Inorganica Chimica Acta, *140* (1987) 21–24

Studies on Organolanthanide Complexes. XVI.* Reduction of Alkenes with Organolanthanide Complexes/Sodium Hydride Systems**

CHANGTAO QIAN†, DAOLI DENG, CHANGQING YE,
ZUOWEI XIE, YUANWEN GE, YUQIN LI
and YONGJIE GU

Shanghai Institute of Organic Chemistry, Academica Sinica,
345 Lingling Lu, Shanghai, China

We reported previously that dicyclopentadienyl lutetium hydride is able to reduce alkenes [1]. The reduction of alkenes and catalytic hydrogenation of alkenes and alkynes with organolanthanide hydrides have also been reported by Evans *et al.* [2, 3] and Marks *et al.* [4–6]. However, the reduction of alkenes with organolanthanide/NaH systems has not yet been reported. Here we wish to report the results of reduction of alkenes with Cp_3Ln/NaH (Cp = C_5H_5; Ln = La, Pr, Nd, Sm, Tb, Y, Er, Yb and Lu), L_2YCl/NaH ($L_2 = (C_5H_5)_2$, $(CH_3C_5H_4)_2$, $C_5H_4(CH_2)_5C_5H_4$, $C_5H_4CH_2CH_2OCH_2CH_2C_5H_4$) and $L'_2MX\cdot THF$/NaH ($L'_2 = C_5H_4(CH_2)_3C_5H_4$; M = La, Dy, Er, Y, Lu; X = Cl, Me_3C, Me_3CCH_2, C_6H_5, $CH_3C_6H_4$, CF_3COO) systems.

Experimental

All operations were performed in an atmosphere of prepurified argon using Schlenk techniques or in a glovebox. Tetrahydrofuran was refluxed and distilled over either finely divided $LiAlH_4$ or blue sodium benzophenone under argon immediately prior to use. Anhydrous lanthanide chlorides were prepared from the hydrate by a literature method [7]. The Cp_3Ln complexes were obtained by the method of Wilkinson and Birmingham [8]. Sodium hydride (E. Merck, with 20% paraffin oil) was washed by THF or pentane and dried in vacuum. 1-Hexene (Fluka) was dried by treatment with Na/K alloy and distilled under argon.

Gas chromatography–mass spectra (GC–MS) were determined on a Finnigan 4021 GC-MS. Gas chromatography–IR spectra were recorded on Digilab FTS-20E Capillary GC-FTIR. Gas chromatographic analysis was carried out on a 103 gas chromatographic instrument utilizing a 4-m PEG-1000 column and a 10-m β,β'-oxydipropionitrile column to determine the content of the product of reduction and isomerization, respectively. To determine products of oxidation and hydrolysis a 2-m XE-60 column was used.

Reduction of 1-Hexene with Cp_3Sm/NaH

The reactor was a 3-ml Schlenk tube with a Teflon stopcock and a stirring bar. The reactor 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. 1-Hexene (6.0 μl, 0.048 mmol) and 0.64 ml of THF were syringed into the Schlenk tube and the stopcock was closed. The reaction mixture was allowed to warm to room temperature and reaction was carried out at 45 °C with stirring. The amount of n-hexane was determined at intervals of 4, 8, 12, 24, 48 and 72 h.

Reduction of 1-Hexene with ($C_5H_4CH_2CH_2OCH_2CH_2C_5H_4$)YCl (A) and NaH

Complex **A** [9] (25.5 mg, 0.0786 mmol) and 3.8 mg (0.158 mmol) of NaH were allowed to react with 9.85 μl (0.0786 mmol) of 1-hexene in 0.96 ml of THF in a 2-ml Schlenk tube with a Teflon stopcock and a stirring bar at 45 °C. The amount of hexane was determined at intervals of 12, 24, 48 and 72 h.

Catalytic Hydrogenation of 1-Hexene by A/NaH

Complex **A** (10.2 mg, 0.0314 mmol) and 4.2 mg (0.175 mmol) of NaH were allowed to react with 39.4 μl (0.314 mmol) of 1-hexene in 1 ml of THF in a 100-ml glass reaction vessel equipped with a stirring bar. The vessel was attached to a vacuum line, cooled to −196 °C and evacuated and then filled with H_2 and sealed. The reaction mixture was stirred for 96 h at 45 °C. Products were analysed by GC–MS and determined by GC to contain 75% n-hexane and 25% 1-hexene.

Reduction of 1-Hexene with [$C_5H_4(CH_2)_3C_5H_4$]LaCl·THF/NaH

[$C_5H_4(CH_2)_3C_5H_4$]LaCl·THF [10] (27.65 mg, 0.066 mmol), 5.5 mg (0.23 mmol) of NaH, 4.2 μl (0.033 mmol) of 1-hexene and 0.42 ml of THF were added to a Schlenk pear flask with a Teflon stopcock and stirring bar, under the protection of argon. Then the Teflon stopcock was closed and the reaction mixture was allowed to heat to 70 °C. Products were identified by GC–MS and determined by GC.

---

*For part XV see ref. 15.

**Project supported by the National Natural Science Foundation of China. Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

†Author to whom correspondence should be addressed.

0020-1693/87/$3.50

Results and Discussion

Reduction of 1-hexene with Cp_3Ln/NaH in THF at 45 °C affords hexane after hydrolysis. The yield of hexane is dependent on Cp_3Ln. The results are depicted in Table I. From Table I, it is found that the activity for 1-hexene reduction with Cp_3Ln/NaH depends strongly 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 activity of nine tricyclopentadienyl lanthanide complexes decreases 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 Cp_3Yb the lowest. The order of reduction activity of seven Cp_3Ln is in agreement with that of decreasing size of radius of rare earth ion Ln^{3+}, except for the variable valency elements Sm^{3+} and Yb^{3+}. Furthermore, 1-hexene cannot be reduced by either Cp_3Ln or NaH alone.

This indicates that the selectivity for 1-hexene reduction by early lanthanides Cp_3Ln is higher than that of heavy lanthanides. For example, in the course of 72 h the selectivity for 1-hexene reduction by Cp_3La is 93%, but the yields of hexane and 2-hexene are nearly equal for Cp_3Er and Cp_3Lu. Cp_3Sm shows not only high activity but also prominent selectivity for 1-hexene reduction. Thus Cp_3Sm is the best reducing agent among the nine Cp_3Ln complexes. This also reveals that the heavy rare earth complexes may probably be used as catalysts for the isomerization of 1-hexene.

The reactivity of a new system of $(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)YCl$/NaH was studied. It was found that this system can reduce an alkene to an alkane in THF at 45 °C. The reducing rate of alkenes with this system depends strongly on the position of the carbon–carbon double bond in the alkenes. Thus the following reactivity order has been established: 1-hexene ≫ 2-hexene > cyclohexene. The influence of the variation of molar ratio in this system on its reactivity for 1-hexene was investigated. The results are listed in Table II. When the molar ratio of **A**:NaH: 1-hexene is changed from 2:7:1 to 1:2:1, no change in the reactivity of this system for 1-hexene reduction is observed. But the reactivity of this system apparently decreases when the molar ratio is equal to 1:1:1. Moreover, this system also isomerizes some 1-hexene to 2-hexene (*trans:cis* = 3:1) at the same time as reducing 1-hexene. This indicates that the reduction and isomerization are competitive reactions in this system.

The influence of the π-ligand on the reactivity of the system L_2YCl/NaH [$L_2 = (C_5H_5)_2$ (**D**) [11], $(CH_3C_5H_4)_2$ (**C**) [11], $[C_5H_4(CH_2)_5C_5H_4]$ (**B**) [12], $[C_5H_4CH_2CH_2OCH_2CH_2C_5H_4]$ (**A**)] was also investigated. The results are listed in Table III. They show that the reactivity of L_2YCl/NaH depends greatly on the π-ligand of complexes under the same reaction conditions, and the reactivity of this system decreases in the following order: **A** > **C** > **D** ≫ **B**. The result may be related to the solubility of these complexes in THF. Although the reactivity of the **C**/NaH and **D**/NaH systems is lower than that of **A**/NaH, their selectivity for 1-hexene reduction is 100%.

From the above results we envisioned that the **A**/NaH system may be used as a catalyst for hydrogenation of olefins due to its higher activity. Indeed, this system is able to catalyze the hydrogenation of 1-hexene. The results are listed in Table IV. No isomerization is observed in the presence of H_2, but in the absence of H_2, 2-hexene is obtained and the conversion of 1-hexene is low.

Moreover, another system, $[C_5H_4(CH_2)_3C_5H_4]$-MX·THF [10] and NaH, is also able to reduce 1-hexene to generate n-hexane in good yield. The yield of hexane varies greatly from complex to complex as metals and/or ligands are changed. The influences of rare earth metals and σ-ligand on the yield of hexane are listed in Table V. The hexane yields strongly depend on the rare earth metals in the complexes. It is worth mentioning that the decreasing order of hexane is in good agreement with the decreasing size of the radii of the rare earth ion. Because the ionic radii of dysprosium, yttrium and erbium are close to each other, these complexes have little influence on

TABLE I. Reduction of 1-Hexene with Cp_3Ln/NaH[a]

Time (h)	Yield (%) of hexane[b] for Ln in Cp_3Ln								
	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(7)	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 figures in parentheses denote the yield of 2-hexene.

TABLE II. Results of A/NaH Reaction with 1-Hexene (45 °C)

A:NaH:1-hexene (mol)	Yield (%) [hexane (2-hexene)[a]] after time (h)			
	12	24	48	72
2:7:1	39(23)	63(23)	64(34)	65(34)
1:7:1	30(24)	50(27)	60(27)	65(30)
1:4:1	28(24)	40(24)	60(26)	65(31)
1:2:1	27(27)	43(29)	63(32)	65(31)
1:1:1	15(trace)	32(8)[b]	38(10)[b]	43(10)[b]

[a] *trans*:*cis* = 3:1. [b] *trans*:*cis* = 1:1.

TABLE III. The Effect of π-Ligands on Reduction of 1-Hexene[a]

L_2YCl	Yield of hexane (%) after time (h)			
	12	24	48	72
$(C_5H_5)_2YCl$ (D)	8	18	29	34
$(CH_3C_5H_4)_2YCl$ (C)	12	26	38	44
$(C_5H_4(CH_2)_5C_5H_4)YCl \cdot THF$ (B)	0	0	0	0
$(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)YCl$ (A)	27(27)[b]	43(29)[b]	63(32)[b]	65(31)[b]

[a] L_2YCl:NaH:1-hexene = 1:2:1 (mol). [b] 2-Hexene, *trans*:*cis* = 3:1.

TABLE IV. Catalytic Hydrogenation of 1-Hexene[a]

A:NaH:1-hexene (mol)	Time (h)	Cat.% (mol)	Yield (%)
1:4:2	136	50	82
1:4:3.3	136	30	85
1:4:5	136	20	84
1:5.3:5	96	20	87
1:5.6:10	96	10	75
[b] 1:4:3.3	136	30	37[c]

[a] 4 atm of H_2, 45 °C. [b] Absence of H_2. [c] Mixture of hexane and 2-hexene.

TABLE V. The Effect of Rare Earth Metals and σ-Ligands on the Reduction of 1-Hexene[a]

Complex[b]	Temperature (°C)	n-Hexane yield (%) over time (h)		
		24	48	72
$L'_2LaCl \cdot THF$	70	73	80	81
$L'_2DyCl \cdot THF$	70	42	59	63
$L'_2ErCl \cdot THF$	45	15	17	21
$L'_2ErCl \cdot THF$	70	35	46	56
$L'_2YCl \cdot THF$	70	42	47	54
$L'_2LuCl \cdot THF$	70	5	6	9
$L'_2YCMe_3 \cdot THF$	70	18	33	39
$L'_2LaCMe_3 \cdot THF$	45	7	10	13
$L'_2LaCMe_3 \cdot THF$	70	32	43	55
$L'_2LaCH_2CMe_3 \cdot THF$	70	18	19	21
$L'_2LaC_6H_5 \cdot THF$	70	2	4	10
$L'_2LaC_6H_4CH_3\text{-}p \cdot THF$	70	2	3	5
$L'_2LaOOCCF_3 \cdot THF$	70	0	0	0

[a] Ln:NaH:1-hexene = 2:7:1 (molar ratio), THF. [b] $L'_2 = C_5H_4(CH_2)_3C_5H_4$.

the rate. The ionic radius of lanthanum is the largest among the above five ions, so its reducing ability for 1-hexene is the highest. The influence of σ-ligands in rare earth complexes on the reduction of alkenes has not been reported yet. We found that σ-ligands in $[C_5H_4(CH_2)_3C_5H_4]LaX \cdot THF/NaH$ affect strongly the reducing ability of complexes for 1-hexene. Reduction does not occur at all for the trifluoroacetyl complex; moreover for phenyl and tolyl complexes the reducing rate is quite low compared with the corresponding chloride complex. Hence, the reducing ability of σ-ligands in rare earth complexes decreases in the order of $Cl > Me_3C > Me_3CCH_2 > C_6H_5 > C_6H_4CH_3\text{-}p \gg CF_3COO$. Lanthanum oxide, chloride and acetyl-acetonate complexes cannot reduce 1-hexene under analogous reaction conditions. The reactivities of rare earth complexes depend not only on the central metals but also on the σ-ligands, therefore the f-transition metals are similar to d-transition metals to some extent.

A probable mechanism for the formation of organolanthanide hydrides by the reaction of the organolanthanide complexes with NaH, followed by the coupling of olefin and hydride insertion via a 'four-center' [6] generating M—C σ-bond is proposed for the reduction of olefins. The neutral dimeric dicyclopentadienyllutetium hydride was successfully prepared by the reaction of $(C_5H_5)_2LuCl$ with NaH, supporting the postulated mechanism for the formation of hydride [1, 13, 14].

Conclusions

Reduction of alkenes with Cp_3Ln/NaH, L_2YCl/NaH and $L'_2MX \cdot THF/NaH$ systems has been studied. The reductive activities of the systems depend strongly on the ionic radius of the trivalent rare earth ion, and the π- and σ-ligands in organolanthanide complexes. For Cp_3Ln/NaH systems, early lanthanides exhibit higher selectivity for 1-hexene reduction than heavy lanthanides. The reducing rate of the $(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)YCl/NaH$ system for different olefins was found to decrease in the order of 1-hexene $\gg$ 2-hexene $>$ cyclohexene. It is worth noting that the $(C_5H_4CH_2CH_2OCH_2CH_2\text{-}C_5H_4)YCl/NaH$ system is able to catalyse the hydrogenation of an alkene.

References

1 C. Qian, D. Deng, Z. Zhang and C. Ni, *Organometallics,* submitted for publication.
2 W. J. Evans, J. H. Meadows, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc., 106,* 1291 (1984).
3 W. J. Evans, J. H. Meadows, W. E. Hunter and J. L. Atwood, *Organometallics., 2,* 1252 (1983).
4 G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc., 107,* 8103 (1985).
5 G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc., 107,* 8091 (1985).
6 G. Jeske, H. Lauke, H. Mauermann, H. Schumann and T. J. Marks, *J. Am. Chem. Soc., 107,* 8111 (1985).
7 C. Qian, C. Ye, H. Lu, Y. Li, J. Zhou, Y. Ge and M. Tsutsui, *J. Organomet. Chem., 247,* 161 (1983).
8 J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc., 78,* 42 (1956).
9 C. Qian, Z. Xie and Y. Huang, *J. Organomet. Chem., 323,* 285 (1987).
10 C. Qian, C. Ye and Y. Li, *J. Organomet. Chem., 302,* 171 (1986).
11 R. E. Maginn, S. Manastyrskyj and M. Dubeck, *J. Am. Chem. Soc., 85,* 672 (1963).
12 C. Qian, Z. Xie and Y. Huang, *Inorg. Chim. Acta, 139,* 195 (1987).
13 P. Cáubere, in F. L. Boschke (ed.), 'Topics in Current Chemistry: Organic Chemistry', Vol. 73, Springer-Verlag, Berlin/Heidelberg/New York, 1978, p. 106.
14 H. Schumann and G. Jeske, *Angew. Chem., 97,* 208 (1985).
15 X. You, W. Wu, C. Li, Z. Li and C. Qian, *Acta Phys. Chim. Sin.,* in press.