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Studies on organolanthanide complexes

XXXV *. Synthesis and reactivity of new organo rare earth hydrides

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Abstract

Four new organo rare earth hydrides $[(CH_2)_3Cp_2LnH(THF)]_2$ ($Cp = C_5H_4$; Ln = Y, Dy, Er, Lu) were synthesized by the hydrogenolysis of the corresponding t-butyl complexes. They were characterized by elemental analyses, IR, MS and ^1H NMR spectroscopy. The reduction and catalytic hydrogenation of 1-hexene by the hydrides were also studied.

Introduction

Organometallic hydrides are important reagents and catalysts in a variety of chemical reactions, therefore research on organometallic hydrides is very active and constantly occupies chemists' attention. Organo *d*-block transition metal and main group metal hydrides have been extensively studied over the last twenty five years, but the first successful synthesis of crystallographically characterized organo yttrium hydride complex was only reported in 1982 [1]. Since then, other kinds of rare earth hydride involving cyclopentadienyl and substituted cyclopentadienyl ligand successively, appeared [2–6]. Only a few examples of bridged dicyclopentadienyl rare earth hydride were known [3,7], moreover the bridges reported in the literature consisted of a silicon atom instead of a carbon atom. 1,1′-Trimethylene bridged dicyclopentadienyl lanthanide chloride, phenylethynyl and t-butyl complexes were previously reported by Tsutsui and our group [8–10]. In the present contribution, we consider this bridged dicyclopentadienyl ligand, 1,1′-trimethylenedicyclopentadienyl, which involves exclusively carbon atims to link two cyclopentadienyls, synthesizing its rare earth hydride complexes, $[(CH_2)_3Cp_2LnH(THF)]_2$ ($Cp = C_5H_4$; Ln = Y, Dy, Er, Lu). The reduction and catalytic hydrogenation of 1-hexene by these hydrides are also investigated.

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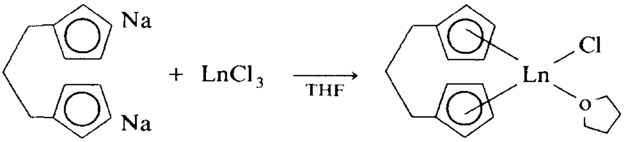
Results and discussion

1,1′-Trimethylenedicyclopentadienyl(t-butyl)lanthanide and yttrium tetrahydrofuran solvated complexes [10] react with hydrogen in toluene at room temperature to afford a new sort of organo rare earth hydride as depicted in eqs. 1 to 3.

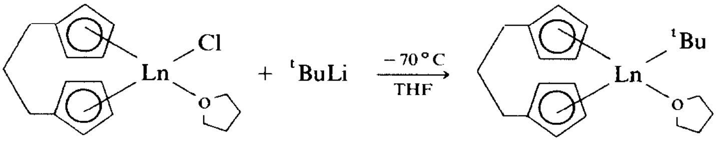
If the standard procedure from the literature is applied, namely the isolation in the solid state of t-butyl complexes, the expected hydride complexes cannot be obtained according to eq. 3 due to the very low concentration of solid t-butyl complexes in toluene. Therefore an improved procedure was introduced in the hydrogenolysis reaction. The purified toluene solution of t-butyl complex, which was prepared from the corresponding chloride in tetrahydrofuran solution and t-butyl lithium [9,10], was directly reacted with hydrogen to generate the desired hydrides under mild conditions (eq. 3). Thus we succeeded in synthesizing the carbon chain bridged dicyclopentadienyl rare earth hydrides for the first time. No dysprosium hydride containing an organic ligand has been reported in the literature until now, therefore this is the first example of organo dysprosium hydride. The data of four hydrides obtained are listed in Table 1.

Because the yield for hydrogenolysis reaction (eq. 3) cannot be calculated, the yields listed in Table 1 are overall yields based on the original starting material $LnCl_3$, from which three steps are required to generate hydrides. The elemental analyses are consistent with the structures. All hydrides are quite sensitive to air and moisture. They cannot sublime even under extremely low pressure and higher temperature. The solubilities of the four hydrides in THF or toluene very low which preclude characterization by other techniques.

The mass spectra of the hydrides are listed in Table 2. Tetrahydrofuran ion peak was present in all hydrides. All except erbium hydrides showed $[M-1]^+$ and



(1)



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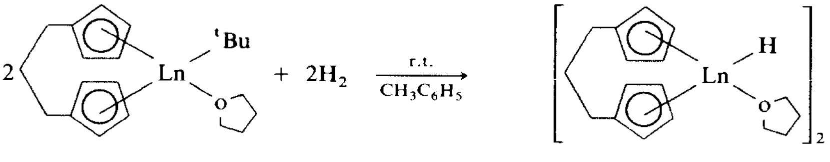

(3)

(Ln = Y (**1**), Dy (**2**), Er (**3**), Lu (**4**))

Table 1

Data of $[(CH_2)_3Cp_2LnH(THF)]_2$

Hydride	Color	Yield [a] (%)	m.p. [b] (°C)	Elemental Analysis (Found (calcd.) (%))		
				C	H	M
$[LYH(THF)]_2$ (**1**) [c]	white	25	162–164	60.90 (61.45)	6.69 (6.98)	26.54 (26.76)
$[LDyH(THF)]_2$ (**2**)	pale yellow	19	160–162	49.92 (50.31)	5.60 (5.71)	40.22 (40.04)
$[LErH(THF)]_2$ (**3**)	pink	30	177–180	49.92 (49.72)	5.28 (5.65)	41.08 (40.73)
$[LLuH(THF)]_2$ (**4**)	white	18	175–177	48.22 (48.81)	5.16 (5.54)	41.69 (41.83)

[a] Based on $LnCl_3$. [b] Decomposition. [c] $L = (CH_2)_3Cp_2$.

$[M - THF - 1]^+$ ion peaks, moreover dysprosium hydride gave $[2M - 1]^+$ and $[2M - 2THF - 1]^+$ ion peaks. These results indicate the metal–hydrogen and metal–oxygen bonds are very weak and first to cleave under the mass spectra conditions. The appearances of $[2M - 1]^+$ and $[2M - 2THF - 1]^+$ for dysprosium

Table 2

Mass spectra of $[(CH_2)_3Cp_2LnH(THF)]_2$ [a]

Characteristic ions	Y (**1**)	Dy (**2**)	Er (**3**)	Lu (**4**)
$[2M-1]^+$ [b]		813 [c] (0.92) [d]		
$[2M-2C_4H_8O-1]^+$		669 (0.94)		
$[>M]^+$	553 (0.87)		504 (3.00)	543 (1.23)
$[M-1]^+$	331 (0.85)	406 (0.68)		417 (0.36)
$[M-C_4H_8O-1]^+$	259 (0.78)	334 (0.83)		345 (2.13)
$[C_5H_5(CH_2)_3C_5H_5+1]^+$				173 (16.28)
$[C_5H_5(CH_2)_3C_5H_5]^+$	172 (2.14)	172 (2.12)	172 (6.00)	
$[C_4H_8O]^+$	72 (29.68)	72 (32.68)	72 (14.62)	72 (23.53)
$[C_5H_6]^+$	66 (6.40)	66 (8.45)	66 (11.89)	66 (33.21)
$[CH_3CH_2CH_3]^+$	44 (6.86)	44 (3.44)		44 (15.79)
$[CH_3CH_2CH_2]^+$			43 (100.00)	
$[CH_2CH_2CH_2]^+$	42 (100.00)	42 (100.00)		42 (100.00)

[a] Recorded at EI, T = 50–300 °C, EM = 1.3 kV. [b] M = monomer. [c] *m/e*, based on the largest abundance of isotopes. [d] Relative intensity.

hydride as well as $[>M]^+$ for the other three hydrides imply that these hydrides are obtained as tetrahydrofuran solvated dimers.

The IR spectral features of these hydrides are very similar. The characteristic absorption peaks of cyclopentadienyl, methylene and tetrahydrofuran vary slightly with the ionic radius of rare earth metals. The characteristic absorption peaks of the coordinated tetrahydrofuran appear at about 896–897 and 1033 cm^{-1}. Evans assigned the 1315 cm^{-1} peak to the characteristic absorption of yttrium–hydrogen bond for $[(C_5H_4)_2YH(THF)]_2$ [1]. Therefore, the strong absorption peak at 1302 cm^{-1} is tentatively assigned to the characteristic absorption of yttrium–hydrogen bond for yttrium hydride. It is difficult to assign the characteristic absorption of metal–hydrogen bond for other three hydrides because of the overlap of absorption peaks.

The ^1H NMR of complexes **1** and **4** were measured using perdeuterotetrahydrofuran as solvent. The ^1H NMR spectra of **4** contain resonances at δ 5.62 and 5.72 assignable to C_5H_4, at δ 1.59 and 3.42 assignable to THF, at δ 2.48 assignable to CH_2 and δ 4.02 assignable to LuH. In addition to the characteristic resonances of C_5H_4, CH_2 and coordinated THF, the spectrum of yttrium hydrides **1** contains a triplet at 2.16 ($J(YHY) = 23.8$ Hz) due to coupling to two equivalent yttrium atoms. Therefore the ^1H NMR data of yttrium hydride supply evidence for a dimeric structure.

All hydrides are able stoichiometrically to reduce 1-hexene as depicted in eq. 4. The hydride reacted with 1-hexene in THF to give the σ-hexyl complex intermediate, then the σ-hexyl complex was hydrolyzed by water generating n-hexane.

$$[(CH_2)_3Cp_2LnH(THF)]_2 + CH_2{=}CH(CH_2)_3CH_3 \xrightarrow[THF]{\Delta} [(CH_2)_3Cp_2Ln\text{-hexyl}] \xrightarrow[H_2O]{} CH_3(CH_2)_4CH_3 \quad (4)$$

Data pertaining to the reduction of 1-hexene are set out in Table 3. The reactivities of hydrides decrease in the order: $[LLuH(THF)]_2 > [LErH(THF)]_2 > [LYH(THF)]_2 > [LDyH(THF)]_2$.

The change in the yield of n-hexane with temperature indicates that the higher reaction temperature benefits the reduction of 1-hexene. 12 h reaction time seems to

Table 3

Reduction of 1-hexene by $[(CH_2)_3Cp_2LnH(THF)]_2$

Hydride	Temperature (°C)	Time (h)	Solvent	Yield [b] (%)
$[LDyH(THF)]_2$ [a]	70	24	THF	38
$[LYH(THF)]_2$	70	24	THF	56
$[LYH(THF)]_2$	45	24	THF	28
$[LErH(THF)]_2$	70	6	THF	57
$[LErH(THF)]_2$	70	12	THF	82
$[LErH(THF)]_2$	70	24	THF	81
$[LLuH(THF)]_2$	70	6	THF	52
$[LLuH(THF)]_2$	70	12	THF	83
$[LLuH(THF)]_2$	70	24	THF	87
$[LLuH(THF)]_2$	70	24	$CH_3C_6H_5$	80

[a] $L = (CH_2)_3Cp$. [b] Based on 1-hexene.

Table 4

Catalytic hydrogenation of 1-hexene

Hydride [a]	Temperature (°C)	Time (h)	Solvent	$\frac{\text{Product}}{\text{Hydride}}$ [b]
$[LDyH(THF)]_2$ [c]	60	24	THF	2.0
$[LYH(THF)]_2$	60	24	THF	2.4
$[LErH(THF)]_2$	60	24	THF	3.0
$[LLuH(THF)]_2$	60	24	THF	2.6
$[LLuH(THF)]_2$	70	24	THF	2.7
$[LLuH(THF)]_2$	60	24	$CH_3C_6H_5$	1.8
$[LLuH(THF)]_2$	r.t.	24	THF	0
$[LLuH(THF)]_2$	60	4	THF	0.6

[a] Hydride : 1-hexene = 1 : 10 (molar ratio). [b] molar ratio. [c] $L = (CH_2)_3Cp_2$.

be enough to complete the reaction. Using toluene as solvent, a similar yield was obtained. It is worth mentioning that the reduction with various hydrides may take place easily in a solvent with strong coordination ability. This behaviour is similar to that of $[(C_5H_4R)_2YH(THF)]_2$ [11], but it is different from that of $[(C_5Me_5)_2NdH]_2$ which reacted with 1-hexene in cyclohexane [3]. The reducing activity of the hydrides obtained also demonstrates the existence of metal–hydrogen bond.

The hydrides, $[(CH_2)_3Cp_2LnH(THF)]_2$, are also capable of catalyzing the hydrogenation of 1-hexene (eq. 5).

$$CH_2{=}CH(CH_2)_3CH_3 + H_2 \xrightarrow[{[(CH_2)_3Cp_2LnH(THF)]_2}]{THF} CH_3(CH_2)_4CH_3 \qquad (5)$$

Table 4 lists the hydrogenation data of 1-hexene catalyzed by the hydrides. The catalytic abilities of different hydrides are nearly the same. The higher reaction temperature leads to only a little enhancement of yield. Tetrahydrofuran appears to be better than toluene as a solvent. If the reaction was performed at room temperature, no n-hexane was detected. The significantly low solubilities of hydrides in organic solvents probably leads to the limited catalytic activities compared with $[(C_5Me_5)_2NdH]_2$ [3]. The catalytic activity indicates the presence of Ln–H bond, although the catalytic activity is not high. The most likely pathway for the catalytic hydrogenation of 1-hexene is proposed as follows. After the dissociation of dimeric hydride to monomer, the olefin then coordinates to the hydride, subsequent insertion generates the Ln–C σ-bond intermediate. The hydrogenolysis of Ln–C σ-bond forms [LLnH] again and 1-hexane.

Experimental

All operations were carried out under prepurified argon by use of Schlenk techniques or in a glovebox. All solvents were refluxed and distilled either over finely divided $LiAlH_4$ or over blue sodium benzophenone under argon immediately before use. 1-Hexene was treated with Na/K alloy, dried and then distilled under argon. Reductive products were determined by gas chromatography-mass spectra (GC-MS) on a Finnigan 4021 GC-MS. Gas chromatographic analysis was carried out on a 102-G gas chromatographic instrument utilizing a 4-m PEG-1000 column.

Melting points were determined in sealed argon-filled capillaries and were uncorrected. Infrared spectra were recorded on Perkin–Elmer 983 Spectrometer with Nujol and Fluorolube mulls and were examined between disc-shaped CsI crystals, the mulls were prepared in an argon-filled glove box. Mass spectra were recorded on a Finnigan 4021 Spectrometer. ^{1}H NMR were performed on a FX-90Q (90 MHz) Spectrometer and referenced to external Me_4Si in THF-d_8. THF-d_8 (E. Merck for NMR spectroscopy) was dried over Na/K alloy and was degassed by freeze-thaw cycles on a vacuum line.

Analyses of rare earth metals were accomplished using a direct complexometric titration procedure with disodium EDTA. Carbon and hydrogen analyses were determined by the combustion method in an aluminium tube.

$[(CH_2)_3Cp_2YH(THF)]_2$ (1)

Anhydrous YCl_3 (3.02 g, 15.4 mmol) reacted with $(CH_2)_3Cp_2Na_2$, followed by the reaction of resulting chloride with an equivalent t-butyl lithium to generate a toluene solution of $(CH_2)_3Cp_2Y(^tBu)(THF)$ according to the procedure we described previously [9]. The toluene solution of $(CH_2)_3Cp_2Y(^tBu)(THF)$ was transferred to a 100-ml glass reaction vessel equipped with a Teflon stopcock and a stirring bar. Then the vessel was attached to a vacuum line, cooled to −78° C, and evacuated. An atmospheric pressure of H_2 was established and the vessel was closed. As the solution slowly warmed, a fine white powder deposited. After the mixture was stirred overnight at ambient temperature, the precipitate was separated, washed with hexane then dried in vacuo to give a white precipitate (1.28 g, 25%). IR (cm^{-1}): 250w, 300w, 380m, 576m, 610m, 676m, 776s, 817m, 897m, 1016m, 1033m, 1302s, 1365m, 1437m, 1602w, 2839m, 2880m, 2927s, 3063m. ^{1}H NMR (ppm): 1.63 (m), 3.47 (m), C_4H_8O; 5.61 (m), 5.73 (m), C_5H_4; 2.52 (m), CH_2; 2.16 (t, $J(YHY) = 23.8$ Hz) YH.

$[(CH_2)_3Cp_2DyH(THF)]_2$ (2)

$[(CH_2)_3Cp_2DyH(THF)]_2$ was synthesized in an analogous manner to that described for **1**. IR (cm^{-1}): 248w, 298w, 388m, 575m, 606m, 673m, 768s, 820m, 896m, 1020m, 1033m, 1363m, 1439m, 1598w, 2840m, 2882m, 2917s, 3061m.

$[(CH_2)_3Cp_2ErH(THF)]_2$ (3)

$[(CH_2)_3Cp_2ErH(THF)]_2$ was synthesized in an analogous manner to that described for **1**. IR (cm^{-1}): 247w, 300w, 376m, 575m, 610m, 676m, 774s, 818m, 897m, 1013m, 1033m, 1365m, 1439m, 1600w, 2841m, 2883m, 2925s, 3061m.

$[(CH_2)_3Cp_2LuH(THF)]_2$ (4)

$[(CH_2)_3Cp_2LuH(THF)]_2$ was synthesized in an analogous manner to that described for **1**. IR (cm^{-1}): 243w, 298w, 386m, 580m, 605m, 674m, 774s, 819m, 897m, 1020m, 1033m, 1364m, 1437m, 1600w, 2842m, 2884m, 2923s, 3062m. ^{1}H NMR (ppm): 1.59 (m), 3.42 (m) C_4H_8O; 5.62 (m), 5.75 (m), C_5H_4; 2.48 (m), CH_2; 4.02 (s), LuH.

Reduction of 1-hexene

$[(CH_2)_3Cp_2LuH(THF)]_2$ (93.4 mg, 0.112 mmol), 1-hexene (14 μl, 0.112 mmol) and tetrahydrofuran (1.4 ml) were added to a Schlenk pear-shaped flask with a Teflon stopcock and a stirring bar. Then the reaction mixture was heated and stirred. The products were identified by GC-MS and determined by GC. Similar procedures were applied to the reduction of 1-hexene using other organo rare earth hydrides.

Catalytic hydrogenation of 1-hexene

$[(CH_2)_3Cp_2YH(THF)]_2$ (56.6 mg, 0.085 mmol), 1-hexene (213 μl, 1.7 mmol) and tetrahydrofuran (5 ml) were added to a 150-ml glass reaction flask equipped with a Teflon stopcock and a stirring bar. The flask was attached to a vacuum line, cooled to $-196°$C, evacuated and then filled with H_2. After the flask had been closed, the reaction mixture was heated and stirred. The products were identified by GC-MS and determined by GC. The hydrogenation reactions catalyzed by other hydrides were performed in a similar way.

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References

1 W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 104 (1982) 2008.
2 W.J. Evans, I. Bloom, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 105 (1983) 1401.
3 G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann and T.J. Marks, J. Am. Chem. Soc., 107 (1985) 8103.
4 H. Schumann, W. Genthe and E.Hahn, J. Organomet. Chem., 299 (1986) 67.
5 M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, J. Am. Chem. Soc., 109 (1987) 203.
6 C. Qian, D. Deng, C. Ni and Z. Zhang, Inorg. Chim. Acta, 146 (1988) 129.
7 E. Bunel, B.J. Burger and J.E. Bercaw, J. Am. Chem. Soc., 110 (1988) 976.
8 J. John and M. Tsutsui, J. Coord. Chem., 10 (1980) 177.
9 C. Qian, C. Ye and Y. Li, J. Organomet. Chem., 302 (1986) 171.
10 C. Qian, C. Ye, H. Lu, Y. Li and Y. Huang, J. Organomet. Chem., 263 (1984) 333.
11 W.J. Evans, J.H. Meadows, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 106 (1984) 1291.
12 C. Qian, D. Zhu and Y. Gu, J. Mol. Catal., 63 (1990) L1.