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Studies on organolanthanide complexes

XVIII *. The reduction and isomerization of olefins with tricyclopentadienyllanthanides / sodium hydride **

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Abstract

Reduction of 1-hexene with Cp_3Ln/NaH (Cp = cyclopentadienyl, Ln = rare earth metals) in THF at 45 °C, after hydrolysis, gives hexane. The reducing activity of Cp_3Ln depends strongly upon the ionic radius of the trivalent rare earth ion. The activity and selectivity of early rare earths for 1-hexene reduction are higher than those of heavy rare earths. The Cp_3Ln/NaH systems can be used to regioselectively reduce dienes which contain a terminal carbon–carbon double bond as well as an internal one with high yield. Selectivity is 100%. Moreover, the Cp_3Ln/NaH systems are able to catalyze the hydrogenation of olefins.

When Cp_3Ln/NaH is used as catalyst, 1-hexene was isomerized at 45 °C to *cis*-2-hexene and to *trans*-2-hexene in excellent yields. In contrast to reducing activity, the catalytic activity of heavy rare earths in the isomerization reaction is higher than that of the early earths. Hence, Cp_3Sm/NaH and Cp_3Y/NaH are new reducing agents and catalysts for 1-hexene reduction and isomerization, respectively.

Introduction

We have reported previously that the neutral dimeric dicyclopentadienyl lutetium hydride, $[Cp_2LuH \cdot OC_4H_8]_2$, was synthesized by the reduction of dicyclopentadienyl lutetium chloride with sodium hydride and that the lutetium hydride thus formed was able to reduce olefins [1]. The reduction of olefins, and the catalytic hydrogenation of alkenes and alkynes with organolanthanide hydrides have also been reported by Evans [2,3] and Marks [4–6]. However, the reaction of olefins with

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* For part XVII see ref. 11.

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tricyclopentadienyl lanthanide/sodium hydride system has not yet been reported. Here we describe the results of reduction and isomerization of olefins with Cp_3Ln/NaH (Ln, La, Pr, Nd, Sm, Tb, Y, Er, Yb and Lu).

Results and discussion

Reduction of 1-hexene with Cp_3Ln/NaH in THF at 45 °C gives hexane after hydrolysis. The yield of hexane is dependent on the Cp_3Ln. The results are listed in Table 1.

From Table 1, it can be seen that the activity for 1-hexene reduction with Cp_3Ln/NaH strongly depends on the ionic radius of the trivalent rare earth ion. Generally, the activity decreases in the order: early rare earths > mid rare earths > heavy rare earths. The activities of the nine tricyclopentadienyl lanthanide complexes decrease in the following order: $Cp_3Sm > Cp_3La > Cp_3Pr > Cp_3Nd > Cp_3Tb > Cp_3Y > Cp_3Er > Cp_3Lu > Cp_3Yb$. The activity of Cp_3Sm is the highest and that of Cp_3Yb the lowest. The order in which the activity of the seven Cp_3Ln decreases is in agreement with that of decrease in radius of the rare earth Ln^{3+} ion. Exceptions to this fact are the ions Sm^{3+} and Yb^{3+}, because they have variable valency. The correlation of decrease in the reducing activity with ionic radius of Ln^{3+} is depicted in Fig. 1. 1-Hexene cannot be reduced by either Cp_3Ln or sodium hydride alone.

When the reaction time was increased, the yield of 1-hexene reduction was improved, but the isomerization product, *cis*- and *trans*-2-hexene, was also formed. The rate of formation of the isomerization product with heavy rare earths is faster than that with early rare earths. So, the reaction activity of some of the heavy rare earth complexes rises rapidly after 24 h. The dependence of conversion of 1-hexene on Ln^{3+} is depicted in Fig. 2.

It has been indicated that the selectivity for 1-hexene reduction by early lanthanides Cp_3Ln is higher than that by heavy lanthanides. For example, during 72 h, whereas the selectivity for 1-hexene reduction by Cp_3La is 93%, the yields of hexane and 2-hexene are nearly equal for both Cp_3Er and Cp_3Lu. Cp_3Sm shows not only high activity but also prominent selectivity for 1-hexene reduction. Thus of the nine Cp_3Ln complexes Cp_3Sm is the best reducing agent. In addition, the heavy rare earth complexes could be used as catalysts for the isomerization of 1-hexene.

Table 1

Reduction of 1-hexene by Cp_3Ln/NaH [a]

Time (h)		Yield of hexane (%) [b]								
	Ln =	La	Pr	Nd	Sm	Tb	Y	Er	Yb	Lu
4		13(0)	11(0)	9(0)	16(0)	3(0)	1(0)	1(0)	0(0)	2(0)
8		31(0)	30(0)	27(0)	41(0)	15(0)	8(0)	4(0)	0(0)	3(0)
12		48(0)	46(0)	47(0)	61(3)	35(0)	15(0)	6(0)	0(0)	5(0)
24		72(3)	68(2)	66(6)	86(4)	62(5)	26(7)	17(5)	0(0)	10(3)
48		86(5)	79(7)	78(11)	90(6)	75(18)	49(25)	42(32)	5(0)	32(14)
72		89(7)	83(7)	80(15)	89(8)	74(18)	52(36)	46(43)	28(0)	39(38)

[a] Reaction conditions: 45 °C, THF, $Cp_3Ln/NaH/alkene = 2/7.8/1$ (molar ratio). [b] The figure in parentheses denotes the yield of 2-hexene (%).

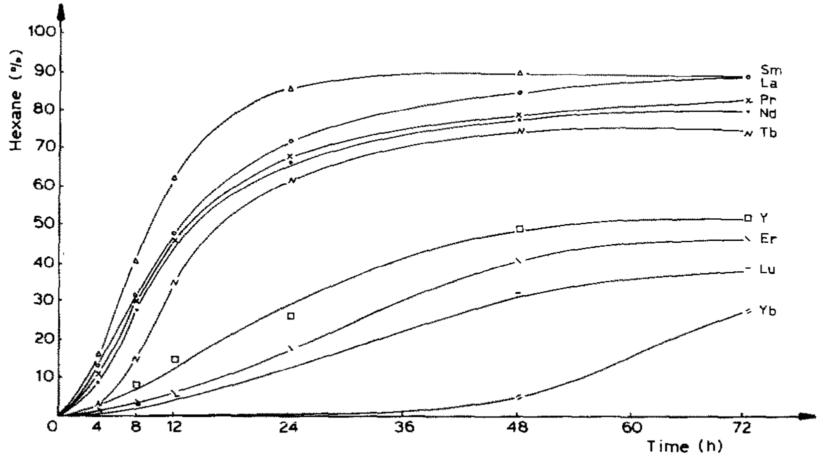


Fig. 1. The correlation of the decrease of reducing activity with decreasing ionic radius of Ln^{3+}.

In the present reaction system, an excess of sodium hydride is necessary and a ratio of 4–8/1, of sodium hydride to 1-hexene, is preferable.

The selectivity for 1-hexene reduction by Cp_3Ln/NaH was strongly affected by molar ratio of Cp_3Ln to 1-hexene. If the ratio of Cp_3Ln/1-hexene decreases from 2 to 1, the decrease in selectivity of 1-hexene reduction is 10–20% (Table 2). Moreover, the conversion of 1-hexene was seen to be slower in the initial stage.

The conversion of 1-hexene was improved but the yield of hexane becoming less as temperature increased. The results are shown in Table 3.

The rates at which internal olefin and cyclohexene are reduced were very low with Cp_3Ln/NaH. Although ethylbenzene was also formed in the reaction of styrene with Cp_3Ln/NaH, such of the styrene polymerized immediately. The rates at which the various olefins were reduced were compared; the results are given in

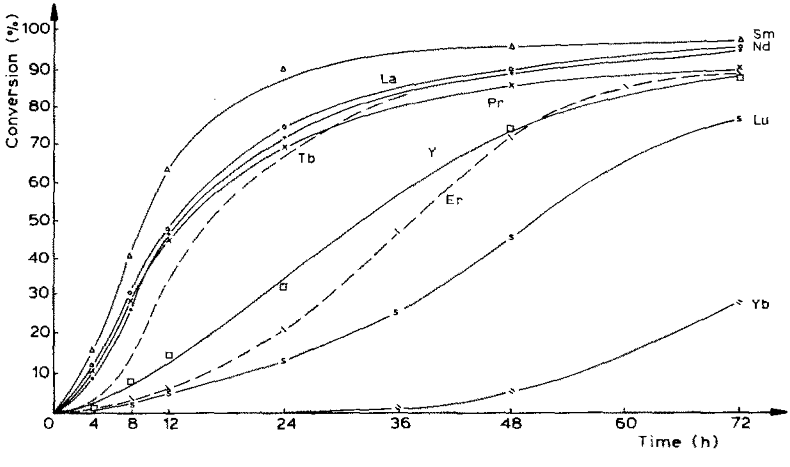


Fig. 2. The rates of conversion of 1-hexene by various Ln^{3+}.

Table 2

Selectivity for 1-hexene, during the reduction by different Cp_3Ln/1-hexene [a] ratios

Ln	Time (h)	Cp_3Ln/1-hexene ratio [b]					
		2/1			1/1		
		Conversion (%)	Product (%)		Conversion (%)	Product (%)	
			Hexane	2-Hexene		Hexane	2-Hexene
Nd	8	27	27	0	11	11	0
	24	72	66	6	57	46	11
	48	89	78	11	82	52	30
Sm	8	41	41	0	39	39	0
	24	90	86	4	78	67	11
	48	96	90	6	95	80	15

[a] Reaction conditions: 45 ° C, THF, concentration; 10 μl 1-hexene/ml THF. [b] NaH/1-hexene = 7.8/1.

Table 3

The influence of temperature on conversion and selectivity for 1-hexene reduction [a]

Ln	Time (h)	45 ° C			60 ° C		
		Conversion (%)	Selectivity (%)		Conversion (%)	Selectivity (%)	
			Hexane	2-Hexene		Hexane	2-Hexene
Nd	4	9	100	0	25	100	0
	8	27	100	0	59	97	3
	24	72	92	8	91	79	21
	48	89	88	12	95	83	17
Sm	4	16	100	0	57	100	0
	8	41	100	0	79	96	4
	24	90	96	4	96	83	17
	48	96	94	6			

[a] Cp_3Ln/NaH/1-hexene = 2/7.8/1; THF; concentration; 10 μl 1-hexene/ml THF.

Table 4. Thus the order of reactivity is as follows: 1-hexene ≫ 2-hexene > cyclohexene. The significant difference in reduction rates was probably due to the steric effects in the substrate.

The reduction rate of internal-olefins was much slower than that of terminal olefins. Thus, the Cp_3Ln/NaH system can be used to reduce dienes, which contain both a terminal and an internal carbon–carbon double bond regioselectively. When Cp_3Sm/NaH was used as the reducing agent, the regioselective reduction of

Table 4

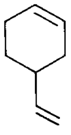
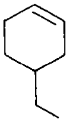
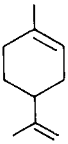
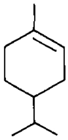
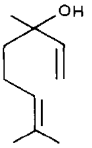
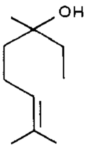
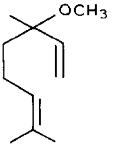
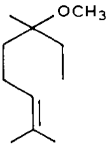
Comparison of rates of at which various olefins are reduced [a]

Olefin	Reaction time (h)	Yield of alkane (%)
1-Hexene	72	80.0
2-Hexene	72	0.6
Cyclohexene	144	0.3
Styrene	48	ethylbenzene + polymer

[a] Cp_3Nd/NaH, 45 ° C, THF.

Table 5

Results of the reduction of dienes by Cp_3Sm/NaH [a]

Diene	Molar ratio (Cp_3Sm/NaH/diene)	Product	Yield (%)
	1.5/7.8/1		90
	2/7.8/1		41 [b]
	2/7.8/1		44 [b]
	2/7.8/1		38 [b]

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[a] THF, 45 °C, 48 h. [b] The starting olefins were recovered at the same time.

4-vinyl-1-cyclohexene, limonene, 3,7-dimethyl-1, 6-octadiene-3-ol and 3,7-dimethyl-3-methoxy-1,6-octadiene was carried out to give product in high yield. The terminal double bond in parent dienes was reduced and the internal double bond remained intact, the regioselectivity is 100%. The results are listed in Table 5.

Table 6

Catalytic hydrogenation of 1-hexene by Cp_3Sm/NaH [a]

Time (h)	Molar ratio [b]			
	0.2/1/1	0.2/2/1	0.2/4/1	0.5/2/1
	Yield of hexane (%) (*cis*/*trans*-hexene-2)			
24				52 (0)
48	4 (5/0)	37 (0)	44 (7/0)	100 (0)
72	39 (5/0)	61 (0)	61 (5/0)	100 (0)
96	44 (0/0)	68 (4/0)	63 (7/3)	100 (0)

[a] 45 °C, 10 μl 1-hexene/ml THF. [b] Cp_3Sm/NaH/1-hexene.

Table 7

Catalytic isomerization of 1-hexene by Cp_3Ln/NaH [a]

Time (h)		Yield of 2-hexene (%) (*cis*/*trans*)								
	Ln =	La	Pr	Nd	Sm	Tb	Y	Er	Yb	Lu
8		0	4 (99/1)	0	13 (47/53)	0	7 (99/1)	23 (70/30)	6 (99/1)	10 (53/47)
12		2 (99/1)	20 (56/44)	0	35 (65/35)	5 (50/50)	29 (65/35)	59 (64/36)	40 (61/39)	30 (52/48)
24		15 (99/1)	54 (56/44)	34 (58/42)	75 (56/44)	33 (61/39)	86 (58/42)	87 (57/43)	69 (59/41)	89 (63/37)
36		29 (55/45)	67 (57/43)	70 (58/42)	87 (52/48)	50 (74/26)	90 (57/43)	87 (52/48)	80 (57/43)	91 (60/40)
48		34 (61/39)	79 (53/47)	82 (59/41)	90 (54/46)	72 (55/45)	91 (56/44)	87 (52/48)	82 (57/43)	91 (55/45)
72		56 (59/41)	84 (56/44)	87 (54/46)	91 (56/44)	79 (59/41)	91 (48/52)	87 (49/51)	82 (52/48)	91 (52/48)

[a] $Cp_3Ln/NaH/1\text{-hexene} = 0.05/7.8/1$, 45 °C, THF, 0.08 *M*.

The Cp_3Ln/NaH system is not only a better reducing agent with higher selectivity, but also a catalyst for catalytic hydrogenation of alkenes. 1-Hexene was completely converted into hexane under 4 atm. pressure of hydrogen in the course of 48 h. Moreover, no isomerization product, 2-hexene, was detected. When the ratio of Cp_3Ln/1-hexene was reduced to 0.2, a small amount of 2-hexene was formed. The results are listed in Table 6.

From the aforementioned results we envisioned that if the ratio of Cp_3Ln/olefin was decreased to a certain extent, then no reduction of olefins should occur, then the Cp_3Ln/NaH system could be used to catalyze the isomerization of olefins. Fortunately, the isomerization of the double bond in 1-hexene occurs solely at a Cp_3Ln/1-hexene ratio of 0.05, 0.1, and 0.25. The *cis*- and *trans*-2-hexenes were

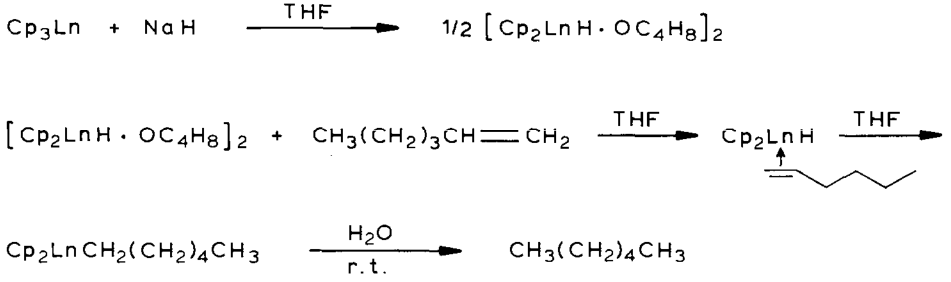
Table 8

Effect of concentration and temperature on the isomerization of 1-hexene [a]

Conc. (*M*)	Temp. (°C)	Time (h)					
		8	12	24	36	48	72
		Yield of 2-hexene (%) (*cis*/*trans*)					
0.08	45	7 (99/1)	29 (65/35)	86 (58/42)	90 (57/43)	91 (56/44)	91 (48/52)
0.08	60	5 (43/57)	15 (60/40)	72 (51/49)	89 (58/42)	90 (57/43)	91 (48/52)
0.16	45	15 (53/47)	47 (62/38)	91 (57/43)	91 (53/47)	91 (49/51)	91 (45/55)
0.32	45	22 (64/36)	52 (67/33)	83 (59/41)	84 (51/49)	90 (49/51)	90 (43/57)

formed in high yield. In general, in initial stages of the reaction more *cis*- than *trans*-2-hexene was formed but during 48 h the amounts of *cis*- and *trans*-2-hexene became nearly equal. The results are given in Table 7. The catalytic activity seems to be related to the ionic radii of rare earth metals. In contrast to reducing activity, isomerization activity of the heavy rare earths is better than that of early rare earths. The catalytic activities of Cp_3Y and Cp_3Lu are highest for the isomerization of 1-hexene. The effect that the concentration of 1-hexene has on the results of isomerization is significant but small after 24 h, and effects by temperature are not evident. The results are listed in Table 8.

The most likely reaction pathway for 1-hexene reduction is depicted in Scheme 1. The organolanthanide hydride is formed by the reaction of Cp_3Ln with NaH [7,8], the olefin then coordinates to the hydride, and subsequent insertion generates the M–C σ bond.



Scheme 1

The presence of the M–C σ bond was shown when hydrolysis of the intermediate gave hexane. To further verify the proposed mechanism, the intermediate product was oxidized with t-BuOOH and MCPBA. In all cases a small amount of 1-hexanol, along with a large amount of hexane, was obtained. This outcome indicates that the M–C σ bond is indeed formed, but it is extremely sensitive to hydrolysis. A known compound, $Cp_2ErC_6H_5$ [9] which contains the rare earth metal M–C σ bond, was oxidized with MCPBA and both oxidation and hydrolysis products, phenol and benzene, respectively, were obtained with the latter predominating. It is indicated that the properties of the rare earth M–C σ bond are different from those with a *d*-block M–C σ bond. The oxidation of the rare earth M–C σ bond was accompanied by hydrolysis of the lanthanide–carbon σ bond.

The reaction of 1-hexene carried out with a catalytic amount of Cp_3Ln and an excess of NaH gave compounds containing a M–C σ bond which underwent β-hydrogen elimination to give 2-hexene with regeneration of the hydride. The isomerization of 1-hexene was thus realized via this addition-elimination cycle.

Experimental

All operations were carried out under prepurified argon by use of Schlenk techniques or in a glovebox. 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 hydrate by a published procedure [9]. The Cp_3Ln complexes were obtained by the method of Wilkinson et al. [10]. Sodium hydride (E. Merck, with 20% paraffin oil) was washed with THF or pentane and dried in vacuum. 1-Hexene (Fluka) was dried by treatment with Na/K alloy and distilled under argon.

GC-MS and GC-IR spectra were recorded on Finnigan 4021 GC-MS and Digilab instruments FTS-20E capillary GC-FTIR. GLC analysis was carried out with a 103-type gas chromatographic instrument equipped with a 4-m PEG 1000-column and a 10-m β,β'-oxydipropionitrile column in order to identify the products of reduction and isomerization, respectively. The products of oxidation and hydrolysis were identified by use of a 2-m XE-60 column.

Reduction of 1-hexene with Cp_3Sm/NaH

A 3-ml Schlenk tube equipped with a Teflon stopcock was charged with 33.4 mg (0.097 mmol) of Cp_3Sm and 9.0 mg (0.38 mmol) of NaH, and cooled to −78 °C, then 6 μl (0.048 mmol) of 1-hexene and 0.64 ml of THF introduced by syringe, and the stopcock was closed. The reaction mixture was allowed to warm to room temperature, with the reaction being carried out at 45 °C with stirring. The amount of hexane generated was determined after 4, 8, 12, 24, 48, and 72 h had elapsed.

Reduction of 4-vinyl-1-cyclohexene with Cp_3Sm/NaH

A similar Schlenk tube was charged with 27.3 mg (0.079 mmol) of Cp_3Sm and 7.39 mg (0.31 mmol) of NaH, and cooled to −78 °C, then 6.34 μl (0.040 mmol) of 4-vinyl-1-cyclohexene and 0.68 ml of THF were introduced to the tube by syringe. The stopcock was closed and the reaction mixture was allowed to warm to room temperature. The reaction was carried out at 45 °C with stirring. After 48 h, the products were determined by GC-IR and GLC.

Cp_3Sm/NaH catalyzed hydrogenation of 1-hexene

A 100 ml-Schlenk flask equipped with a Teflon stopcock was charged with 19.8 mg (0.0573 mmol) of Cp_3Sm and 5.5 mg (0.23 mmol) of NaH, cooled to −78 °C, and 14.3 μl (0.115 mmol) of 1-hexene and 1.52 ml of THF were introduced by syringe. The flask was cooled to −196 °C and evacuated. H_2 was passed into the flask until atmospheric pressure was achieved, then the stopcock was closed. The reaction mixture was allowed to warm to room temperature, with the reaction being carried out at 45 °C with stirring. The pressure of hydrogen is equal to 4 atm. The product was determined by GLC.

Isomerization of 1-hexene with Cp_3Y/NaH

The aforementioned Schlenk tube was charged with 3.0 mg (0.0106 mmol) of Cp_3Y and 39.0 mg (1.63 mmol) of NaH, cooled to −78 °C, and 26.3 μl (0.21 mmol) of 1-hexene and 0.70 ml of THF were then introduced by a syringe to the tube. The reaction mixture was allowed to warm to room temperature, with the reaction being carried out at 45 °C with stirring. The products were determined by GLC.

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