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Studies on Organolanthanide Complexes. XVII.* Syntheses and Identification of 1,1′-Pentamethylenedicyclopentadienyl Lanthanide Chlorides, Yttrium Chloride and Yttrium Cyclopentadienyl Derivative**

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Recently, the stabilization of early organolanthanide complexes has been achieved by using carbon or silicon chain bridged dicyclopentadienyl as a ligand [1–4]. Their derivatives have been also synthesized for identification of the structures and investigation of their reactivities. However, until now the bridged chain was limited to less than three atoms, and no report had appeared in the literature concerning longer chain bridged dicyclopentadienyl as ligand.

Herein, we would like to report the syntheses of seven new THF-solvated complexes using 1,1′-pentamethylenedicyclopentadienyl as ligand. Unfortunately, under similar conditions, we did not succeed in obtaining the early lanthanocene chloride with this chelating ligand.

Experimental

All operations for the preparation of organolanthanide complexes were performed under prepurified argon using Schlenk techniques and in a glove box. 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 [5]. The syntheses of $(C_5H_5)_2LnCl$ (Ln = Lu, Y) were carried out by the literature method [6]. Thermal decomposition temperatures 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. ^1H and ^{13}C NMR spectra were obtained on a Varian XL-200 (200 MHz) spectrometer referenced to external Me_4Si, and on an FX-90 (90 MHz) 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.

Analyses of rare earth metals of complexes were accomplished using a direct complexometric titration procedure with disodium EDTA [5]. Carbon and hydrogen analyses were performed by the combustion method in an aluminium tube.

1,1′-Pentamethylenedicyclopentadienyldysprosium Chloride·THF (3)

C_5H_5Na (0.108 mol) was prepared in the usual manner from cyclopentadiene and sodium sand in 40 ml of THF at 0 °C. The solution was cooled to −10 °C and 12.80 g (0.055 mol) of 1,5-dibromopentane in 15 ml of THF was added dropwise and stirred for 1.5 h at −10 °C. The mixture was centrifuged to give a pale yellow solution, which reacted again with an excess of sodium sand in 160 ml of THF at 45 °C overnight. The 1,1′-pentamethylenedicyclopentadienyl disodium salt/THF solution was 0.222 M by titration with standard hydrochloric acid, and was stored under argon for use as an intermediate.

22.5 ml of the disodium salt/THF solution (0.222 M, 5.00 mmol) was added slowly to 1.48 g (5.50 mmol) of $DyCl_3$ in 45 ml of THF at −50 °C. The reaction mixture was stirred for 2 h between −50 and 30 °C, then allowed to warm to room temperature and stirred overnight. The Schlenk flask was centrifuged to give a transparent THF solution, which was reduced in volume to about 15 ml. Addition of 5 ml of n-hexane gave a crude product, which was washed twice with 10 ml portion of n-hexane and then dried *in vacuo* to afford a yellow solid (**3**), 1.57 g. Its physical properties and elemental analyses are shown in Table I.

1,1′-Pentamethylenedicyclopentadienyl-erbium chloride·THF (**4**), -lutetium chloride·THF (**5**) and -yttrium chloride·THF (**6**) were synthesized in a similar way.

1,1′-Pentamethylenedicyclopentadienylsamarium Chloride·THF (1)

THF (20 ml) was added to 1.65 g (6.42 mmol) of $SmCl_3$ and the reaction mixture was stirred for 26 h at room temperature. To this suspension was added dropwise with stirring 1,1′-pentamethylenedicyclopentadienyl disodium salt/THF solution (5.06 mmol) at −50 °C. The subsequent operations were similar to that for **3**. 0.89 g of **1** was obtained. The physical

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TABLE I. Physical Properties and Elemental Analyses

Complex (Ln)	Color	Decomposition temperature (°)	Yield[a] (%)	Analysis [Found (calc.) (%)]			
				Ln	C	H	Cl
1 (Sm)	yellow	120	38.5	33.15 (32.99)	50.32 (50.01)	5.65 (5.70)	7.50 (7.79)
2 (Gd)	white	152	66.2	33.55 (33.98)	49.91 (49.27)	5.72 (5.62)	7.97 (7.67)
3 (Dy)	pale-yellow	133	66.8	34.49 (34.72)	49.09 (48.72)	5.61 (5.56)	7.32 (7.59)
4 (Er)	orange–red	130	75.4	34.14 (35.34)	48.25 (48.25)	6.09 (5.50)	8.17 (7.51)
5 (Lu)	pale-yellow	100	75.8	35.71 (36.42)	47.55 (47.45)	5.53 (5.41)	7.60 (7.39)
6 (Y)	pale-yellow	120	73.2	22.03 (22.56)	57.99 (57.79)	6.86 (6.59)	8.91 (9.00)
7 (Y)	white	100	38.9	19.45 (20.99)	67.04 (67.93)	7.29 (7.31)	

[a] Based on the disodium salt.

properties and the elemental analyses are shown in Table I.

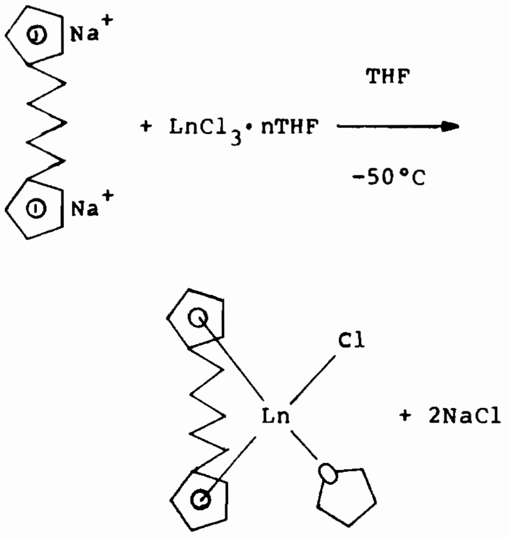
The synthesis of 1,1′-pentamethylenedicyclopentadienylgadolinium chloride·THF (2) was similar to that for **1**.

1,1′-Pentamethylenedicyclopentadienylcyclopentadienylyttrium·THF (7)

Anhydrous YCl_3 (1.90 g, 9.72 mmol) reacted with 1,1′-pentamethylenedicyclopentadienyl disodium salt/THF solution (8.88 mmol) to give 6.84 mmol of complex **6**. An equivalent cyclopentadienyl sodium/THF solution was added to the resulting 1,1′-pentamethylenedicyclopentadienylyttrium chloride/THF solution at −30 °C. The reaction mixture was then allowed to warm to ambient temperature and stirred overnight. The Schlenk flask was centrifuged. After removal of the solid, the THF solution was concentrated to give a crude product, which was washed with 8 ml portion of n-hexane thrice, then dried *in vacuo* to afford **7**, a white solid, 1.47 g (38.9% yield based on the disodium salt).

Results and Discussion

The preparation of 1,1′-pentamethylenedicyclopentadienyl disodium salt/THF solution is similar to those reported in the literature [2, 7]. It could be stored for over one month with exclusion of moisture and oxygen. The disodium salt/THF solution reacts with anhydrous lanthanide chlorides in THF at −50 °C to give complexes **1**–**6**, which are shown in eqn. (1).

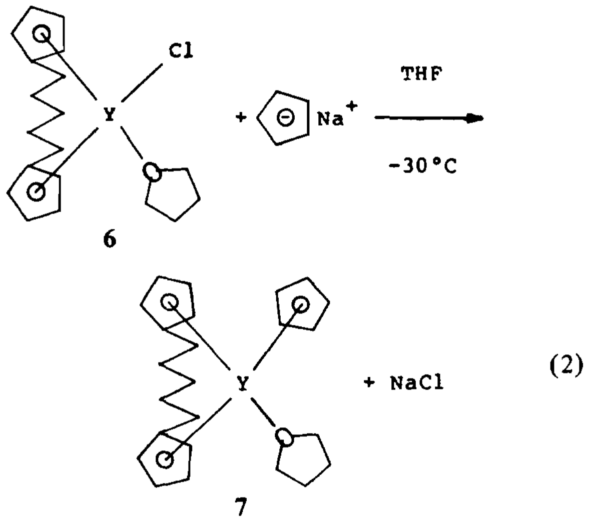


(1)

$n = 3$, Ln = Sm (**1**), Gd (**2**).
$n = 0$, Ln = Dy (**3**), Er (**4**), Lu (**5**), Y (**6**).

Unfortunately, we failed to isolate 1,1′-pentamethylenedicyclopentadienylneodymium chloride·THF in a similar manner or by using $NdCl_3·2THF$ instead of $NdCl_3$ as starting material, or by changing the molar ratio of the disodium salt and neodymium trichloride. The reason may probably be due to either the disproportionation of dicyclopentadienylneodymium chloride occurring during its synthesis [6, 8, 9] or to it being partly further replaced by another cyclopentadienyl. For further investigation of the stabilization of early lanthanocene chlorides, the heteroatom-containing ring-bridged dicyclopentadienyl was used as ligand, so as to change the flexibility of the chain on one hand and to form an intramolecular coordination bond to satisfy the requirement of coordination saturation on the other. An oxygen-containing ring-bridged dicyclopentadienylneodymium chloride was successfully synthesized. The result has been reported [10].

Complex **6** was allowed to react with cyclopentadienyl sodium/THF solution at –30 ℃ to give complex 7. The reaction is shown in eqn. (2).



(2)

In Table I are listed the physical properties and elemental analyses of seven new complexes. Their elemental analyses are consistent with the structures and the thermal stabilities are lower than the corresponding complexes with a three-carbon bridge, $[C_5H_4(CH_2)_3C_5H_4]LnCl·THF$ [2].

Thermoanalysis of complex **4** was carried out from 20 to 600 ℃ in an atmosphere of nitrogen and the weight loss was equal to 16.5% between 70–150 ℃, which is consistent with the loss of one mole of THF, showing that six new chloride complexes are THF-solvated neutral ones.

The data of major absorption peaks of infrared spectra (4000–200 cm^{-1}) of complexes **1**–**7** are listed in Table II. The characteristic absorption peaks due to the coordinated THF, cyclopentadienyl and ring-bridged methylene are evidently present, and their wave-numbers and shapes are all similar. However, in the low frequency region the characteristic absorption peaks are different to some extent, especially with complexes **6** and **7**, and the band at 250 cm^{-1} is assigned to a characteristic absorption of a π-bonded cyclopentadienyl group to the Ln metal [2]. But when Ln is yttrium, the characteristic absorptions of π-bonded complexes **6** and **7** are shifted to 277 and 293 cm^{-1} respectively, which are in accord with the results reported by us previously [4, 10]. Further investigation, to decide whether the result is related to the absence of an f-orbital, is necessary.

The mass spectra of complexes **1**, **2**, **5** and **7** did not show a parent molecular ion. However, they show THF, 1,1′-pentamethylenedicyclopentadiene, cyclopentadiene ions and fragments which may be attributed to the moieties containing the above-mentioned groups connected to the metal.

^1H and ^{13}C NMR spectra of complexes **5**, **6** and **7** were also measured, and the results are listed in Tables III and IV, respectively. For comparison, the ^1H and ^{13}C NMR data of related ring-bridged complexes are also listed. Table III reveals that the C_5H_5 in complex **7** shows only a single peak at δ 5.86 ppm,

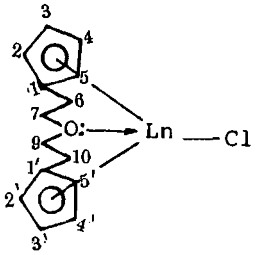
TABLE II. IR Data of Complexes 1–7 (4000–200 cm^{-1})

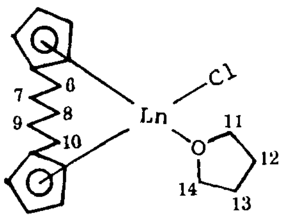
Complex	1	2	3	4	5	6	7
Low-frequency region							228m
	220s	225s	221s	228s	228s	233m	255s
	250s	242s	245m	259s	254s	277m	293s
	334m	338m	350w	356m	337m	300m	324w
	370m	419m	377s	405m	415m	367s	416s
						408s	441s
Coordinated-THF	867m	864s	867s	866s	865m	866m	855m
	1048s	1045s	1047s	1046s	1050s	1046s	1049s
Cyclopentadienyl	772vs	766vs	768vs	778vs	768vs	770vs	780vs(br.)
	1017s	1017s	1015s	1014s	1010s	1015s	1016s
	1440s	1439s	1447m	1444s	1444s	1439m	1440s
	3067m	3061m	3065m	3070m	3073m	3067m	3065s
Methylene	2851vs	2852vs	2852vs	2852vs	2861vs	2852vs	2852vs
	2927vs	2925vs	2922vs	2929vs	2929vs	2924vs	2925vs

which indicates that the C_5H_5 is most probably η^5-bonded to Y.

The Δδ value implies the distribution of charge on the cyclopentadienyl and the torsional ring mobility of the cyclopentadienyl [11]. With complexes **12** to **11** to **5** to **9**, the Δδ values decrease gradually from 0.4 to 0, which shows that the torsional ring mobility of the cyclopentadienyl in complex **5** is very near to that in $(C_5H_5)_2LuCl$. The ^{13}C NMR spectra give the same result. This may be the reason why we failed to obtain 1,1'-pentamethylenedicyclopentadienyl early lanthanide chlorides. From complexes **6** to **7**, the Δδ values increase from 0.07 to 0.15, which indicates that the distance between C(1) and C(1') is shortened because of the steric crowding of the C_5H_5 in complex 7.

According to the Δδ value, we may conclude that the ability of ring-bridged dicyclopentadienyl, which we studied, on stabilization of early lanthanocene chlorides decreases in the order: trimethylenedicyclopentadienyl > (3-oxa-pentamethylene)dicyclopentadienyl > pentamethylenedicyclopentadienyl ~ cyclopentadienyl. Our experimental results support this suggestion [2, 10].





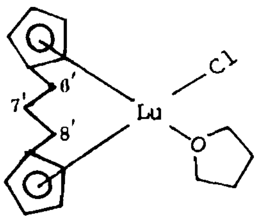


TABLE III. ^1H NMR Proton Shift (δ, ppm, TMS, 25 °C)

Complex	Ring protons	Δδ[a]	6,10-CH_2 6',8'-CH_2	7,9-CH_2 7'-CH_2	THF	Reference
$(C_5H_5)_2YCl$ (8)	6.20	0				
$(C_5H_5)_2LuCl$ (9)	6.11	0				
$[C_5H_4(CH_2)_5C_5H_4]YCl\cdot THF$ (6)	6.04	0.07	2.59	1.60[b]	3.71	
	5.97				1.85	
$[C_5H_4(CH_2)_5C_5H_4]Y(C_5H_5)\cdot THF$ (7)	5.86[c]					
	5.80	0.15	2.57	1.60[b]	3.63	
	5.65				1.78	
$[C_5H_4(CH_2)_5C_5H_4]LuCl\cdot THF$ (5)	5.96	0.07	2.56	1.56[b]	3.62	
	5.89				1.77	
$(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)YCl$ (10)	5.98	0.14	2.64	4.18		10
	5.84			3.79		
$(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)LuCl$ (11)	5.87	0.09	2.63	4.24		10
	5.78			3.79		
$(C_5H_4CH_2CH_2CH_2C_5H_4)LuCl\cdot THF$ (12)	6.25	0.40	2.80	2.47	3.50	2
	5.85				1.63	

[a] Δδ = δ(2,5-CH)−δ(3,4-CH). [b] 7,8,9-CH_2 overlap. [c] $\delta(\eta^5\text{-}C_5H_5)$.

TABLE IV. ^{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)	Reference
8	113.5	113.5	113.5						
9	112.9	112.9	112.9						
6	135.3	112.6	110.9	33.9	32.3	31.7	70.8	27.8	
5	131.6	113.3	111.8	33.9	32.2	31.7	70.8	27.8	
10	128.1	110.7	105.8	30.7	77.9				10
11	126.8	110.3	104.6	30.6	77.7				10

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