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# Studies on organolanthanide complexes

## XXVI *. Synthesis, identification and bonding properties of {1,1′-(3-oxa-pentamethylene)dicyclopentadienyl} (cyclopentadienyl) lanthanide derivatives

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### Abstract

Right new complexes, {1,1′-(3-oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)lanthanide derivatives, have been synthesized. They are all unsolvated monomers showing an intramolecular coordination of ether oxygen and can be sublimed at 200-240 °C/$10^{-4}$ mmHg. The cyclopentadienyl ligand is \$-bonded to the lanthanide metal. These complexes have been fully characterized by elemental analyses, IR, MS, $^1$H and $^{13}$C NMR spectroscopy.

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### Introduction

Tricyclopentadienyl lanthanide complexes were synthesized by the reaction of cyclopentadienyl sodium salt with $LnCl_3$ in THF [1]. The X-ray diffraction study shows that they are polymeric or tetrameric in the solid states involving $\mu$-$\eta^5:\eta^2$-$C_5H_5$ or $\mu$-$\eta^5:\eta^1$-$C_5H_5$ units [2–6]. Their THF-coordinated complexes, $Cp_3Ln \cdot$ THF, show pseudo-tetrahedral coordination containing only $\eta^5$-bonded cyclopentadienyl ligands [7–11]. In addition, in d-block transition metal complexes, for example in $Cp_4Ti$ two cyclopentadienyls are $\eta^1$-bonded to Ti and $\eta^1$ and $\eta^5$ cyclopentadienyls can exchange each other at room temperature [12–14]. However, 1,1′-trimethylenedicyclopentadienyl ligand can effectively prevent this exchange to give $[(CH_2)_3(\eta^5$-$C_5H_4)_2]Ti(\eta^1$-$C_5H_5)_2$ [15].

We have reported the synthesis of the {1,1′-pentamethylenedicyclopentadienyl}-(cyclopentadienyl)yttrium complex and suggested that the $C_5H_5$ is $\eta^5$-bonded to Y

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* For part XXV see ref. 23.

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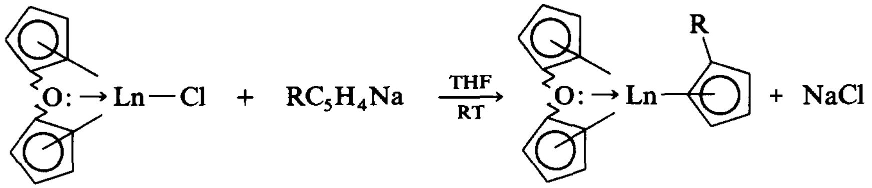
[16]. When the heteroatom-containing ring-bridged dicyclopentadienyl is used as ligand, is there any intramolecular coordination of that oxygen with the lanthanide metal atom in the complexes? Is the $C_5H_5$ still $-bonded to the lanthanide? To answer these questions, {1,1′(3-oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)lanthanide derivatives were synthesized and their properties were studied.

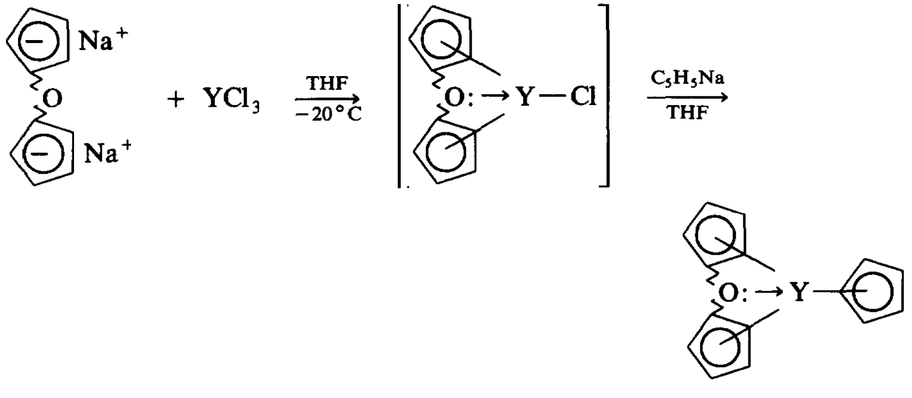
## Results and diision

1,1′-(3-Oxa-pentamethylene)dicyclopentadienyllanthanide chlorides were allowed to react with $RC_5H_4Na$ (R = H, CH,) in THF at room temperature to give lanthanocene cyclopentadienyl derivatives in high yields (eq. 1). These complexes can also be synthesized by a one-pot reaction as shown in eq. 2.



(1)

R = H, Ln = Nd (1), Gd (2), Er (3), Yb (4), Lu (5), Y (6).
R = CH,, Ln = Yb (7), Y (8).



(2)

Furthermore, the 1,1′-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt reacts with lanthanocene chlorides to afford $[(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)Ln\text{-}C_5H_4CH_2CH_2]_2O$. The results of this reaction will be published elsewhere [17].

The new complexes all sublime at 240°C/$10^{-4}$ mmHg, to give crystals of different colors depending on the lanthanide metal present. They are stable up to 300 ° C, but are sensitive to air and moisture.

The reaction rate was found to depend upon the concentration of substrate in THF solution. When the concentration of chloride was less than 0.08 *M* and [CpNa] was less than 0.4 *M in the* solution of starting material, the reaction of lanthanocene

Table 1

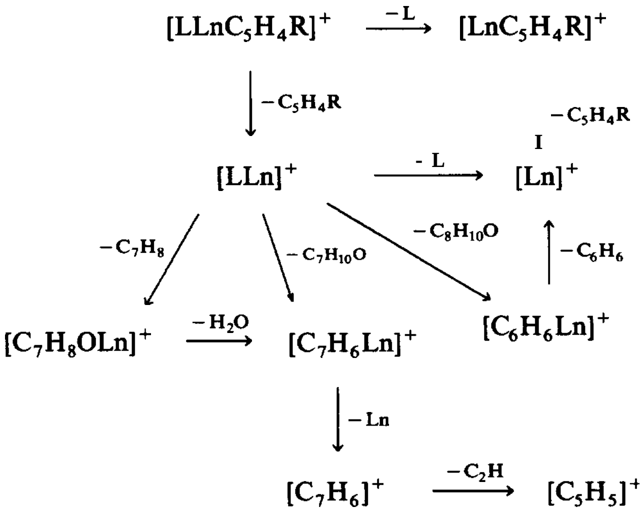
Mass spectral data for complexes **1–8**[a]

| Fragment | Complex m/e (relative intensity) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **1** (Nd) | **2** (Gd) | 3 (Er) | 4 (Yb) | **5** (Lu) | **6** (Y) | 7 (Yb) | **8** (Y) |
| $M^+$ | 407 (11.11) | 423 (1.75) | 432 (5.07) | 439 (0.85) | 440 (3.60) | 354 (27.39) | 453 (3.57) | 368 (2.37) |
| [M-65]+ | 342 (100.0) | 358[c] (7.89) | 367[c] (88.25) | 374[c] (21.25) | 375 (100.0) | 289 (100.0) | 374[b] (100.0) | 289[b] (100.0) |
| $[C_7H_8OLn]^+$ | 250 (16.73) | 266 (2.01) | 275 (21.81) | 282 (3.07) | 283 (16.54) | 197 (61.58) | 282 (1.43) | 197 (36.26) |
| $[C_7H_6Ln]^+$ | 232 (1.58) | 248 (0.53) | 257 (4.26) | 264 (3.34) | 265 (5.59) | 179 (14.45) | 264 (1.55) | 179 (6.43) |
| $[C_6H_6Ln]^+$ | 220 (5.88) | 236 (0.60) | – | 252 (3.56) | 253 (3.64) | 167 (26.48) | 252 (1.96) | 167 (15.38) |
| $[C_5H_5Ln]^+$ | 207 (4.60) | 223 (1.78) | 232 (5.45) | 239 (4.46) | 240 (6.72) | 154 (16.56) | 239 (1.13) | 154 (3.74) |
| $[Ln]^+$ | 142 (2.39) | – | 167 (7.72) | 174 (13.89) | 175 (4.50) | 89 (2.10) | 174 (10.24) | 89 (1.28) |

[a] Recorded at EI.*T* 50–300° C, EM = 1.3 kV, based on the largest abundance. of isotopes; [b] $[M-79]^+$; [c] $[C_5H_6]$ = base peak.

chlorides with CpNa is slow and after 24 hours the substrate was partially recovered.

Salient mass spectral data for the eight complexes are listed in Table 1. All the complexes showed a parent molecular ion $[M]^+$ and related fragments including $[M-C_5H_4R]^+$ (R = H, CH,), $Ln^+$ and $[M-L]^+$ (L = ligand), No m/e greater than $M^+$ or equal to 72 or 71 was detected. The data indicate that the complexes



Scheme 1. L = $C_5H_4CH_2CH_2OCH_2CH_2C_5H_4$; R = H, CH,; Ln = rare earth metal.

Table 2

C-O-C Asymmetric stretching vibrational frequency ($cm^{-1}$)

| Complex | Disodium salt | 1 (Nd) | 2 (Gd) | 3 (Er) | 4 (Yb) | 5 (Lu) | 6 (Y) | 7 (Yb) | 8 (Y) |
|---|---|---|---|---|---|---|---|---|---|
| $\nu$ | 1093 [a] | 1057 | 1058 | 1059 | 1052 | 1051 | 1064 | 1065 | 1049 |
| $\Delta\nu$ [b] | | 36 | 35 | 34 | 41 | 41 | 29 | 28 | 44 |

[a] See ref. 21. [b] $\Delta\nu = \nu(\text{salt}) - \nu(\text{complex})$.

are solvent-free and monomeric, and that the $Ln-C_5H_4R$ bond is the first cleaved, giving very high relative, intensity peaks of $[M-C_5H_4R]^+$, resulting from the intramolecular coordination bond. The fragmentation of these complexes is shown in Scheme 1.

The IR spectra of these complexes exhibit absorption peaks typical of $\eta^5$-cyclopentadienyl at about 775, 1020, 1440, 3085 cm-‘, and a single peak of middle intensity in the olefinic C-H stretching region (3000-3100 cm-‘), indicating that the cyclopentadienyl is most probably $-bonded to the lanthanide metal in these complexes [18–20].

Compared with the absorption peak of the C-O-C asymmetric stretching vibration of 1,1′-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt, that of complex is shifted to lower frequency and lies between 29-44 cm-’ (Table 2). This suggests the existence of the above supposed intramolecular coordination of that oxygen and lanthanide metal [21].

The $^1H$ and $^{13}C$ NMR data of complexes 5 and 6 are listed in Tables 3 and 4. Table 3 shows that $\delta(C_5H_5)$ and $\delta$(2,5-CH) overlap, giving a group of multiple

Table 3

$^1H$ NMR data ($\delta$, TMS, ppm)

| Complex [a] | $C_5H_5$ | $(C_5H_4)_2$ | $\Delta\delta$ [b] | 6,10-$CH_2$ | 7,9-$CH_2$ | Ref. |
|---|---|---|---|---|---|---|
| LLuCl | | 5.87 | | 2.63 | 4.24 | |
| | | 5.78 | 0.09 | | 3.79 | 21 |
| $LLu(C_5H_5)$ | 5.95 | 5.95 | | 2.55 | 4.10 | |
| | | 5.72 | 0.23 | | | |
| LYCl | | 5.98 | | 2.64 | 4.18 | |
| | | 5.84 | 0.14 | | 3.79 | 21 |
| $LY(C_5H_5)$ | 5.74 | 5.74 | | 2.60 | 4.08 | |
| | | 5.55 | 0.19 | | | |

[a] L = $C_5H_4CH_2CH_2OCH_2CH_2C_5H_4$. [b] $\Delta\delta = \delta$(2,5-CH) − $\delta$(3,4-CH).

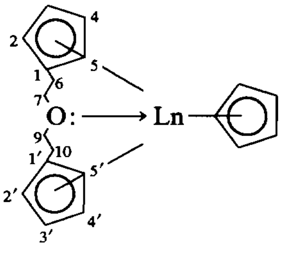


Table 4

$^{13}$C NMR data (6, THF-$d_8$ = 26.7 ppm, 25° C)

| Complex | C-1 | C-2,5 | C-3,4 | C-6,10 | c-7,9 | $C_5H_5$ | Ref. |
|---|---|---|---|---|---|---|---|
| LLuCl | 126.8 | 110.3 | 104.6 | 30.6 | 77.7 | | 21 |
| LLu($C_5H_5$) | 135.0 | 110.9 | 107.0 | 29.9 | 82.9 | 112.7 | |
| LYCl | 128.1 | 110.7 | 105.8 | 30.7 | 77.9 | | 21 |
| LY($C_5H_5$) | 127.9 | 111.8 | 109.6 | 29.5 | 81.3 | 113.1 | |

peaks at 5.95 (Lu) and 5.74 (Y), respectively. The $^{13}$C NMR data also indicate that the $C_5H_5$ in complexes gives only a single peak. In addition the data show that the $C_5H_5$ is \$-bonded to the lanthanide metal in {1,1′-(3-oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)lanthanide derivatives [15,22].

The $\Delta\delta$ value gives an indication of the distribution of charge on the cyclopentadienyl and the torsional ring mobility of the cyclopentadienyl [21,22]. When chlorine is replaced by cyclopentadienyl, the $\Delta\delta$ values are increased owing to the bulk of the $C_5H_5$, showing that the torsional ring mobility of the cyclopentadienyl has been decreased and the rigidity of the bridged chain has been enhanced.

Carbon tetrachloride can selectively attack the $\sigma$ bond of $[(CH_2)_3(\eta^5\text{-}C_5H_4)_2]Ti(\eta^1\text{-}C_5H_5)_2$ to give the complex, $[(CH_2)_3(\eta^5\text{-}C_5H_4)_2]TiCl_2$[15]. However, the starting material was recovered in the case of the reaction of complex 6 with $CCl_4$ under similar conditions. This outcome is consistent with the fact that the $C_5H_5$ is $\eta^5$-bonded to the lanthanide metal. However, we have not yet obtained single crystals suitable for X-ray crystallography.

In conclusion, {1,1′-(3-oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)lanthanide derivatives share the characteristic features of the tricyclopentadienyl lanthanides; viz., they have the same thermal stability, color, and behavior in sublimation. The IR, $^1$H, $^{13}$C NMR and MS spectra all show the $\eta^5$-bonding between the cyclopentadienyl and the lanthanide metal, and the presence of an intramolecular coordination bond between oxygen and lanthanide metal.

## Experimental

All operations for these organolanthanide complexes were performed under prepurified argon by use of Schlenk techniques or 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 and 1,1′-(3-oxa-pentamethylene)dicyclopentadienyllanthanide chlorides were prepared by a published procedure [21]. Infrared spectra were recorded on Perkin-Elmer 983 or Digilab FTS-20/E Fourier Transform IR spectrometers in Nujol or Fluorolube mulls, in CsI disks or polyethylene plates; the mulls were prepared in an argon-filled glovebox. Mass spectra were recorded on a Firmigan 4021 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were obtained on a Varian XL-200 (200 MHz) spectrometer referenced to external $Me_4Si$, and on an FX-90Q(90 MHz) spectrometer referenced to internal THF-d,. THF-$d_8$ was dried over Na/K alloy and was degassed by freeze-thaw cycles on a vacuum line.

The rare earth complexes were analyzed by direct complexometric titration with disodium EDTA. Carbon and hydrogen analyses were carried out by the combustion method in an aluminium tube.

### *{1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)neodymium (1)*

A tetrahydrofuran solution of an equivalent CpNa (1.0 *M*, 3.10 ml) was added to 1.17 g (3.08 mmol) of {1,1′-(3-oxa-pentamethylene)dicyclopentadienyl}neodymium chloride in 20 ml of THF at room temperature and the reaction mixture was stirred overnight. The Schlenk flask was centrifuged to give a clear THF solution, which was reduced in volume to about 8 ml. Addition of 10 ml of n-hexane gave a product, which was washed twice with 5 ml portion of hexane and then dried in vacuum to afford a blue solid (1): 1.17 g; yield 92.8%. The product was purified by sublimation at 190–210 °C/$10^{-4}$ mmHg, giving blue crystals. Anal. Found: C, 56.42; H, 5.51; Nd, 35.50. $C_{19}H_{21}ONd$ calc.: C, 55.75; H, 5.13; Nd, 35.21%. IR (cm-‘): 115w, 143m, 218s, 256s, 295s, 348s, 486s, 759vs, 825s, 843m, 887m, 971s, 988s, 1020s, 1030s, 1047s, 1057s, 1181s, 1193s, 1241m, 1275m, 1323m, 1377s, 1442m, 2880s, 2923s. 3085m.

### *{1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)gadolinium (2)*

*The* procedure followed was similar to that for **1**. Complex 2 was obtained as pale-yellow crystals in 90.8% yield. Sublimes at 180-200” C/$10^{-4}$ mmHg. Anal. Found: C, 53.22; H, 4.66; Gd, 37.71. $C_{19}H_{21}OGd$ calc.: C, 54.00; H, 4.97; Gd, 37.24%. IR (cm-‘): 145w, 219s, 250m, 345m, 395m, 490m, 775vs, 830s, 891s, 971s, 1012s, 1058s, 1105m, 1183s, 1193s, 1236m, 1252m, 1272s, 1324s, 1377s, 1437s, 2880s, 2930s, 3077s.

### *{1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)erbium (3)*

The procedure followed was similar to that for **1**. Complex 3 was obtained as pink crystals in 91.2% yield. Sublimation at 180–210 °C/$10^{-4}$ mmHg. Anal. Found: C, 51.76; H, 4.79; Er, 38.57. $C_{19}H_{21}OEr$ calc.: C, 52.75; H, 4.86; Er, 38.69%. IR (cm-‘): 214s, 255m, 375m, 777vs, 834s, 891s, 927s, 1015s, 1059s, 1105s, 1183s, 1194s, 1237m, 1253m, 1271s, 1364s, 1438m, 2880s, 2935s, 3080m.

### *{1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)ytterbium (4)*

*The* procedure followed was similar to that for **1**. Complex 4 was obtained as dark green crystals in 89.6% yield. Sublimes at 200–220 °C/$10^{-4}$ mmHg. Anal. Found: C, 52.43; H, 4.85; Yb, 39.24. $C_{19}H_{21}OYb$ calc.: C, 52.06; H, 4.80; Yb, 39.50%. IR (cm-‘): 206s, 250m, 345m, 398s, 488s, 541m, 766vs, 837vs, 855s, 890s, 973s, 1021s, 1052s, 1112s, 1184s, 1195s, 1236m, 1253m, 1272m, 1325m, 1376s, 1439m, 2880s, 2910s, 3081m.

### *{1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)lutetium (5)*

*The* procedure followed was similar to that for **1**. White crystals, 5, were obtained in 60.6% yield. Sublimes at 200–220 °C/$10^{-4}$ mmHg. Anal. Found: C, 50.90; H, 4.83; Lu, 40.80. $C_{19}H_{21}OLu$ calc.: C, 51.82; H, 4.77; Lu, 39.77%. IR (cm-‘): 140m, 155m, 200s, 250s, 345m, 400w, 490m, 789vs, 837s, 856s, 889s, 971s, 1019s, 1033s, 1051s, 1183s, 1195s, 1235m, 1253m, 1270s, 1324m, 1331m, 1377s, 1439s, 2875s, 2913s, 3081s.

*{1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl}(cyclopentadienyl)yttrium (6)*

*Anhydrous* $YCl_3$ (2.34g, *11.97* mmol) was treated with 1,1′-(3-oxa-pentamethylene)dicyclopentadienyl disodium salt in THF (11.21 mmol) to give a THF solution containing 8.97 mmol of {1,1′-(3-oxa-pentamethylene)dicyclopentadienyl}yttrium chloride. An equivalent CpNa/THF solution was added to the resulting yttrocene chloride in THF at room temperature. The procedure followed was similar to that for 1. Colorless crystals, 6, were obtained in 69.8% yield (based on the disodium salt). Sublimes at 220-240" $C/10^{-4}$ mmHg. Anal. Found: C, 64.72; H, 5.84; Y, 25.54. $C_{19}H_{21}OY$ calc.: C, 64.41; H, 5.93: Y, 25.14. IR (cm-‘): 265m, 375s, 387s, 765vs, 891s, 973m, 1040s, 1064s, 1106s, 1194m, 1272m, 1376s, 1440m, 2871s, 2920s, 3069m.

*{1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl}(methylcyclopentadienyl)ytterbium (7)*

Except for the use of methylcyclopentadienylsodium salt as starting material, the procedure followed was similar to that for **1.** Complex 7 was obtained as dark-green crystals in 73.7% yield. Sublimes at 220–250 °$C/10^{-4}$ mmHg. Anal. Found: C, 52.71; H, 4.93; Yb, 38.79. $C_{20}H_{23}OYb$ calc.: C, 53.10; H, 5.09; Yb, 38.27%. IR (cm-‘): 206m, 250w, 350s, 395s, 487m, 763vs, 813s, 835s, 897s, 929m, 947m, 972s, 1020m, 1036s, 1048s, 1065s, 1113s, 1166m, 1184m, 1194ms, 1237m, 1272m, 1365s, 1376s, 1440m, 2882s, 2930s, 3095m.

*{1,1′-(3-Oxa-pentamethylene)dicyclopentadienyl}(methylcyclopentadienyl)yttrium (8)*

*The* procedure followed was similar to that for 7. White crystals, 8, were obtained in 72.1% yield. Sublimes at 220–250 °$C/10^{-4}$ mmHg. Anal. Found: C, 65.55; H, 6.36; Y, 24.66. $C_{20}H_{23}OY$ calc.: C, 65.22; H, 6.25; Y, 24.18%. IR (cm-‘): 225s, 260s, 342m, 362m, 395s, 488s, 765vs, 834s, 853m, 885m, 906m, 970s, 1020s, 1032s, 1049s, 1125w, 1183s, 1194s, 1236m, 1252m, 1271s, 1325m, 1377s, 1437s, 2881s, 2929s, 3092s.

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