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Carbon–Halogen Bond Cleavage Reaction Catalyzed by Organoyttrium Hydride (*in situ*) and Lanthanide Alkoxides

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Organic halides can be ubiquitous long-lived contaminants to the environment. Dehalogenation of organic halides with sodium hydride (NaH) as reductant catalyzed by two varieties of lanthanides was reported in respect of environmental remediation. The first catalyst is a dicyclopentadienyl yttrium halide, and organoyttrium hydride was thought to be the reactive species. The second catalyst is a lanthanide isopropoxide which showed higher catalytic reactivity, and an aggregate is involved in the suggested mechanism.

Keywords: organic halide; carbon–halogen bond cleavage; sodium hydride; organoyttrium complex; lanthanide isopropoxides

INTRODUCTION

Carbon–halogen bond cleavage is an issue of fundamental as well as practical, importance: it has played a major role in the elucidation of the mechanism of organometallic transformations, and it is important for organic synthesis.[1,2] The practical interest of dehalogenation derives from the genetic toxicity and carcinogenicity of this ubiquitous class of organic materials.[3-5] Some of the major classes of pesticides which persist in the environment, and the most common chemical warfare agent, mustard gas,[6] are chlorocarbons while the deleteriousness of chlorofluorocarbons with respect to the ozone layer derives largely from their chlorine content. The quest for environmentally friendly catalysis and technology, in general, has given rise to a substantial thrust to move away from chlorocarbons and halogenated materials altogether.

Sodium hydride (NaH) is commonly used as a Lewis base in organic chemistry and its reducing properties are masked by its basic ones;[7] only a few substrates can be reduced by NaH alone, the reactions are slow and the yields are far from excellent.[8] Fortunately, Caubere and co-workers have developed reducing agents complexed with sodium hydride (NaH–RONa–MXn),[9] which greatly promote the reducing ability of sodium hydride. A number of other approaches for dehalogenation have been reported, especially with metal hydrides and transition-metal salts, for instance, $LiAlH_4$–$CeCl_3$, $NaBH_4$–$PdCl_2$ etc.,[10] but most of the activating reagents for these systems must be present in stoichiometric amounts, or a third component may even be needed.

We have found that Cp_3Ln–NaH systems showed high reactivity to the carbon–carbon double bond.[11,12] Here we report the reaction of organic halides with NaH, catalyzed by Cp_2LnCl and lanthanide alkoxides respectively.

EXPERIMENTAL

All operations were carried out under prepurified argon by Schlenk techniques. Tetrahydrofuran was refluxed and distilled either over finely divided $LiAlH_4$ or over blue sodium benzophenone under argon, immediately before use. Anhydrous lanthanide chlorides were prepared from the oxides by a published procedure.[13] Cp_2YCl complex was obtained by the method of Maginn *et al.*[14] Sodium hydride (with 20% paraffin oil; E. Merck) was washed with THF and dried under vacuum. Sodium isopropoxide (i-PrONa) was prepared by the reaction of sodium metal with isopropanol (i-PrOH) in THF, and the concentration was titrated by standard aqueous HCl solution. The products generated were identified

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Table 1 Dehalogenation of organic halides catalyzed by organoyttrium hydride (*in situ*)[a]

Entry	Halide	Time (h)	Yield (%)
1	*p*-Bromotoluene	24	87
2	*m*-Bromotoluene	24	98
3	*o*-Bromotoluene	24	100
4	*o*-Bromoanisole	12	100
5	α-Bromonaphthalene	10	100
6	Benzyl chloride	30	92
7	Phenethyl chloride	36	98
8	Benzyl bromide	20	100
9	Bromodecane	32	93
10	Diphenylchloromethane	12	92[b]

[a] In THF at 60 °C; Cp_2YCl/Na/Halide = 0.1 : 4.0 : 1.0.
[b] Isolated yield.

on Finngun 4021 GC–MS and Digilab instruments Frs-20E and by capillary GC–FTIR. The GC yields were determined by a 103-type chromatographic instrument equipped with a 2 m XE-60 column, and hexadecane was used as an internal standard.

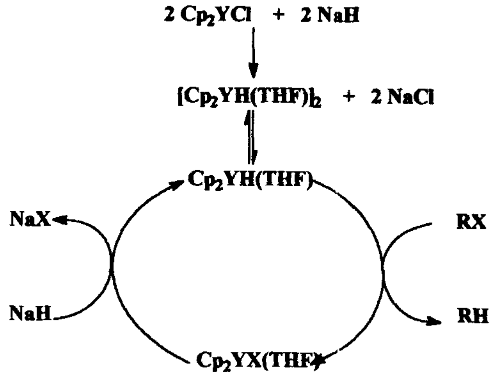
A typical procedure catalyzed by Cp_2YCl

Cp_2YCl (13.0 mg, 0.051 mmol) and NaH (49 mg, 2.04 mmol) were loaded into a Schlenk tube under argon, then THF and bromodecane (0.11 ml, 0.51 mmol) were introduced by a syringe and the stopcock was closed. The reaction was carried out with stirring at 60 °C for 32 h. The product was confirmed by GC–FTIR and GC–MS, and the yield was determined by GC.

A typical synthesis procedure of $Ln(i\text{-}PrO)_3$

i-PrONa–THF solution (16.8 ml; 0.91 M, 15.3 mmol) was added dropwise to the suspension of $SmCl_3$ (1.32 g 5.1 mmol) in 20 ml THF. After stirring at room temperature overnight, the suspension was centrifuged and the colorless liquor was filtered and evaporated to remove the solvent. The solid was extracted with n-hexane (2 × 25 ml) and the combined extracts were evaporated to dryness *in vacuo*; 1.70 g of white solid was obtained; yield 84%.

Analysis: calcd. for $C_9H_{21}O_3Sm$: for Sm, 38.11; H, 5.36; C: 27.40. Found: Sm, 37.72; H, 5.68; C, 27.83%.



R=aryl, alkyl; X=Cl, Br

Scheme 1

A typical procedure catalyzed by $Ln(i\text{-}PrO)_3$

A 5 ml Schlenk tube containing 2 ml THF was charged with 27.6 mg (0.07 mmol) of $Sm(i\text{-}PrO)_3$ and 67.3 mg of NaH (2.8 mmol), then 119 mg of 4-bromotoluene (0.7 mmol) was introduced and the stopcock was closed. The reaction mixture was stirred at 60 °C for 24 h. The product was confirmed by GC–IR and GC–MS, and the yield was determined by GC.

RESULTS AND DISCUSSION

Dehalogenation by Cp_2YCl/NaH system

It has been reported that the reaction of Cp_2LuCl with NaH in THF formed the hydride $[Cp_2LuH(THF)]_2$,[15,16] so we tried to use the organolanthanide hydride species generated *in situ* from the Cp_2LnCl–NaH system, which avoided the difficult preparation and manipulation of reactive organolanthanide hydrides, to catalyze the carbon–halogen bond cleavage of organic halides; we chose Cp_2YCl as catalyst (Eqn [1]).

Table 2 $Ln(i\text{-}PrO)_3$-catalyzed dehalogenation of *p*-bromotoluene with NaH[a]

$Ln(i\text{-}PrO)_3$	La	Pr	Nd	Sm	Gd	Dy	Er	Yb	Y
Yield (%)	52	34	66	82	60	57	72	47	37

[a] In THF at 60 °C, 6 h, $Ln(i\text{-}PrO)_3$/NaH/Halide = 0.1 : 4 : 1.0.

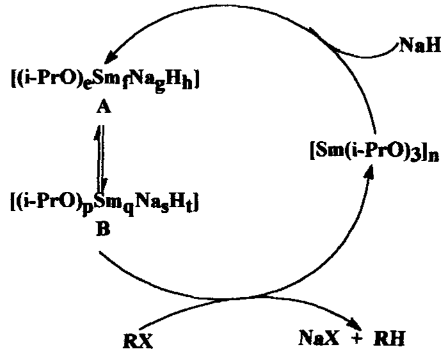
Table 3 Dehalogenation of organic halides catalyzed by Sm(i-PrO)$_3$–NaH system[a]

Entry	Halide	Time (h)	Sm(i-PrO)$_3$/NaH/S	Yield (%)
1	Chlorobenzene	48	0.1:4:1	81
2	1,2-Dichlorobenzene	48	0.1:8:1	61 (benzene) 17 (C_6H_5Cl)
3	1,3-Dichlorobenzene	48	0.1:8:1	41 (benzene) 7 (C_6H_5Cl)
4	1-Chloronaphthalene	48	0.1:4:1	83
5	4-Bromotoluene	10	0.1:4:1	100
6	2-Bromotoluene	10	0.1:4:1	100
7	Bromobenzene	10	0.1:4:1	100
8	1-Chlorobutane	48	0.1:4:1	94
9	2-Chloro-2-methylpropane	48	0.1:4:1	99
10	n-Butyl bromide	10	0.1:4:1	99
11	t-Butyl bromide	10	0.1:4:1	100
12	n-Butyl iodide	1.5	0.1:4:1	100

[a] In THF at 60 °C.

$$R\text{—}X + NaH \xrightarrow[\text{THF, 60 °C}]{Cp_2YCl\text{ (10 mol \%)}} RH + NaX \qquad [1]$$

The results are summarized in Table 1. As expected, the Cp$_2$YCl–NaH system showed high reactivity to catalyze the carbon–halogen bond cleavage of organic halides (both alkyl and aryl) and no coupling products were detected. Unlike the Cp$_3$Ln–NaH systems, wherein alkylcyclopentadienes were obtained instead of the dehalogenation products in the reaction with alkyl halides due to the generation of Cp$^-$ anion, the Cp$_2$YCl–NaH system should give no alkylcyclopentadienes in the product, because the reaction of Cp$_2$LnCl with NaH produces [Cp$_2$LnH(THF)]$_2$ without formation of anion. A plausible catalytic cycle for the formation of an organoyttrium hydride species by the reaction of Cp$_2$YCl with NaH has been proposed in Scheme 1.



R=aryl, alkyl; X=Cl, Br

Scheme 2

Dehalogenation catalyzed by Ln(i-PrO)$_3$–NaH systems

Use of lanthanide alkoxides as catalysts in some organic reactions seems to be very promising,[18–20] so we tried to use lanthanide tri-2-propoxides as the catalysts for carbon–halide bond cleavage. The Ln(i-PrO)$_3$ complexes were prepared by the reaction of *i*-PrONa with LnCl$_3$ in THF at room temperature.

At first, we used a variety of lanthanide metal ions in Ln(i-PrO)$_3$ in the dehalogenation of *p*-bromotoluene (Eqn [2]) and the yield of toluene was determined after 6 h (Table 2). We were pleased to find that all of the lanthanide 2-propoxides used could catalyze the reaction effectively and Sm(i-PrO)$_3$ was the most active catalyst.

$$p\text{-}CH_3C_6H_4Br + NaH \xrightarrow[\text{THF, 60 °C}]{Ln(i\text{-}PrO)_3\text{ (10\%)}} C_6H_5CH_3 + NaBr \qquad [2]$$

The dehalogenation of some organic halides was examined by using Sm(i-PrO)$_3$ as catalyst. The results are summarized in Table 3. The yield is high not only for bromide substrate but also for chloride substrate; even the dichloride organic compound has a moderate transfer ratio. In these reactions no coupling products were discovered.

Although there are different reports in the literature, most of the evidence supports the proposition that Ln(i-PrO)$_3$ exists as a polymer.[21] A plausible mechanism is depicted in Scheme 2. NaH mixes with Sm(i-PrO)$_3$ into aggregates, and there is an equilibrium between the insoluble aggregate A and the soluble aggregate B. The hydride ion (H^-) in a mixed aggregate has a good probability of being more reactive than in the solid sodium hydride.

Comparing the Ln(i-PrO)$_3$–NaH system with Cp$_2$LnCl–NaH, we found that Ln(i-PrO)$_3$ showed higher catalytic reactivity in dehelogenation than Cp$_2$LnCl: this might have resulted from the difference that H^- in the aggregate B [$(\text{i-PrO})_p\text{Sm}_q\text{Na}_y\text{H}_t$] is more active than in Cp$_2$LnH. Easy preparation of Ln(i-PrO)$_3$ is the other advantage of the Ln(i-PrO)$_3$–NaH reductive system.

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