

## Studies on organolanthanide complexes

### LIV \*. Syntheses and X-ray crystal structures of bis-(2-methoxyethylcyclopentadienyl) rare earth iodides $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnI}$ (Ln = La or Y)

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#### Abstract

Reaction of bis-(2-methoxyethylcyclopentadienyl) rare earth chlorides with sodium iodide in tetrahydrofuran (THF) affords bis(2-methoxyethylcyclopentadienyl) rare earth iodide complexes  $\text{Cp}'_2\text{LnI}$  (Ln = La (1) or Y (2);  $\text{Cp}' = \text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4$ ). They crystallize from THF–hexane in the orthorhombic space group  $P2_12_12_1$  with unit cell parameters  $a = 11.266(7)$  Å,  $b = 12.350(10)$  Å,  $c = 13.075(9)$  Å and  $V = 1819(2)$  Å<sup>3</sup> with  $Z = 4$ , for  $D_{\text{calc}} = 1.870$  g cm<sup>-3</sup> for 1 and  $a = 12.237(4)$  Å,  $b = 10.965(9)$  Å,  $c = 12.805(1)$  Å and  $V = 1718.3(8)$  Å<sup>3</sup> with  $Z = 4$  for  $D_{\text{calc}} = 1.786$  g cm<sup>-3</sup> for 2. The central metal  $\text{Ln}^{3+}$  is coordinated by two  $\text{Cp}'$  ring centroids, one iodine atom and two oxygen atoms of  $\text{Cp}'$ , forming a distorted trigonal bipyramid. The La–O and Y–O bond distances average 2.584 Å and 2.48 Å, respectively. The average La–C( $\eta^5$ ) bond length is 2.805 Å and the Y–C( $\eta^5$ ) 2.68 Å.

**Key words:** Lanthanum; Yttrium; Iodide; Crystal structure

#### 1. Introduction

In recent years, unprecedented structural features and spectacular reactivity have been reported in organolanthanide chemistry [2–5]. Organolanthanide complexes are very active in such important processes as alkene and alkyne reduction [6–10], alkene polymerization [10–14], carbonyl [15–17] and saturated C–H activation [18,19], hydrosilylation [20,21] and olefin hydroamination [22]. As basic precursors to organolanthanide alkyl and hydride species, the biscyclopentadienyl lanthanide halides have received considerable attention. However, very few biscyclopentadienyl lanthanide iodides have been studied up to now [23–26]. As we know, the organolanthanide iodides are quite different from chlorides in the bond energies and reactivity of Ln–X [27]. Therefore we are interested in

syntheses of organolanthanide iodides. Generally, the syntheses of organolanthanide iodides have been realized by the reaction of  $\text{LnI}_3$  with cyclopentadienyl salt [23,25], of hydrides with MeI [24] and of divalent organolanthanide complexes with  $\text{I}_2$  [26]. We herein report a simple method for syntheses of  $\text{Cp}'_2\text{LnI}$  (Ln = La or Y) by the reaction of bis(2-methoxyethylcyclopentadienyl) lanthanide chlorides with NaI and their X-ray crystal structures.

#### 2. Experimental details

The complexes described below are extremely air and moisture sensitive. Therefore, both the syntheses and the subsequent manipulations of these compounds were conducted under argon with rigorous exclusion of air and water using the Schlenk vacuum-line techniques. Tetrahydrofuran (THF) and hexane were predried with  $\text{LiAlH}_4$  and freshly distilled from blue sodium benzophenone ketyl under Ar immediately

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\* For Part LIII, see ref. 1.

prior to use. The compounds  $[\text{Cp}'_2\text{LaCl}]_2$  and  $\text{Cp}'_2\text{YCl}$  were prepared according to methods in the literature [1,28]. Mass spectra were obtained on a Finnigan 4021 spectrometer at EI,  $T = 50\text{--}300^\circ\text{C}$ ,  $\text{EM} = 1.3\text{ kV}$ .  $^1\text{H}$  NMR spectra were obtained on a FX-90Q (90 MHz) spectrometer referenced to extral  $\text{Me}_4\text{Si}$  in  $\text{THF-}d_8$  (E. Merck for NMR spectroscopy).  $\text{THF-}d_8$  was dried over an Na–K alloy and degassed by freeze–thaw cycles on a vacuum line. The rare earth metals were analysed by direct complexometric titration with disodium EDTA. Carbon and hydrogen analyses were carried out by the combustion method in an aluminium tube.

### 2.1. $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LaI}$ (1)

NaI (0.340 g, 2.2 mmol) was added to a THF solution of  $[\text{Cp}'_2\text{LaCl}]_2$  (0.924 g, 1.1 mmol) and then the suspension was stirred for 20 h at room temperature. The mixture was centrifuged to remove NaCl, and the THF was removed *in vacuo* to a quarter volume; 2 ml of hexane were added. After filtration, the clear solution was crystallized at room temperature, giving white crystals  $\text{Cp}'_2\text{LaI}$  (0.732 g) with a 65% yield. Anal. Found: C, 37.69; H, 4.38; La, 27.13.  $\text{C}_{16}\text{H}_{22}\text{O}_2\text{LaI}$  calc.: C, 37.52; H, 4.33; La, 27.12%. MS: 512 ( $\text{M}^+$ , 15.40), 385 ( $[\text{M}-\text{I}]^+$ , 100.00), 124 ( $[\text{Cp}' + \text{H}]^+$ , 32.64). IR: 3070 s, 2921 vs, 1608 m, 1599 m, 1448 s, 1420 s, 1080 s, 1046 s, 1032 s, 998 s, 808 s, 762 vs, 369 m, 318 m, 216  $\text{s cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{THF-}d_8$ , TMS): 5.70 (s, 4H); 3.63 (t, 2H); 3.44 (s, 3H); 2.62 (t, 2H) ppm.

### 2.2. $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{YI}$ (2)

In an analogous manner, this substance was obtained from NaI (0.152 g, 1.0 mmol) and  $\text{Cp}'_2\text{YCl}$  (0.372 g, 1.0 mmol) as white crystals (0.278 g) with a 60% yield. Anal. Found: C, 41.15; H, 4.64; Y, 19.52.  $\text{C}_{16}\text{H}_{22}\text{O}_2\text{YI}$  calc.: C, 41.60; H, 4.80; Y, 19.24%. MS: 462 ( $\text{M}^+$ , 17.20), 335 ( $[\text{M}-\text{I}]^+$ , 100.00), 124 ( $[\text{Cp}' + \text{H}]^+$ , 22.16). IR: 3080 s, 2916 s, 1597 m, 1447 s, 1418 s, 1075 s, 1057 vs, 1035 s, 991 s, 812 s, 779 s, 380 m, 333 m, 249  $\text{s cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{THF-}d_8$ , TMS): 6.10 (t, 2H); 5.90 (t, 2H); 3.90 (t, 2H); 3.52 (s, 3H); 2.60 (t, 2H) ppm.

### 2.3. X-Ray crystallography

A suitable single crystal was sealed under Ar in the thin-walled glass capillary. Intensity data were collected on a Siemens R3m/V diffractometer for **1** and on an Enraf–Nonius CAD4 diffractometer for **2**, using graphite-monochromated  $\text{Mo K}\alpha_2$  radiation in the  $2\theta\text{--}\theta$  scan mode for **1** and the  $\omega\text{--}2\theta$  scan mode for **2**. Final lattice parameters were obtained by a least-squares refinement of the  $2\theta$  values of 25 reflections. The space group  $\text{P}2_12_12_1$  were identified from the systematic absences. The crystal data and the data collected parameters are listed in Table 1. The intensi-

TABLE 1. Crystallographic data for  $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnI}$  (Ln = La (1) or Y (2))

Compound	1	2
Molecular weight	512.1	462.1
Crystal systems	Orthorhombic	Orthorhombic
Space group	$\text{P}2_12_12_1$	$\text{P}2_12_12_1$
Crystal size (mm $\times$ mm $\times$ mm)	$0.4 \times 0.3 \times 0.2$	$0.4 \times 0.2 \times 0.1$
Cell constants		
$a$ ( $\text{\AA}$ )	11.266(7)	12.237(4)
$b$ ( $\text{\AA}$ )	12.350(10)	10.965(9)
$c$ ( $\text{\AA}$ )	13.075(9)	12.805(1)
$V$ ( $\text{\AA}^3$ )	1819(2)	1718.3(8)
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.870	1.786
$Z$	4	4
Scan technique	$2\theta\text{--}\theta$	$\omega\text{--}2\theta$
$2\theta$ range ( $^\circ$ )	$3 < 2\theta < 50.0$	$0 < 2\theta < 50.0$
Reflections	1874	1664
Number of observed data	1566 (for $F_o \geq 4\sigma(F)$ )	1063 (for $F_o \geq 3\sigma(F)$ )
$F(000)$	976	904
$R, R_w$	0.050, 0.067	0.064, 0.077

ties were corrected for Lorentz and polarization effects, but not for absorption effects for complex **1** and for Lorentz, polarization and absorption effects for complex **2**.

The metal atom was located by the Patterson method and the other non-hydrogen atoms were carried out by difference Fourier synthesis. All positional parameters and anisotropic thermal parameters for non-hydrogen atoms were refined by the full-matrix least-squares technique. Finally, all hydrogen atoms were introduced in calculated positions. All calculations for **1** were performed on a micro Vax-II computer with Siemens SHELXTL PLUS (VMS) programs and all calculations for **2** were made on a MicroVAX-II computer with SDP plus ORTEP programs. The atomic coordinates for complexes **1** and **2** are listed in Tables 2 and 3 respectively.

## 3. Results and discussion

### 3.1. Synthesis

The complexes  $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnI}$  (Ln = La (1) or Y (2)) were synthesized by the reaction of bis-(2-methoxyethylcyclopentadienyl) lanthanide chlorides with NaI in THF at room temperature (RT) according to eqns. (1) and (2):

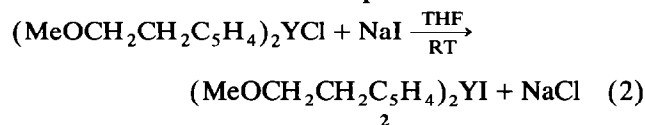
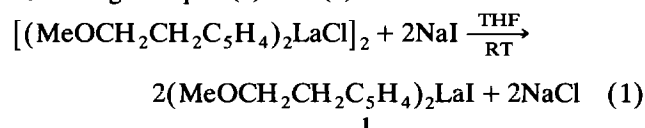


TABLE 2. Atomic coordinates and equivalent isotropic displacement coefficients for 1

Atom	$x(\times 10^4)$	$y(\times 10^4)$	$z(\times 10^4)$	$U_{eq}^a(\times 10^3 \text{ \AA}^3)$
La	648(1)	5014(1)	9537(1)	39(1)
I	1021(1)	3120(1)	11181(1)	77(1)
O(1)	-1238(9)	5303(11)	10626(9)	68(4)
O(2)	2565(9)	4105(8)	8876(10)	62(4)
C(11)	-1528(13)	4994(15)	8539(11)	57(4)
C(12)	-851(20)	5760(18)	8018(13)	80(7)
C(13)	15(24)	5263(24)	7470(15)	94(10)
C(14)	-54(19)	4178(25)	7628(16)	92(9)
C(15)	-997(20)	3961(13)	8287(14)	65(5)
C(16)	-2570(15)	5117(31)	9264(18)	107(10)
C(17)	-2340(18)	5166(32)	10296(19)	126(13)
C(18)	-1196(22)	5409(23)	11731(13)	111(10)
C(21)	2724(18)	6206(15)	9682(21)	82(8)
C(22)	2025(20)	6884(16)	9089(17)	82(7)
C(23)	1111(23)	7240(14)	9667(17)	82(7)
C(24)	2282(18)	6255(17)	10662(15)	72(6)
C(25)	1301(21)	6898(15)	10678(20)	92(9)
C(26)	3785(17)	5617(20)	9307(25)	110(11)
C(27)	3615(22)	4566(23)	9043(38)	434(66)
C(28)	2540(21)	2968(14)	8578(17)	89(8)

<sup>a</sup> Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

All these complexes can be crystallized from THF-hexane to give single crystals of different colours depending on the lanthanide metal present. They are

TABLE 3. Positional parameters and their estimated standard deviations for 2

Atom	$x$	$y$	$z$	$B(\text{ \AA}^2)$
Y	0.2427(2)	0.1895(2)	0.2955(2)	3.62(3)
I	0.4268(2)	0.1556(2)	0.1368(2)	5.43(4)
O(1)	0.214(1)	0.364(2)	0.178(1)	5.4(4) <sup>a</sup>
O(2)	0.342(1)	0.006(2)	0.360(1)	4.3(3) <sup>a</sup>
C(11)	0.260(2)	0.404(2)	0.388(2)	4.5(5) <sup>a</sup>
C(12)	0.355(2)	0.350(3)	0.414(2)	4.8(6) <sup>a</sup>
C(13)	0.327(3)	0.251(3)	0.485(3)	5.8(7) <sup>a</sup>
C(14)	0.218(2)	0.243(3)	0.497(3)	6.0(7) <sup>a</sup>
C(15)	0.169(2)	0.341(3)	0.440(2)	5.6(7) <sup>a</sup>
C(16)	0.246(3)	0.507(3)	0.312(3)	7.8(8) <sup>a</sup>
C(17)	0.228(3)	0.484(3)	0.210(2)	6.4(7) <sup>a</sup>
C(18)	0.202(2)	0.361(3)	0.065(2)	6.4(7) <sup>a</sup>
C(21)	0.129(2)	-0.015(2)	0.282(2)	4.8(6) <sup>a</sup>
C(22)	0.123(2)	0.033(2)	0.179(2)	4.4(6) <sup>a</sup>
C(23)	0.063(2)	0.143(2)	0.174(2)	4.2(5) <sup>a</sup>
C(24)	0.029(2)	0.149(3)	0.288(2)	6.4(7) <sup>a</sup>
C(25)	0.067(3)	0.059(3)	0.351(2)	6.1(7) <sup>a</sup>
C(26)	0.185(3)	-0.126(3)	0.314(3)	6.7(8) <sup>a</sup>
C(27)	0.453(2)	0.005(3)	0.389(2)	6.4(7) <sup>a</sup>
C(28)	0.305(3)	-0.108(3)	0.339(3)	7.5(9) <sup>a</sup>

<sup>a</sup> Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $\frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$ .

soluble in ethers and moderately soluble in aromatic solvents, but sensitive to air and moisture as other organolanthanides.

These new complexes are thermally stable and have better volatility. In the EI mass spectra, two complexes showed a parent molecular ion  $M^+$  and related fragments; no  $m/e$  greater than  $M^+$  was detected. This suggests that the complexes are monomeric, and the Ln-I bond is cleaved first, giving base peak of  $[M-I]^+$ . The monomeric structures of **1** and **2** were confirmed by the X-ray diffraction analyses.

The IR spectra of two complexes exhibit absorption peaks typical of  $\eta^5$ -cyclopentadienyl at about 3075, 1440, 1030 and 770.  $\text{cm}^{-1}$  [1,29]. Compared with the absorption peak of the C-O-C asymmetric stretching vibration of  $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{Na}$  ( $\nu = 1080 \text{ cm}^{-1}$ ) [1,29], that of complexes is shifted to lower frequency and  $\Delta\nu$  lies between 23 and 34  $\text{cm}^{-1}$ . These imply the existence of the intramolecular coordination bond from oxygen atom of ether-substituted cyclopentadienyl to the metal [1,29].

The  $^1\text{H}$  NMR data of two complexes **1** and **2** were measured using perdeuterotetrahydrofuran as solvent. The signals of  $\text{OCH}_3$  and  $\text{OCH}_2$  shifted to lower fields compared with those of sodium salt (3.05 ppm (s, 3H) for  $\text{OCH}_3$ , and 3.28 ppm (t, 2H) for  $\text{OCH}_2$ ). These results show that an intramolecular coordination bond (Ln ← O) forms. It is noteworthy that the four hydrogen atoms of cyclopentadienyl ring gave a single  $^1\text{H}$  NMR peak at 5.70 ppm (s, 4H) in complex **1**, but two peaks at 6.10 ppm (t, 2H) and 5.90 ppm (t, 2H) in complex **2**. Analogous cases are known in chloride complexes  $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnCl}$  [1,29]. Possibly a larger "twinkling" effect of the cyclopentadienyl protons led to their equality and a single  $^1\text{H}$  NMR peak in a larger lanthanum complex **1**.

### 3.2. Molecular structure of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnI}$ (**1** and **2**)

The X-ray structure of **1** is illustrated in Fig. 1, and selected bond distances and angles are given in Table 4. The lanthanum atom is coordinated by two cyclopentadienyl ligands, one iodine atom and two oxygen atoms. The bond parameters indicate that the structure has a trigonal bipyramidal coordination geometry if the  $\eta^5$ -cyclopentadienyl ring is regarded as occupying a single polyhedral vertex. Therefore **1** is a monomer and the formal coordination number of  $\text{La}^{3+}$  is nine. This is the first unsolvated monomeric example of organolanthanum halide complexes in which intramolecular coordination bond (Ln ← O) are formed effectively to avoid occurrence of disproportionation reaction. However, when the iodine ion is replaced by smaller chlorine ion, the lanthanum chloride complex

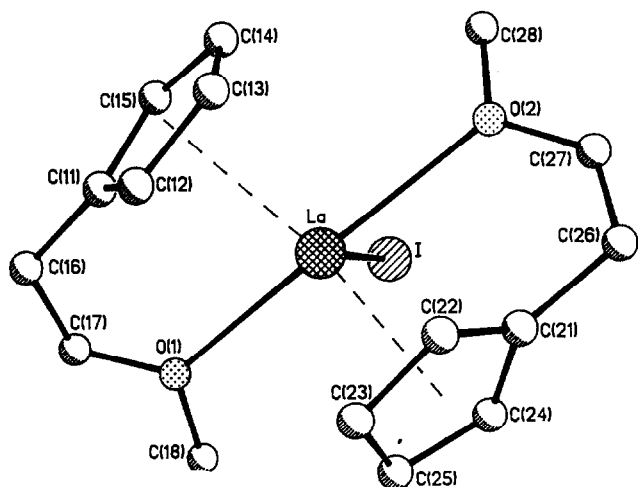


Fig. 1. The molecular structure of  $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LaI}$ .

is a dimer containing a chloride bridge; the formal coordination number of  $\text{La}^{3+}$  is ten [29]. This indicates that the size of anion also affects the coordination

TABLE 4. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1** and **2**

	<b>1</b> (Ln = La)	<b>2</b> (Ln = Y)
<i>Bond lengths</i>		
M-I	3.206(3)	3.057(4)
M-O(1)	2.583(11)	2.47(2)
M-O(2)	2.584(11)	2.49(2)
M-C(11)	2.777(14)	2.64(2)
M-C(12)	2.764(20)	2.71(3)
M-C(13)	2.812(20)	2.72(3)
M-C(14)	2.815(23)	2.66(3)
M-C(15)	2.792(20)	2.65(3)
M-C(21)	2.771(20)	2.65(3)
M-C(22)	2.842(21)	2.70(3)
M-C(23)	2.802(17)	2.74(2)
M-C(24)	2.861(21)	2.65(3)
M-C(25)	2.812(20)	2.68(4)
M-cent(1)	2.529	2.39
M-cent(2)	2.564	2.39
<i>Bond angles</i>		
cent(1)-M-cent(2)	124.5	125.6
O(1)-M-O(2)	158.8(4)	154.2(6)
O(1)-M-I	80.7(3)	78.1(5)
O(2)-M-I	78.3(3)	76.3(5)
I-M-cent(1)	123.3	121.1
I-M-cent(2)	112.1	113.3
O(1)-M-cent(1)	88.1	92.7
O(2)-M-cent(2)	88.2	92.6
C(11)-C(16)-C(17)	118.2(16)	120(3)
C(16)-C(17)-O(1)	120.1(19)	119(3)
C(17)-O(1)-M	125.0(13)	
C(21)-C(26)-C(27)	116.1(19)	114(3)
C(26)-C(27)-O(2)	125.2(22)	119(3)
C(27)-O(2)-M	120.2(16)	

Cent(1) is the centroid of cyclopentadienyl ring defined by C(11)-C(15); cent(2) is the centroid of the cyclopentadienyl ring defined by C(21)-C(25).

number and coordination geometry of the central metal ion.

The La-I distance is 3.21  $\text{\AA}$  in **1**, about 0.05  $\text{\AA}$  shorter than that in complex  $(\text{C}_5\text{Me}_5)_2\text{CeI}(\text{NCCCH}_3)_2$  after the difference between the rare earth ion radii is taken into account [30]. The La-C( $\eta^5$ ) bond distances range from 2.76 to 2.84  $\text{\AA}$ , similar to the values for  $[\text{Cp}_2^*\text{LaCl}]_2$  [29],  $(\eta^5\text{-C}_5\text{H}_5)_3\text{La} \cdot \text{THF}$  [28] and  $[(\text{C}_5\text{H}_5)_3\text{La}]_n$  [31].

The average La-O bond length in complex **1** is 0.14  $\text{\AA}$  shorter than the equivalent distance in the complex  $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LaCl}]_2$ . The cent(1)-La-cent(2) angle 124.5 $^\circ$  in **1** is significantly larger than that in complex  $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LaCl}]_2$  (113.9 $^\circ$ ), where cent(1) and cent(2) mean the centroids of cyclopentadienyl ligands. These may well arise from the less-crowded molecular structure of **1**.

The geometry of the yttrium compound **2** is similar to that of the lanthanum complex **1**, except that bond distances involving the metal atom are generally shorter for Y than for La. The selected bond lengths and angles are given in Table 4. However, the average Y-C( $\eta^5$ ) distance in **2**, 2.68  $\text{\AA}$ , agrees well with that found in other Y(III) cyclopentadienyl complexes, such as 2.66(2)  $\text{\AA}$  in  $[(\text{C}_5\text{H}_5)_2\text{Y}(\text{CH}_3)_2]$  [32], 2.69(2)  $\text{\AA}$  in  $[(\text{MeC}_5\text{H}_4)_2\text{Y}(\mu\text{-H})\text{THF}]_2$  [33], 2.674(5)  $\text{\AA}$  in  $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-N}_2\text{C}_3\text{HMe}_2)(\mu\text{-OH})\text{Y}(\text{C}_5\text{H}_4\text{-CH}_2\text{CH}_2)_2\text{O}]$  [34] and 2.655  $\text{\AA}$  in  $(\text{C}_5\text{Me}_5)_2\text{YCl}(\text{THF})$  [35]. The mean Y-O distance, 2.48  $\text{\AA}$  in **2**, is comparable with the value of 2.460(8)  $\text{\AA}$  in  $[(\text{MeC}_5\text{H}_4)_2\text{YH}(\text{THF})_2]$  [32] and 2.491(5)  $\text{\AA}$  in  $[(\text{Me}_2\text{C}_5\text{H}_3)_2\text{YH}(\text{THF})_2]$  [36].

On comparison of **1** and **2**, the mean La-O and La-I distances in **1** are in agreement with those in **2** when the differences between the ionic radii are taken into account [30]. The angles cent(1)-Ln-cent(2) and O(1)-Ln-O(2) are about the same in both compounds (124.5 $^\circ$  and 158.8(4) $^\circ$  for La *vs.* 125.6 $^\circ$  and 154.2(6) $^\circ$  for Y).

The most striking feature of these compounds is the formation of the intramolecular coordination bond from the oxygen atom of the ligand to the central rare earth metal. A chelating coordination is formed from each ether substituted cyclopentadienyl. For example, in **1**, two chelated five-membered rings are composed of C(16), C(17), cent(1), O(1) and La, and C(26), C(27), cent(2), O(2) and La respectively. Moreover, the sums of interior angles are 541.4 $^\circ$  and 539.7 $^\circ$  respectively, only deviating slightly from 540 $^\circ$ . This indicates that chelated rings are planes.

It is obvious that the synthesis of biscyclopentadienyl lanthanide iodides by the reaction of biscyclopentadienyl lanthanide chlorides with NaI is very simple and convenient. Moreover, the X-ray crystal structures

of these complexes will provide useful basic structural data in the area of biscyclopentadienyl lanthanide chemistry.

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