STUDIES ON ORGANOLANTHANIDE COMPLEXES

XII *. SYNTHESIS, IDENTIFICATION AND REACTIVITY OF ORGANO-LANTHANIDE AND -YTTRIUM CHLORIDES WITH THE CHELATING 1,1'-(3-OXA-PENTAMETHYLENE)DICYCLOPENTADIENYL LIGAND

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Summary

Seven new 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl lanthanide and yttrium chlorides, $(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)LnCl$ (Ln = Nd, Gd, Ho, Er, Yb, Lu and Y) were synthesized by using 1,1'-(3-oxa-pentamethylene)biscyclopentadienyl as ligand. Disproportionation of dicyclopentadienyl neodymium chloride is thus successfully prevented, and a stable early lanthanocene chloride is obtained. All seven complexes are unsolvated monomers, containing an intramolecular coordination bond. Their structures were verified by elemental analyses, and IR, MS, XPS, ^1H NMR and ^{13}C NMR spectroscopy. They are readily soluble in various solvents and more stable towards air and moisture than other related complexes without an intramolecular coordination bond. The complex/NaH system hydrogenates 1-hexene catalytically in hydrogen.

Introduction

In order to prevent disproportionation of dicyclopentadienyl early lanthanide chlorides, bridged dicyclopentadienyl [1–4] or bulky pentamethylcyclopentadienyl [5,6] have been used as ligands. But in either case solvated or anionic coordination products were obtained so as to achieve coordination saturation. However, no report has been published, concerning the heteroatom-containing bridged dicyclopentadienyl as a ligand, which prevents disproportionation on one hand and forms an intramolecular coordination bond for satisfy the requirement of coordination saturation on the other.

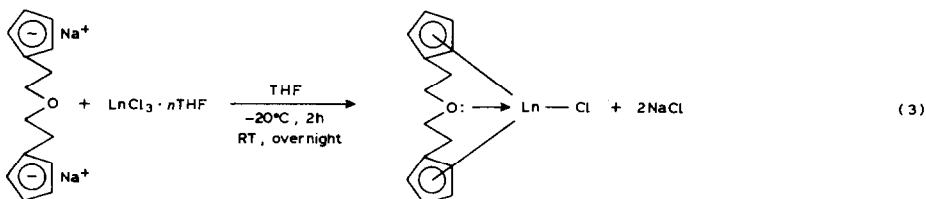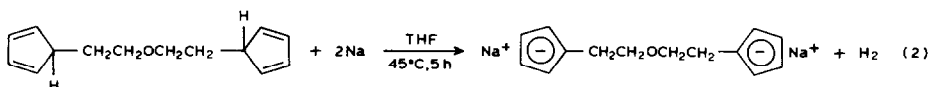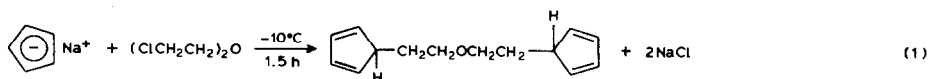Herein, we would like to report the first example of an oxygen-containing

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* Part XI. see ref. 17; Part X. see ref. 18.

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bridged dicyclopentadienyl as a ligand for synthesizing solvent-free neutral complexes. The new complexes have good solubility, higher stability and better reactivity.

Results and discussion

CpNa reacts with 2,2'-dichlorodiethyl ether in THF at $-10\,^{\circ}$C to give a new type of ligand — 1,1'-(3-oxa-pentamethylene)dicyclopentadiene, which reacts with an excess of sodium sand in THF at $45\,^{\circ}$C to yield 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt. It can be stored for one month in a moisture- and oxygen-free atmosphere. Because this ligand is extremely sensitive to the size of the lanthanide ion, a different reaction conditions are necessary for different lanthanide ions. For the mid lanthanide Gd^{3+} and light lanthanide Nd^{3+}, $LnCl_3 \cdot n$THF ($n = 2$, 3) must be used instead of solvent-free chlorides. The reactions are shown in eqs. 1–3.

$$
\begin{array}{c}
\text{Cp}^{-}\text{Na}^{+} + (\text{ClCH}_2\text{CH}_2)_2\text{O} \xrightarrow[1.5\,h]{-10^{\circ}C} \text{Cp}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{Cp} + 2\,\text{NaCl} \qquad (1)
\end{array}
$$

$$
\begin{array}{c}
\text{Cp}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{Cp} + 2\,\text{Na} \xrightarrow[45^{\circ}C,\,5\,h]{THF} \text{Na}^{+}\text{Cp}^{-}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{Cp}^{-}\text{Na}^{+} + \text{H}_2 \qquad (2)
\end{array}
$$

$$
\begin{array}{c}
\text{[ligand](Na}^{+})_2\text{O} + \text{LnCl}_3 \cdot n\text{THF} \xrightarrow[\substack{-20^{\circ}C,\,2h \\ RT,\,overnight}]{THF} \text{O:} \rightarrow \text{Ln}-\text{Cl} + 2\,\text{NaCl} \qquad (3)
\end{array}
$$

$n = 2$, Ln = Nd (1)

$n = 3$, Ln = Gd (2)

$n = 0$, Ln = Ho (3) , Er (4) , Yb (5) , Lu (6) , Y (7)

The seven new complexes are all unsolvated monomers containing an intramolecular coordination bond. The elemental analyses are consistent with the structures. Although these complexes are still sensitive to air and moisture, their stabilities are much improved, when compared with the corresponding Cp_2LnCl and $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot OC_4H_8$ complexes. For example, when complex 4 was exposed to air for 45 min, no obvious hydrolysis was observed, as shown by the fact that the characteristic absorption peaks recorded with KBr pellets were fundamentally in accord with those of a sample prepared in a glovebox. All the complexes possess good thermal stability and do not sublime even under extremely low pressures.

Very little knowledge about mass spectra of organolanthanide complexes has appeared in the literature [7–9]. Our investigation of the MS(EI) spectra of Cp_2LnCl and $(CH_3C_5H_4)_2LnCl$ shows that they are dimers in the solid state and cyclopentadienyl is the fragment which is first cleaved [10]. On the other hand the mass spectrum of 1,1'-trimethylenebiscyclopentadienyl lanthanide chlorides gave only

some fragments [1]. Furthermore, we fortunately obtained the complete mass spectra of seven new complexes of which the major data are listed in Table 1. They all showed a parent molecular ion $[M]^+$ and related fragments including $[M - Cl]^+$, $[LnCl]^+$, Ln^+; and m/e larger than M^+ or equal to 72 or 71 did not appear. This indicates that they are solvent-free monomeric complexes and the Ln–Cl bond is probably first cleaved, giving very high relative intensity peaks of $[M - Cl]^+$, resulting from the intramolecular coordination bond.

Fragmentation of these complexes is shown in Scheme 1.

The coordination function of 2,2'-bipyridyl to Cp_2LnCl has been studied [11]. XPS of the complexes 1–7 were measured and the results are listed in Table 2. This shows that the binding energies of the rare earth metal atoms all decrease, and that those of Cl_{2p} are unchanged on complexation as compared with those in the dicyclopentadienyl rare earth chlorides, and that the binding energies of O_{1s} increase in these complexes compared with that in $Na^+(C_5H_4CH_2CH_2OCH_2CH_2$-$C_5H_4)Na^+$. Thus the lone pair of electrons of the oxygen atom in these complexes is partly transferred from oxygen to the rare earth metal centre. The scheme of electron transfer in the complexes can be shown as follows:
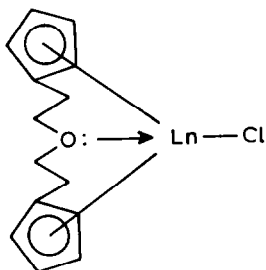
But there is no obvious relationship between the change in binding energy and radius of rare earth ion.

The IR spectra of complexes 1–7 were measured from 4000 to 50 cm^{-1}. The spectral features of these complexes are very similar. The IR spectrum of 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt was also measured from 4000 to 400 cm^{-1}.

The complexes exhibit five characteristic absorption peaks in the low frequency region, and the absorption peak at about 250 cm^{-1} was assigned to a characteristic absorption of π-bonded cyclopentadienyl group to Ln metal [12]. It is worth noting that the characteristic absorption of π-bonded complex 7 is shifted to 287 cm^{-1}, which is in accord with those of Cp_2YCl, $(CH_3C_5H_4)_2YCl$ and $[C_5H_4(CH_2)_3C_5H_4]YBu^t \cdot THF$ [3] reported in our previous work. However further investigation to decide whether the result is related to an f-orbital is necessary. The absorption peak at about 220 cm^{-1} may be the characteristic absorption of Ln–Cl bonds.

The characteristic absorption peaks due to cyclopentadienyl and ring-bridged 3-oxa-pentamethylene are evidently present. The characteristic cyclopentadienyl absorptions appear at 770, 1010, 1435 and 3080 cm^{-1} in the complexes, but at 722, 1003, 1464 and 3095 cm^{-1} in the disodium salt. The absorption peak of the C–O–C asymmetric stretching vibration, which shifts to lower frequency, lies between 33–37 cm^{-1}. It also implies that an intramolecular coordination bond is present [13]. Moreover, the characteristic absorption peaks of Cp are in relation to the type of bond between it and metal.

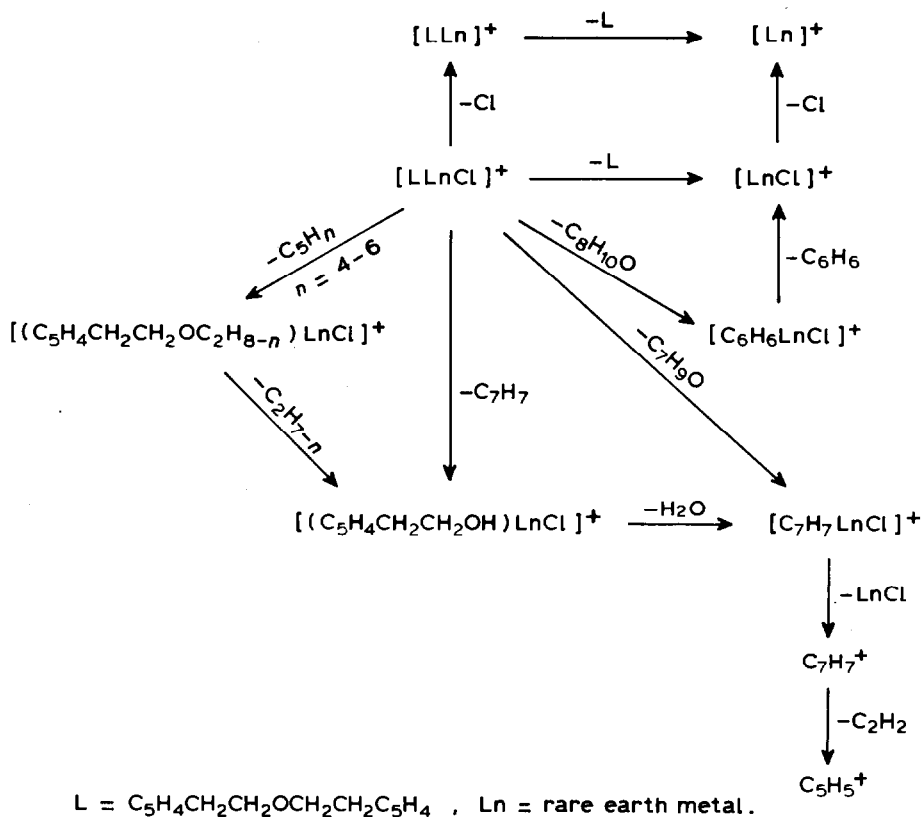TABLE 1

MASS SPECTRA OF COMPLEXES 1–7 [a]

Fragment	Complex (Ln) m/e (rel. intensity)						
	1 (Nd)	**2** (Gd)	**3** (Ho)	**4** (Er)	**5** (Yb)	**6** (Lu)	**7** (Y)
M^+	377 (1.21)	393 (42.48)	400 (56.15)	401 (39.38)	409 (30.63)	410 (41.76)	324 (33.83)
$[M-Cl]^+$	342 (9.51)	358 (59.15)	365 (100.0)	366 (49.85)	374 (30.92)	375 (100.0)	289 (27.52)
$[M-64]^+$	313 (1.39)	329 (25.12)	336 (0.90)	337 (26.53)	345 (2.39)	346 (0.30)	260 (0.30)
$[M-65]^+$	312 (1.00)	328 (8.62)	335 (6.50)	336 (27.08)	344 (1.77)	345 (1.70)	259 (4.10)
$[M-66]^+$	311 (1.69)	327 (32.74)	334 (43.54)	335 (31.18)	343 (8.25)	344 (9.91)	258 (28.22)
$[M-91]^+$	286 (0.41)	302 (10.82)	309 (11.51)	310 (12.46)	318 (0.91)	319 (4.10)	231 (3.80)
$[C_7H_7LnCl]^+$	268 (1.22)	284 (52.03)	291 (43.24)	292 (30.39)	300 (5.66)	301 (9.71)	215 (24.82)
$[C_6H_6LnCl]^+$	255 (0.58)	271 (18.62)	278 (11.61)	279 (8.88)	287 (1.26)	288 (4.10)	202 (9.41)
$[LnCl]^+$	177 (2.31)	193 (14.74)	200 (48.64)	201 (18.95)	209 (36.90)	210 (5.20)	124 (8.60)
Ln^+	142 (1.27)	158 (0)	165 (10.21)	166 (3.19)	174 (5.72)	175 (0.80)	89 (1.20)
$C_7H_7^+$	91 (18.10)	91 (100.0)	91 (36.83)	91 (100.0)	91 (62.30)	91 (28.32)	91 (20.22)
$C_4H_8O^+$	72 (0)	72 (0)	72 (0)	72 (0)	72 (0.53)	72 (0)	72 (0)
$C_5H_6^+$	66 (100.0)	66 (57.27)	66 (20.32)	66 (34.58)	66 (100.0)	66 (28.62)	66 (100.0)
$C_5H_5^+$	65 (0)	65 (49.49)	65 (21.82)	65 (33.50)	65 (79.54)	65 (25.12)	65 (71.47)

[a] Recorded at EI. T 50–300 °C, EM = 1.3 kV, based on the largest abundance of isotopes.

TABLE 2

BINDING ENERGY DATA (eV) FOR COMPLEXES AND Cp_2LnCl

Complex	O_{1s}		Ln_{4d}	
	B.E.	ΔE [a]	B.E.	ΔE [b]
$Na^+ C_5H_4CH_2CH_2OCH_2CH_2C_5H_4Na^+$	531.6			
1 (Nd)	532.4	+0.8	982.9 [c]	
2 (Gd)	532.6	+1.0	143.8	−0.1
Cp_2GdCl			143.9	
3 (Ho)	532.8	+1.2	163.4	−0.4
Cp_2HoCl			163.8	
4 (Er)	532.3	+0.7	170.0	−1.0
Cp_2ErCl			171.0	
5 (Yb)	532.4	+0.8	186.6	−0.5
Cp_2YbCl			187.1	
6 (Lu)	532.4	+0.8	9.6 [d]	−0.3
Cp_2LuCl			9.9 [d]	
7 (Y)	533.0	+1.4	158.0 [e]	−0.4
Cp_2YCl			158.4 [e]	

[a] $\Delta E = B.E.$ $(O_{1s}(1-7)) - 531.6$. [b] $\Delta E = B.E.$ $(Ln(2-7)) - B.E.$ $(Ln(Cp_2LnCl))$. [c] $Nd_{3d_{5/2}}$. [d] Lu_{4f}. [e] $Y_{3d_{5/2}}$.

$$[LLn]^+ \xrightarrow{\ -L\ } [Ln]^+$$

$$\uparrow -Cl \qquad\qquad \uparrow -Cl$$

$$[LLnCl]^+ \xrightarrow{\ -L\ } [LnCl]^+$$

$$\xleftarrow[n=4-6]{-C_5H_n} \qquad \xrightarrow{-C_8H_{10}O} \qquad \uparrow -C_6H_6$$

$$[(C_5H_4CH_2CH_2OC_2H_{8-n})LnCl]^+ \qquad\qquad [C_6H_6LnCl]^+$$

$$\searrow{-C_2H_{7-n}} \qquad \downarrow -C_7H_7 \qquad \swarrow{-C_7H_9O}$$

$$[(C_5H_4CH_2CH_2OH)LnCl]^+ \xrightarrow{-H_2O} [C_7H_7LnCl]^+$$

$$\downarrow -LnCl$$

$$C_7H_7^+$$

$$\downarrow -C_2H_2$$

$$C_5H_5^+$$

$$L = C_5H_4CH_2CH_2OCH_2CH_2C_5H_4 \ , \ Ln = \text{rare earth metal.}$$

SCHEME 1

Except for Lu^{3+} and Y^{3+}, the other five complexes are paramagnetic. Therefore, the ^1H NMR and ^{13}C NMR spectra of complexes 6, 7 and disodium salts were measured using perdeuterotetrahydrofuran as solvent. The results are listed in Tables 3 and 4, respectively. For comparison, the ^1H NMR and ^{13}C NMR data of related trimethylene and pentamethylene ring-bridged complexes are also listed in Tables 3 and 4.

Moreover, Tables 3 and 4 show that when the complexes are formed, the Cp signals shift to lower field, which indicates that negative charge of the ring is transferred to Ln^{3+}. The signals of hydrogen and carbon at positions 7 and 9 also shift to lower field and the four hydrogens at positions 7 and 9 exhibit two groups of equal proton peaks, indicating the presence of an intramolecular coordination bond, these hydrogens, however, are not homomagnetic.

Furthermore, the $\Delta\delta$ value implies the distribution of charge on cyclopentadienyl. The $\Delta\delta$ value changes from 0.40 to 0.07 in going from a trimethylene bridge to a pentamethylene bridge, which indicates that the flexibility of the chain in complex is increased. However, the decrease in flexibility of the chain, as revealed by the $\Delta\delta$, increases in the case of 3-oxa-pentamethylene which is contrary to that of the pentamethylene bridge [14]. The ^{13}C NMR spectra gave similar results.

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TABLE 3

^{1}H NMR PROTON SHIFT (δ, TMS, ppm, 25°C)

Complex	$(C_5H_4)_2$	$\Delta\delta$ [a]	6, 10-CH$_2$ 6', 8'-CH$_2$	7, 9-CH$_2$ 7'-CH$_2$	THF	Ref.
$(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)LuCl$ (6)	5.87	0.09	2.63	4.24		
	5.78			3.79		
$(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)YCl$ (7)	5.98	0.14	2.64	4.18		
	5.84			3.79		
$NaC_5H_4CH_2CH_2OCH_2CH_2C_5H_4Na$ (8)	5.33	0	2.62	3.58		
$[C_5H_4(CH_2)_5C_5H_4]LuCl\cdot THF$ [b] (9)	5.96	0.07	2.56	1.56 [c]	3.62	
	5.89				1.77	
$[C_5H_4(CH_2)_5C_5H_4]YCl\cdot THF$ [b] (10)	6.04	0.07	2.59	1.60 [c]	3.71	
	5.97				1.85	
$[C_5H_4(CH_2)_3C_5H_4]LuCl\cdot THF$ (11)	6.25	0.40	2.80	2.47	3.50	1
	5.85				1.63	
$[C_5H_4(CH_2)_3C_5H_4]LaCl$ [d] (12)	5.95	0.17				2
	5.78					
$[C_5H_4(CH_2)_3C_5H_4]LaBu^t\cdot THF$ (13)	5.76	0.16	2.33 [e]		3.43	3
	5.60				1.57	

[a] $\Delta\delta = \delta(2,5\text{-CH}) - \delta(3,4\text{-CH})$. [b] This work will be published in another paper. [c] 7,8,9-CH$_2$ overlap. [d] In THF. [e] 6',7',8'-CH$_2$ overlap.
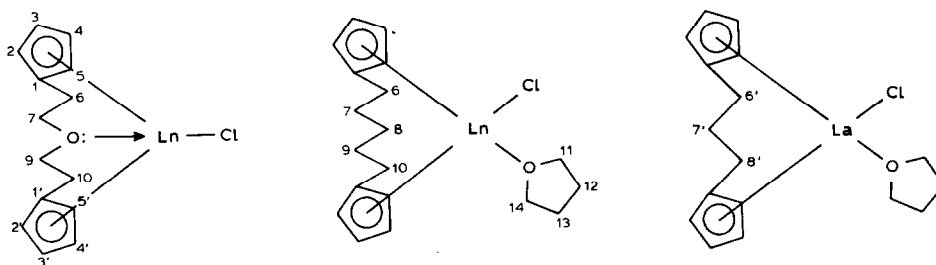
In the study of the protolysis reactions of complexes we found that the ^{1}H NMR spectra the products were in good agreement with that of 3-oxa-pentamethylene-dicyclopentadiene which polymerized partly at room temperature.

TABLE 4

^{13}C NMR CARBON SHIFT (δ, THF-d_8 = 26.7 ppm, 25°C)

Complex	C-1	C-2,5	C-3,4	C-6,10 C-6',8'	C-7,9	C-8 C-7'	C-11,14	C-12,13	Ref.
6	126.8	110.3	104.6	30.6	77.7				
7	128.1	110.7	105.8	30.7	77.9				
8	117.2	104.1	104.0	32.7	75.1				
9 [a]	131.6	113.3	111.8	33.9	32.2	31.7	70.77	27.77	
10	135.3	112.6	110.9	33.9	32.3	31.7	70.77	27.77	
13	124.5	108.5					63.83	19.05	16

[a] See Table 3.

TABLE 5

SOLUBILITIES OF COMPLEXES 4 AND 14 (15°C)

Solvent	4/14 (mol/mol)
THF	11
CH_3COCH_3	51
C_6H_6	27
$CH_3COOC_2H_5$	16
CCl_4	12
$(C_2H_5)_2O$	9

The solubilities of the complexes in various solvents are of great importance for further investigation of the reactions of these complexes. The solubility of complex 4 was thus measured in a variety of solvents, showing that the solubility decreases in the order: THF > CH_3COCH_3 > CH_3COOEt ≫ C_6H_6 > CCl_4 > Et_2O > $CH_3(CH_2)_4CH_3$. The solubilities of complex $[C_5H_4CH_2CH_2CH_2C_5H_4]ErCl \cdot OC_4H_8$ (14) [1] and 4 were compared, the results of which are listed in Table 5. It shows that the solubility of complex 4 in the different solvents is much greater than that of complex 14.

Recently, Qian et al. found that a Cp_3Ln/NaH system can reduce an alkene to an alkane in high yield [15]. In order to further investigate the reactivity of this system, we studied the reducing ability of the new $(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)$-YCl/NaH system and found that this system reduces an alkene to an alkane with rates falling in the order: 1-hexene > 2-hexene ≫ cyclohexene. Notable features are that this system is more reactive and selective, and smaller amounts of NaH are required compared with those in $(C_5H_4CH_2CH_2CH_2C_5H_4)YCl \cdot THF/NaH$ and Cp_2YCl/NaH systems. It is noteworthy that this system is able to catalyze the hydrogenation of an alkene below 1 atm. of H_2 and at 45°C. Preliminary results have shown that the nature of the rare earth metal and π and σ ligands all influence the reducing ability of this type of system. Further studies are in progress.

Experimental

All operations on these organolanthanide complexes were performed under prepurified argon using Schlenk techniques, or in a glovebox. All solvents were refluxed and distilled over finely divided $LiAlH_4$ or blue sodium benzophenone under argon immediately before use. Anhydrous lanthanide chlorides were prepared from the hydrates by a published method [12]. Melting points and thermal decomposition temperatures were determined in sealed argon-filled capillaries and were uncorrected. Infrared spectra were recorded on Perkin–Elmer 983 or Digilab FTS-20/E Fourier Transform IR spectrometers with Nujol and Fluorolube mulls and were examined between disk-shaped CsI crystals or polyethylene plates; the mulls were prepared in an argon-filled glovebox. Mass spectra and GC/MS were recorded on a Finnigan 4021 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained on a Varian XL-200 (200MHz) spectrometer referenced to external Me_4Si, and on an FX-90Q (90MHz) spectrometer referenced to internal 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. X-ray photoelectron spectra were recorded on an Np-1 spectrometer equipped with a Mg-K_α X-ray source. Gas chromatographic analysis was carried out on a 102G gas chromatographic instrument.

Analyses of rare earth metals complexes were accomplished using a direct complexometric titration procedure with disodium EDTA [12]. Carbon and hydrogen analyses were performed by the combustion method in an aluminium tube.

1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl disodium salt

C_5H_5Na (0.118 mol) was prepared in the usual manner from cyclopentadiene and sodium sand in 40 ml of THF at room temperature. The solution was cooled to $-10°C$ and 8.00 g (0.056 mol) of 2,2′-dichlorodiethyl ether in 10 ml of THF was added. The reaction mixture was stirred for about 1.5 h at $-10°C$. The mixture was centrifuged and the precipitate was separated from the solution. The brown-yellow solution thus obtained was allowed to react again with an excess of sodium sand in 150 ml of THF at 45°C for about 5 h. The concentration of this solution was 0.216 M by titration with standard hydrochloric acid. The 1,1′-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt/THF solution was stored under argon for use as an intermediate. IR (cm^{-1}): 722vs, 891w, 1003s, 1023s, 1037s, 1093s, 1464s, 3059m.

1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl yttrium chloride (7)

A tetrahydrofuran solution of an equivalent 1,1′-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt was added slowly to 3.82 g (19.54 mmol) of anhydrous YCl_3 in 50 ml of THF at $-25°C$. The reaction mixture was stirred for 2 h between -20 and $-25°C$, then allowed to warm up to ambient temperature, and stirred overnight. The Schlenk flask was centrifuged, the precipitate separated from solution, and the THF solution reduced in volume to about 10 ml. Addition of 30 ml of n-hexane gave a pale green solid, which was extracted with 20 ml of THF. Concentration of the THF solution followed by addition of n-hexane afforded a solid product which was washed with 15 ml of n-hexane and then dried in vacuo to give a pale green solid 5.57 g. Yield 87.8%; melting point 130°C. Anal. Found: C, 50.88; H, 5.28; Y, 26.93; Cl, 10.39. $C_{14}H_{16}OClY$ calc: C, 51.77; H, 4.93; Y, 27.43; Cl, 10.94%. IR (cm^{-1}): 182m, 227s, 287s, 365m, 400w, 770vs, 827s, 891w, 1013s, 1038s, 1045s, 1060s, 1438s, 2880s, 2927s, 2947s, 3080m.

1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl lutetium chloride (6)

The procedure followed was similar to that for 7. A white solid, 6, was obtained; yield 49.0%; decomposition temperature 222°C. Anal. Found: C, 40.13; H, 4.91; Lu, 43.12; Cl, 8.91. $C_{14}H_{16}OClLu$ calc: C, 40.93; H, 3.90; Lu, 42.63; Cl, 8.65%. IR (cm^{-1}): 178w, 220s, 250s, 365m, 400m, 775vs, 826s, 888w, 1010s, 1030s, 1040s, 1056s, 1436s, 2878s, 2920s, 2945s, 3080m.

1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl ytterbium chloride (5)

The procedure followed was similar to that for 7. A red solid, 5, was obtained; yield 77.2%; melting point 115°C. Anal. Found: C, 41.26; H, 4.35; Yb, 42.17; Cl, 8.25. $C_{14}H_{16}OClYb$ calc: C, 41.13; H, 3.92; Yb, 42.35; Cl, 8.69%. IR (cm^{-1}): 177w, 220s, 260s, 365m, 400m, 780vs, 827s, 888w, 1010s, 1030s, 1041s, 1057s, 1435s, 2880s, 2920s, 2943s, 3080m.

1,1'-(3-Oxa-pentamethylene)dicyclopentadienyl erbium chloride (4)

The procedure followed was similar to that for 7. An orange-red solid, **4**, was obtained; yield 63.6%; decomposition temperature 240°C. Anal. Found: C, 41.98; H, 3.98; Er, 41.56; Cl, 8.85. $C_{14}H_{16}OClEr$ calc: C, 41.74; H, 3.96; Er, 41.49; Cl, 8.82%. IR (cm^{-1}); 178w, 220s, 250s, 365m, 390m, 770vs, 826s, 888w, 1010s, 1034s, 1041s, 1056s, 1435s, 2878s, 2925s, 2945s, 3080m.

1,1'-(3-Oxa-pentamethylene)dicyclopentadienyl holmium chloride (3)

The procedure followed was similar to that for 7. A pale yellow solid, **3**, was obtained; yield 65.1%; decomposition temperature 270°C. Anal. Found: C, 41.94; H, 4.22; Ho, 41.67; Cl, 8.56. $C_{14}H_{16}OClHo$ calc: C, 41.95; H, 4.00; Ho, 41.20; Cl, 8.86%. IR (cm^{-1}): 177w, 220s, 250s, 365m, 400m, 770vs, 825s, 887w, 1010s, 1034s, 1040s, 1056s, 1435s, 2880s, 2920s, 2945s, 3080m.

1,1'-(3-Oxa-pentamethylene)dicyclopentadienyl gadolinium chloride (2)

THF (26 ml) was added to 1.05 g (3.98 mmol) of anhydrous GdCl$_3$ and the reaction mixture stirred for 25.5 h at room temperature. To this suspension was added dropwise with stirring an equivalent 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt-THF solution at -20°C. The subsequent operations were similar to that for 7. Complex **2** was obtained as a white solid. Yield 59.2%; decomposition temperature 230°C. Anal. Found: C, 43.26; H, 4.40; Gd, 40.51; Cl, 8.67. $C_{14}H_{16}OClGd$ calc.: C, 42.80; H, 4.08; Gd, 40.00; Cl, 9.04%. IR (cm^{-1}): 178m, 213s, 255s, 360w, 390w, 770vs, 825s, 890w, 1013s, 1035s, 1044s, 1058s, 1438m, 2875m, 2927s, 2945s, 3080m.

1,1'-(3-Oxa-pentamethylene)dicyclopentadienyl neodymium chloride (1)

THF (60 ml) was added to 3.29 g (13.13 mmol) anhydrous NdCl$_3$ and the reaction mixture stirred for 20.5 h at room temperature. The Schlenk flask was centrifuged, and the solution was separated from the solid. The solution contained 2.11 mmol NdCl$_3$ of chlorine by analysis. One equivalent of 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt-THF solution was added dropwise to the solid (11.02 mmol) in 50 ml of fresh THF at -30°C and worked up. Complex **1** was obtained as a pale green solid. Yield 44.9%; decomposition temperature 280°C. Anal. Found: C, 43.12; H, 4.47; Nd, 38.23; Cl, 9.01. $C_{14}H_{16}OClNd$ calc: C, 44.27; H, 4.22; Nd, 37.94; Cl, 9.35%. IR (cm^{-1}): 175m, 212s, 250s, 358w, 412m, 770vs, 820s, 889w, 1010s, 1035s, 1042s, 1059s, 1437s, 2875s, 2930s, 2950s, 3080m.

Catalytic hydrogenation of 1-hexene by $(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)YCl/NaH$ system

Complex 7, 10.2 mg (0.0314 mmol), and 4.2 mg (0.175 mmol) of NaH were allowed to react with a 10-fold excess of 1-hexene in 1 ml of THF in a 100 ml glass reaction vessel equipped with a stirrer bar. The vessel was attached to a vacuum line, cooled to -178°C and evacuated and then filled with H$_2$ at atmospheric pressure and sealed. The reaction mixture was stirred for 48 h at 45°C. The solution was analyzed by GC/MS and GC to contain 90% n-hexane and 10% 1-hexene.

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