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Studies on organolanthanide complexes

XXIII. Reaction of organic halides with tricyclopentadienyllanthanides/sodium hydride

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Abstract

The reductive dehalogenation of aryl and vinyl halides with tricyclopentadienyllanthanide/sodium hydride systems affords, respectively, the corresponding aromatics and alkenes in excellent yields under mild conditions. However, the reaction with alkyl halides generates alkylated products, which yield alkyl cyclopentadienes after hydrolysis. The reaction mechanism has been briefly investigated.

Introduction

Sodium hydride is commonly used as a base [1]. The reducing properties of this compound in organic chemistry are not well-known and only a few publications about them have been reported [2–4]. In the course of our studies on organolanthanide complexes, we have discovered that the Cp_3Ln/NaH systems are not only able to reduce olefins, but also to catalyze the isomerization of 1-alkenes into internal olefins [5,6]. This led us to think that these systems may have potential as reducing reagents.

The reduction of organic halides to the corresponding hydrocarbons plays an important role in organic synthesis [7], so we have applied the Cp_3Ln/NaH systems to halide reduction to examine their reducing properties. Here we wish to report the results of the reaction of the Cp_3Ln/NaH systems with organic halides.

Results and discussion

Reductive dehalogenation of aryl and vinyl halides by Cp_3Ln/NaH systems

p-Bromotoluene was reduced by Cp_3Ln/NaH systems giving toluene in excellent yield under mild conditions. The results are presented in Table 1.

The results in Table 1 show that the activity of Cp_3Ln/NaH in *p*-bromotoluene reduction strongly depends on the central metal of tricyclopentadienyllanthanide complexes. The reductive activity of light rare earth is higher than that of heavy

Table 1

Effect of reaction conditions on the reduction of *p*-bromotoluene with Cp_3Ln/NaH in THF at 45 °C

Entry	Ln of Cp_3Ln	Molar ratio $Cp_3Ln:NaH:ArX$	Yield(%) [a], Overtime (h)					
			4	8	12	24	48	72
1	La	1:4:1		72	90	100		
2	Sm	1:4:1		27	43	100		
3	Gd	1:4:1		12	32	95	100	
4	Y	1:4:1		7	11	51	100	
5	Lu	1:4:1		3	4	54	100	
6	La	1:0:1		0	0	0	0	
7	La	1:2:1		33	62	100		
8	La	1:6:1		55	94	100		
9	La	1:8:1		55	97	100		
10	La	0:4:1		0	0	0	0	5
11	La	2:4:1		68	97	100		
12	La	1:4:1 [b]				21	85	100
13	La	1:4:1 [c]	59	98				
14	La	1:4:1 [d]		13	100			
15	La	1:4:1 [e]	3	10	34	95		
16	La	1:4:1 [f]	42	95				
17	La	1:4:1 [g]	74	100				

[a] GC yield of toluene based on *p*-bromotoluene. [b] At 25 °C; [c] At 65 °C. [d] At 65 °C, in THF/HMPA, the molar ratio of HMPA to substrate is 6:1, similar results were obtained when molar ratio is 1:1 and 2:1. [e] At 65 °C, in DME. [f] At 65 °C, in diglyme. [g] At 85 °C, in diglyme.

ones. The activities of these tricyclopentadienyllanthanide complexes decrease in the following order: $Cp_3La > Cp_3Sm > Cp_3Gd > Cp_3Y > Cp_3Lu$. This order of activity is different from that of Cp_3Ln/NaH in the reduction of olefins [5]. It has been found that Cp_3Ln alone has no reducing power for aryl halides, no toluene is formed when only Cp_3Ln is allowed to react with p-bromotoluene at 45 °C for 72 h. In the absence of Cp_3Ln, the treatment of *p*-bromotoluene with NaH at 45 °C yields toluene only in 5% yield after 72 h. The yield of toluene rises to 100% in the presence of Cp_3Ln. It appears clear that the reducing powers of Cp_3Ln/NaH systems are much higher than that of NaH alone in THF. Our result indicates that the suitable molar ratio of reactants is 1 : 4 : 1 ($Cp_3Ln:NaH:ArBr$).

Hexamethylphosphoric triamide (HMPA) strongly promoted the reduction of organic halides by SmI_2–THF solution [8]. The promoting effect of HMPA on photoreduction has recently also been reported [9]. We have found, however, HMPA has no promoting effect on the reduction of *p*-bromotoluene with the Cp_3La/NaH system, and even inhibits this reaction to some extent. The reduction speed of Cp_3La/NaH on aryl halides depends notably on the reaction temperature. For example, the reaction rate at 65 °C is three times as fast as that at 45 °C and nine times as fast as that at 25 °C. Rate of reduction is also affected by solvent. The activities of Cp_3Ln/NaH system in the various solvents decrease in the following order: THF > Diglyme > DME.

Furthermore, a series of aryl and vinyl halides has been smoothly reduced by Cp_3La/NaH (Eq. 1). The results are summarized in Table 2.

$$R\text{-}X \xrightarrow[\text{THF}]{Cp_3La/NaH} R\text{-}H \qquad (1)$$

(R = aryl, vinyl; X = F, Cl, Br, I)

Table 2

Reduction of aryl and vinyl halides with Cp_3La/NaH system in THF [a]

Entry	Organic halide	Time (h)	Product	Yield (%) [b]
1	*p*-Bromotoluene	8	Toluene	98
2	*o*-Bromotoluene	8	Toluene	100
3	*m*-Bromotoluene	8	Toluene	96
4	*p*-Bromoanisole	6	Anisole	100
5	β-Bromonaphthalene	6	Naphthalene	100
6	*p*-Bromoacetophenone	48	Methyl phenyl ketone	100
7	Iodobenzene	1	Benzene	98
8	Bromobenzene	8	Benzene	100
9	Chlorobenzene	12	Benzene	66
10	Fluorobenzene	12	Benzene	44
11	*p*-Bromochlorobenzene	4	Chlorobenzene	100
12	β-Bromostyrene [c]	24	Styrene	100
13	1-Bromoisobutene [c]	48	Isobutene	60
14	1-Iodopentyne-1 [c]	1	1-pentyne	99

[a] At 65 °C, $Cp_3La:NaH:substrate = 1:4:1$. [b] GC yield based on the substrate. [c] At 45 °C.

From Table 2, it can be seen that the order of ease of reductive dehalogenation of aryl halides by Cp_3La/NaH system is in agreement with that of usual reductive dehalogenation of organic halides, i.e. $I > Br > Cl > F$. It is worthy of note that the Cp_3La/NaH system can selectively reduce *p*-bromochlorobenzene to chlorobenzene.

Reaction of alkyl halides with Cp_3Ln/NaH

The surprising thing is that the reaction pattern of alkyl halides with Cp_3Ln/NaH systems is quite different from that of aryl and vinyl halides. The treatment of alkyl halides with Cp_3La/NaH followed by hydrolysis does not generate the corresponding alkanes, but the substituted products, alkyl cyclopentadienes, are obtained (Eq. 2). The results are listed in Table 3.

$$Cp_3Ln + RX + NaH \xrightarrow{THF} \xrightarrow{H_2O} CpR \qquad (2)$$

(R = alkyl; X = Cl, Br, I)

As shown in Table 3, in the absence of sodium hydride, tricyclopentadienyllanthanum does not react with alkyl halides. The larger the amount of NaH that is used, the faster is the reaction. Obviously, sodium hydride is necessary for this reaction. The temperature also strongly affects the rate of the reaction. For example, the reaction of Cp_3La/NaH with 1-bromobutane was finished at 65 °C in 1 h, but at 45 °C in 6 h and at 20 °C in 24 h. From Table 3, it can also be seen that the reaction rate order conforms with the ease of leaving of X^-: $I > Br > Cl$. The position of halogen in alkyl halides has very strong effect on this reaction. The reactions of benzyl and allyl halides with Cp_3La/NaH are faster. The length of chain of alkyl group does not have any noticeable effect on this reaction.

Approach to the reaction mechanism

We have previously reported that dicyclopentadienyllutetium chloride reacts with sodium hydride in THF at ambient temperature generating a neutral dimer of

Table 3

Results of the reaction of Cp_3La/NaH with RX [a]

Entry	Alkyl Halide	Time (h)	Yield of C_5H_5R [b](%)
1	1-Bromohexane	1 [c]	96
2	1-Bromohexane	6 [d]	93
3	1-Bromohexane	24 [e]	0
4	1-Bromobutane	1 [c]	98
5	1-Bromobutane	6	96
6	1-Bromobutane	24 [f]	96
7	1-Chlorohexane	24	77
8	1-Iodobutane	5	98
9	s-Bromobutane	30	65 [g]
10	t-Bromobutane	36	53 [h]
11	Benzyl bromide	4	98
12	Allyl chloride	4 [i]	98
13	Allyl iodide	2	98
14	5-Bromopentene	4	99
15	1-Bromooctane	6	99
16	1-Bromolaurane	6	94

[a] At 45 °C, in THF, molar ratio of $Cp_3La:NaH:RX = 1:4:1$. [b] Yield was determined by GC and based on RX, 1–2% RH was also obtained. [c] At 65 °C. [d] $Cp_3La:NaH:RX = 1:2:1$, at 65 °C. [e] $Cp_3La/NaH/RX = 1:0:1$, at 65 °C. [f] At 20 °C. [g] 31% diisobutylcyclopentadiene was obtained. [h] 17% di-t-butylcyclopentadiene was obtained. [i] In diglyme.

dicyclopentadienyllutetium hydride, $[Cp_2LuH(THF)]_2$[10]. It has been reported that the Ln–Cp bond is cleaved by RLi ($R = t\text{-}C_4H_9$, $s\text{-}C_4H_9$) [11]. We therefore first supposed that the Ln–Cp bond of Cp_3Ln is cleaved by NaH to form dicyclopentadienyllanthanide hydride (I) and cyclopentadienyl sodium (Scheme 1).

Using alkyl halides as substrates, there is competition between the reduction and the replacement reactions. Cyclopentadienyl sodium readily undergoes nucleophilic substitution with alkyl halides yielding alkyl cyclopentadienes as the major products. But cyclopentadienyl sodium is not able to effect nucleophilic substitution with vinyl and aryl halides, they react only with dicyclopentadienyllanthanide hydride affording the corresponding alkenes and aromatics, respectively.

On the other hand, Schumann has reported that Cp_3Lu reacts with NaH in THF to form μ-hydride $[Na(THF)_6][Cp_3LuHLuCp_3]$ [12]. So the reaction pathway shown in Scheme 2 is also possible.

When aryl and vinyl halides are the substrates, they are reduced by the μ-hydride II. For alkyl halides, direct alkylation on the cyclopentadienyl ligand of μ-hydride II takes place to form μ-hydride III and IV, which afford alkyl cyclopentadienes after hydrolysis.

$$2Cp_3Ln + 2NaH \xrightarrow{THF} \underset{(I)}{[Cp_2LnH(THF)]_2} + 2CpNa$$

$$CpNa + RX \longrightarrow CpR + NaX \quad (R = \text{alkyl})$$

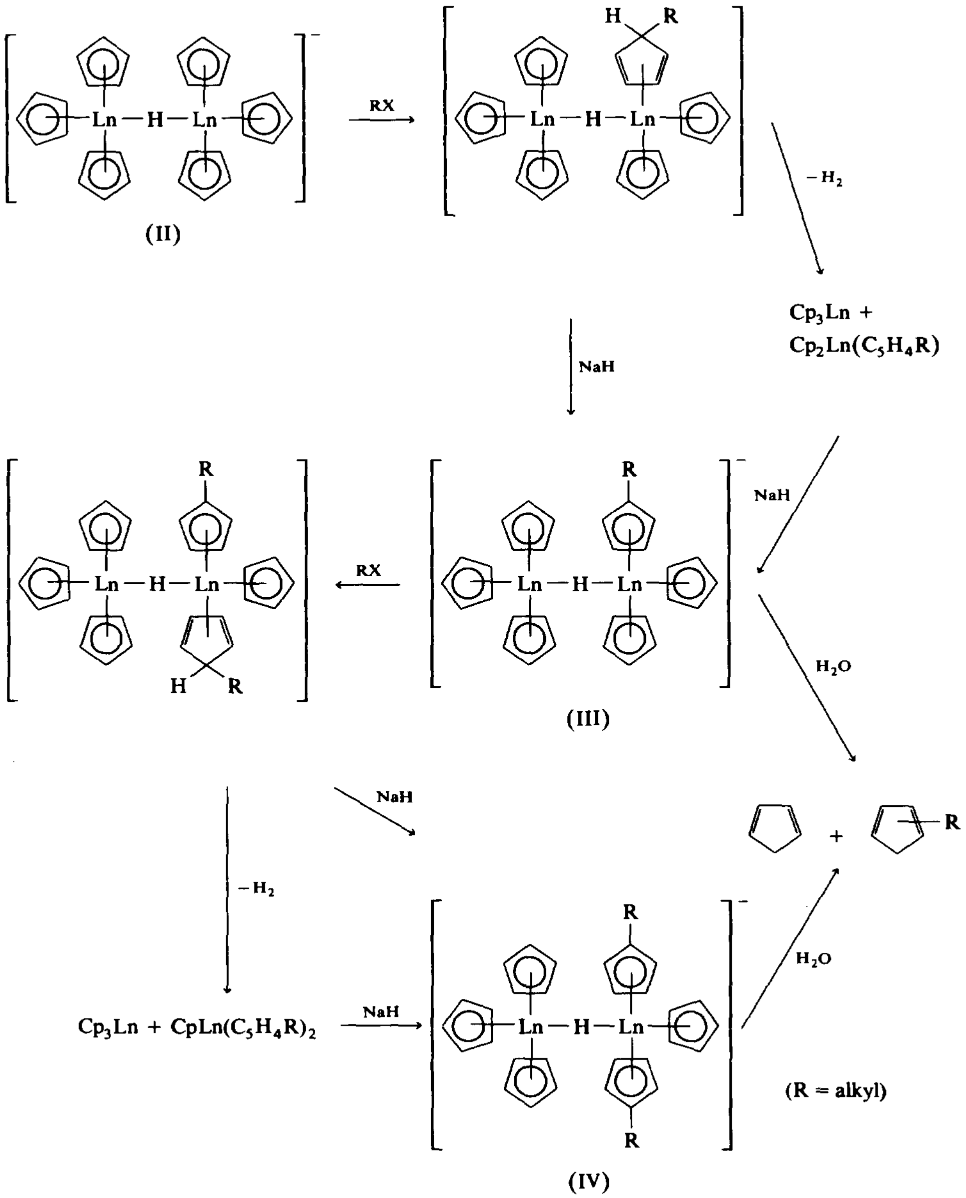
$$I + 2RX \longrightarrow 2RH + 2Cp_2LnX \quad (R = \text{aryl, vinyl})$$

Scheme 1

$$2\mathrm{Cp_3Ln} + \mathrm{NaH} \xrightarrow{\mathrm{THF}} [\mathrm{Na(THF)_6}][\mathrm{Cp_3LnHLnCp_3}]$$

(II)

$$\mathrm{II} + \mathrm{RX} \longrightarrow \mathrm{RH} + 2\mathrm{Cp_3Ln} + \mathrm{NaX} \quad (\mathrm{R} = \text{aryl, vinyl})$$



Scheme 2

mass spectrum appeared the peaks of $[CpGd(C_5H_4C_4H_9)_2]^+$, $[Cp_2Gd(C_5H_4C_4H_9)]^+$ and $[Cp_3Gd]^+$ (MS data are listed in Experimental section). This indicates that the Gd–Cp bond of Cp_3Gd is not cleaved. It has also been shown that the neutral hydride $[Cp_2YH(THF)]_2$ is less powerful than the corresponding system, Cp_3Y/NaH (see Entry 4 in Table 1 and last paragraph of Experimental section). Therefore, the reaction mechanism depicted in Scheme 2 is more reasonable.

Experimental

All operations were performed in an atmosphere of prepurified argon using Schlenk techniques. Tetrahydrofuran was refluxed and distilled over either finely divided $LiAlH_4$ or blue sodium benzophenone under argon immediately prior to use. The Cp_3Ln complexes were prepared by the literature method [13]. Sodium hydride (E. Merck, with 20% paraffin oil) was washed by THF or pentane and dried in vacuum. Organic halides were dried by CaH_2 and then distilled under argon.

Gas chromatography-mass spectra were determined on a Finnigan 4021 GC-MS. Gas chromatography-IR spectra were determined on the Digilab FTS-20E capillary GC-FTIR. Gas chromatographic analysis was carried out on a 103 gas chromatographic instrument utilizing 4-m XE-60 or 2-m OV-1 column to determine the yields of products.

Reduction of aryl and vinyl halides with Cp_3Ln/NaH

The typical procedure was as follows: A 3 ml Schlenk tube equipped with a Teflon stopcock was charged with 33.4 mg (0.0999 mmol) of Cp_3La and 9.6 mg (0.400 mmol) of NaH, then 17.1 mg (0.0999 mmol) of *p*-bromotoluene was added and 1 ml of THF was introduced by a syringe. Then the stopcock was closed and the reaction was carried out at 65 °C with stirring. The toluene generated was verified by GC-IR and GC-MS. The amount of toluene was determined by GC after 4 and 8 h.

Reaction of alkyl halides with Cp_3La/NaH

The typical procedure was as follows: A 3 ml Schlenk tube was charged with 28.6 mg (0.0856 mmol) of Cp_3La, 8.3 mg (0.346 mmol) of NaH under argon, then 14.1 mg (0.0856 mmol) of 1-bromohexane and 1 ml of THF were added into the tube, the stopcock was closed. The reaction mixture was stirred for 1 h at 65 °C and then hydrolyzed under cooling. The product was verified by GC-MS and GC-IR. The yield of product was determined by GC.

Reaction of Cp_3Gd with n-bromobutane and NaH

439.8 mg (1.25mmol) of Cp_3Gd, 123.2 mg (5.13mmol) of NaH, 171.1 mg (1.25mmol) of n-bromobutane and 12 ml of THF were added into a Schlenk tube. The mixture was stirred for 4 h at 50–60 °C and the precipitate was separated. Then THF was removed and the residue was washed with a little hexane, affording a light yellow solid. Its mass spectrum was as follows: *m/e* (relative intensity and assignment) 465 (0.4, $[CpGd(C_5H_4Bu\text{-}n)_2]^+$), 409 (0.4, $[Cp_2Gd(C_5H_4Bu\text{-}n)]^+$), 400 (1.2, $[Gd(C_5H_4Bu\text{-}n)_2]^+$), 353 (0.4, $[Cp_3Gd]^+$), 344 (1.7, $[CpGd(C_5H_4Bu\text{-}n)]^+$), 288 (1.1, $[Cp_2Gd]^+$), 281 (0.4, $[Gd(C_5H_4Bu\text{-}n)]^+ + 1$), 223 (0.5, $[CpGd]^+$), 122 (28.0, $[n\text{-}BuC_5H_4]^+$), 79 (100.0, $[C_5H_4CH_2]^+$), 66 (54.0, $[C_5H_6]^+$), 65 (31.0, $[C_5H_5]^+$).

Reaction of dicyclopentadienylyttrium hydride with p-*bromotoluene*

A 3 ml Schlenk tube was charged with 17.1 mg (0.059 mmol) of $[Cp_2YH(THF)]_2$ and 10.1 mg (0.059 mmol) of *p*-bromotoluene, then 0.5 ml of THF was added by a syringe. The stopcock was closed and the reaction was carried out at 45 °C with stirring. After 16 h, the yield of toluene was less than 1%.

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