

# Anionic dichlorolanthanocene compounds. X-ray crystal structures of $[\{(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\}_2\text{LnCl}_2][\text{Li}(\text{THF})_4]$ (Ln = Er, Yb) and $\{(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\}_2\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$

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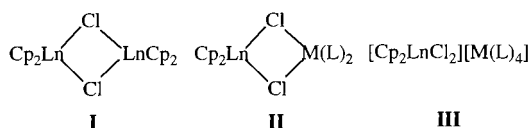
## Abstract

Treatment of  $\text{LnCl}_3$  with two equivalents of  $\text{Cp}^*\text{Li}$  ( $\text{Cp}^* = (\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ ) in THF gave, after crystallization from a THF–*n*-hexane solution at  $-30^\circ\text{C}$ , ionic compounds  $[\text{Cp}_2^*\text{LnCl}_2][\text{Li}(\text{THF})_4]$  (Ln = Er (1), Yb (2)) in good yield. Recrystallization of 2 from a toluene solution afforded an ‘ate’ compound  $\text{Cp}_2^*\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$  (3). Interestingly, recrystallization of 3 from a mixed solvent of THF–*n*-hexane did not give compound 2, and only 3 was isolated, indicating that the dissociation of THF may be an irreversible process or 3 is a thermodynamically more stable compound. All three compounds were fully characterized by various spectroscopic data and single-crystal X-ray analyses. Compounds 1 and 2 are the rare structurally characterized examples of an anionic dichlorolanthanocene stabilized by an alkali metal complex ion. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Alkali; Lanthanocene; Metallocene; Organolanthanide; Structure

## 1. Introduction

As key intermediates to various kinds of organolanthanide compounds, a large number of lanthanocene(III) chlorides have been prepared and structurally characterized [1]. The molecular structures of these compounds fall into types I, II and III.



Ln = lanthanide ion; M = alkali metal ion

However, no crystal data on type III compounds have yet been reported in the literature, presumably due to their poor stability<sup>1</sup>. Only in the case where  $\text{M}^+$  is replaced by bulky cations such as ammonium, phosphonium or arsenium, compound  $[\text{R}_4\text{A}][\text{Cp}_2^*\text{LnCl}_2]$

( $\text{Cp}^* = (\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ ) can be stabilized and  $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Cp}_2^*\text{NdCl}_2]$  has been subjected to X-ray diffraction study [2]. We report herein the rare structurally characterized example of the type III compound  $[\text{Cp}_2^*\text{LnCl}_2][\text{Li}(\text{THF})_4]$  (Ln = Er, Yb) and the X-ray crystal structure of  $\text{Cp}_2^*\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ .

## 2. Results and discussion

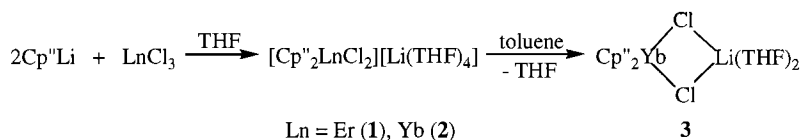
### 2.1. Synthesis

Treatment of  $\text{LnCl}_3$  with two equivalents of  $\text{Cp}^*\text{Li}$  in THF gave, after crystallization from a THF–*n*-hexane solution at  $-30^\circ\text{C}$ , ionic compounds  $[\text{Cp}_2^*\text{LnCl}_2][\text{Li}(\text{THF})_4]$  (Ln = Er (1), Yb (2)) in about 70% yield. The <sup>1</sup>H-NMR spectra of the hydrolysis products support the ratio of two THF molecules per ligand. The coordinated THF molecules in these compounds are very labile and can be easily lost by keeping the crystals away from the mother liquor for a while even at room temperature, which may explain why the values of carbon and hydrogen analyses on these solids were generally lower than the theoretical ones.

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<sup>1</sup> Compound  $[\{(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\}_2\text{LaCl}_2][\text{Li}(\text{THF})_4]$  was communicated with no structural data, see Ref. [2].



Scheme 1.

Table 1  
Crystal data and details of data collection and structure refinement for **1–3**

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>38</sub> H <sub>74</sub> Cl <sub>2</sub> ErLiO <sub>4</sub> Si <sub>4</sub>	C <sub>38</sub> H <sub>74</sub> Cl <sub>2</sub> LiO <sub>4</sub> Si <sub>4</sub> Yb	C <sub>30</sub> H <sub>58</sub> Cl <sub>2</sub> LiO <sub>2</sub> Si <sub>4</sub> Yb
Crystal size (mm <sup>3</sup> )	0.34 × 0.25 × 0.20	0.80 × 0.40 × 0.24	0.28 × 0.25 × 0.13
<i>M</i>	952.4	958.2	814.0
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	11.599(1)	11.608(1)	12.972(1)
<i>b</i> (Å)	21.856(1)	21.826(1)	19.584(2)
<i>c</i> (Å)	20.664(1)	20.552(1)	16.872(2)
<i>β</i> (°)	95.72(1)	95.77(1)	92.06(1)
<i>U</i> (Å <sup>3</sup> )	5212.4(5)	5180.6(4)	4283.5(7)
<i>Z</i>	4	4	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.214	1.229	1.262
2 $\theta$ range (°)	3.0–51.0	3.0–50.0	3.0–50.0
$\mu$ (mm <sup>-1</sup> )	1.835	2.032	2.441
<i>F</i> (000)	1980	1988	1668
No. of observed reflections	8053	8009	4958
No. of parameters refined	483	452	362
Goodness-of-fit	1.084	1.109	1.082
<i>R</i> <sub>1</sub>	0.066	0.060	0.052
<i>wR</i> <sub>2</sub>	0.187	0.166	0.108

Recrystallization of **2** from a toluene solution afforded an ‘ate’ compound Cp<sub>2</sub>Yb(μ-Cl)<sub>2</sub>Li(THF)<sub>2</sub> (**3**). It is noteworthy that recrystallization of **3** from a THF–*n*-hexane solution still afforded **3**, and no compound **2** was isolated, which perhaps indicate that the dissociation of THF molecules from **2** is an irreversible process or **3** is thermodynamically more stable than **2**. It is further noted that compounds **1** and **2** can only be obtained by an initial attempt. Recrystallization always causes loss of the coordinated THF molecules leading to the formation of the ‘ate’ compounds of the type **II**. Scheme 1 summarizes the above-mentioned transformations.

Table 2  
Selected bond distances (Å) and angles (°) for **1–3**

Compound (Ln)	<b>1</b> (Er <sup>3+</sup> )	<b>2</b> (Yb <sup>3+</sup> )	<b>3</b> (Yb <sup>3+</sup> )
Average Ln–C	2.667(3)	2.641(3)	2.630(3)
Average Ln–Cl	2.563(1)	2.546(1)	2.590(1)
Average Li–O	1.925(8)	1.937(7)	1.913(7)
Average Li–Cl			2.372(6)
Cl–Ln–Cl	103.11(3)	102.77(3)	84.89(3)
Cent–Ln–Cent <sup>a</sup>	129.9	130.1	127.5

<sup>a</sup> Cent, the ring centroid of the cyclopentadienyl.

## 2.2. Molecular structures

Crystal data and details of data collection and structure refinement for **1–3** are listed in Table 1. Table 2 lists selected bond distances and angles. The solid-state structures of both **1** and **2** as derived from single-crystal X-ray analyses reveal that they are isostructural and

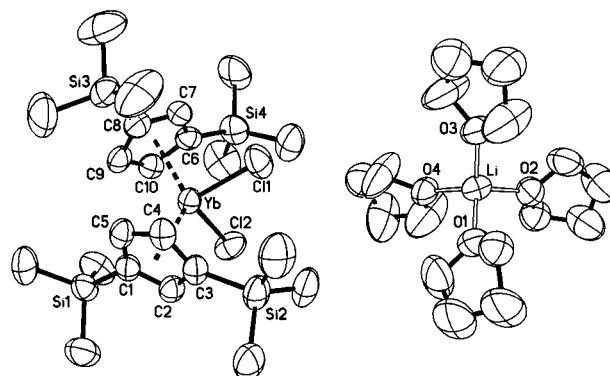


Fig. 1. Perspective view of the molecular structure of [Cp<sub>2</sub>YbCl<sub>2</sub>][Li(THF)<sub>4</sub>] (**2**). The thermal ellipsoids are drawn at the 35% probability level.

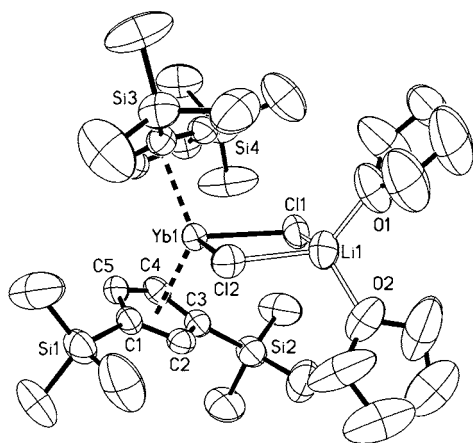


Fig. 2. Perspective view of the molecular structure of  $\text{Cp}_2\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$  (**3**). The thermal ellipsoids are drawn at the 35% probability level.

isomorphous. Their representative structure is shown in Fig. 1. It consists of well-separated, alternating layers of discrete tetrahedral anions  $[\text{Cp}_2^-\text{LnCl}_2]^-$  and tetrahedral cations  $[\text{Li}(\text{THF})_4]^+$ , a typical ionic lattice. In the anion, the  $\text{Ln}^{3+}$  ion is  $\eta^5$ -bound to two cyclopentadienyl rings and  $\sigma$ -bound to two terminal chloride ions in a distorted-tetrahedral geometry. The average Ln–C distances are 2.667(3) Å in **1** and 2.641(3) Å in **2**, respectively. The 0.026 Å difference in the above distances is comparable to the 0.019 Å difference in Shannon's ionic radii of eight-coordinate  $\text{Er}^{3+}$  (1.004 Å) and  $\text{Yb}^{3+}$  (0.985 Å) [3]. The average Ln–Cl distance of 2.563(1) Å in **1**, 2.546(1) Å in **2**, and 2.668(3) Å in  $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Cp}_2^-\text{NdCl}_2]$  [2] are all comparable to each other if Shannon's ionic radii are taken into account. The Cl–Ln–Cl angle of 103.11(3)° in **1** and 102.77(3)° in **2**, and the Cent–Ln–Cent angle of 129.9° in **1** and 130.1° in **2** are all larger than the corresponding values of 99.3(1)° and 126.3° in  $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Cp}_2^-\text{NdCl}_2]$  [2], respectively, perhaps due to crystal packing forces.

An X-ray diffraction study reveals that  $\text{Cp}_2\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$  (**3**) is similar in structure to  $\text{Cp}_2\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$  [4], but they are not isomorphous. As shown in Fig. 2, the  $\text{Yb}^{3+}$  ion is  $\eta^5$ -bound to two cyclopentadienyl rings and  $\sigma$ -bound to two doubly bridging chloride ions in a distorted-tetrahedral geometry. The Cl–Yb–Cl angle of 84.89(3)° is similar to that of 82.10(1)° in  $\text{Cp}_2\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$  and other type **II** compounds [5], but is significantly smaller than that of 102.77(3)° in **2** probably due to the bridging unit  $\text{Yb}(\mu\text{-Cl})_2\text{Li}$  that forces the Cl–Yb–Cl angle to be smaller. The Cent–Yb–Cent angle of 127.5° is also smaller than that of 130.1° in **2**. The doubly bridging Cl atoms result in that the average Yb–Cl distance of 2.590(1) Å in **3** is 0.044 Å longer than that in **2**. The average Yb–C distance of 2.630(3) Å is close to that of 2.641(3) Å in

**2** and is comparable to that of 2.76(1) Å in  $\text{Cp}_2\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ .

In summary, the rare structurally characterized example of an anionic dichlorolanthanocene stabilized by an alkali metal complex ion is reported. Such a compound can only be prepared by an initial attempt. Any recrystallization will cause loss of the coordinated solvent molecules leading to the formation of an 'ate' compound of the type **II**.

### 3. Experimental

#### 3.1. General procedure

All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk or cannula techniques. Organic solvents were freshly distilled from sodium benzophenone ketyl prior to use.  $\text{Cp}^*\text{Li}$  [4,6] and  $\text{LnCl}_3$  [7] were prepared according to the literature methods. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin–Elmer 1600 Fourier transform spectrometer.  $^1\text{H-NMR}$  spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 MHz, and chemical shifts are reported in  $\delta$  units with reference to the residual protons of the deuterated solvent. Elemental analyses were performed by MEDAC Ltd, Brunel University, Middlesex, UK.

#### 3.2. Preparation of $[\text{Cp}_2^-\text{ErCl}_2][\text{Li}(\text{THF})_4]$ (**1**)

To a suspension of  $\text{ErCl}_3$  (0.50 g, 1.84 mmol) in 30 ml of THF was slowly added a THF solution of  $\text{Cp}^*\text{Li}$  (0.79 g, 3.66 mmol) at  $-30^\circ\text{C}$  under stirring, and the reaction mixture was allowed to warm to room temperature and then stirred overnight. The precipitate was filtered off, and the resulting pink solution was concentrated. After addition of *n*-hexane, this pink THF–*n*-hexane solution was then cooled to  $-30^\circ\text{C}$  and this temperature was kept for several days, giving **1** as pink crystals (1.22 g, 70%).  $^1\text{H-NMR}$ :  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ )  $-1.9$  (br s),  $-20.4$  (br, s) ( $\text{Cp}^*$ ),  $-8.3$  (m),  $-17.7$  (m) (THF),  $-14.4$  (s),  $-18.8$  (s) (TMS). IR (KBr,  $\text{cm}^{-1}$ ): 3050w, 2959m, 2900w, 1258m, 1090s, 1025s, 801s. Anal. Found: C, 44.59; H, 7.27. Calc. for  $\text{C}_{30}\text{H}_{58}\text{Cl}_2\text{ErLiO}_2\text{Si}_4$  (**1**–2THF): C, 44.58; H, 7.23%.

#### 3.3. Preparation of $[\text{Cp}_2^-\text{YbCl}_2][\text{Li}(\text{THF})_4]$ (**2**)

This compound was prepared as orange–red crystals from  $\text{YbCl}_3$  (0.91 g, 3.27 mmol) and  $\text{Cp}^*\text{Li}$  (1.41 g, 6.53 mmol) in 50 ml of THF using procedures used above for **1**: yield 2.39 g (76%).  $^1\text{H-NMR}$ :  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 17.8 (s),  $-5.8$  (br, s) ( $\text{Cp}^*$ ) 2.47 (m), 0.74 (m) (THF), 0.29 (s),  $-0.04$  (s) (TMS). IR (KBr,  $\text{cm}^{-1}$ ): 3060w, 2958m,

2893w, 1255s, 1089s, 1038s, 837s. Anal. Found: C, 44.31; H, 6.97. Calc. for  $C_{30}H_{58}Cl_2LiO_2Si_4Yb$  (**2**-2THF): C, 44.26; H, 7.18%.

#### 3.4. Preparation of $Cp^*_2Yb(\mu-Cl)_2Li(THF)_2$ (**3**)

Recrystallization of **2** from a toluene solution at  $-30^\circ C$  gave **3** as orange–red crystals.

Compound **3** can also be prepared according to the literature method [4] except using toluene as a crystallization solvent.  $^1H$ -NMR:  $\delta_H$  ( $C_6D_6$ ) 17.6 (s),  $-5.7$  (br, s) ( $Cp^*$ ), 2.45 (m), 0.72 (m) (THF), 0.26 (s),  $-0.01$  (s) (TMS). IR (KBr,  $cm^{-1}$ ): 3055w, 2950m, 2890w, 1255s, 1089s, 1035s, 832s. Anal. Found: C, 44.16; H, 7.09. Calc. for  $C_{30}H_{58}Cl_2LiO_2Si_4Yb$ : C, 44.26; H, 7.18%.

#### 3.5. X-ray structure determination

All single crystals were sealed with mother liquor under  $N_2$  in thin-walled glass capillaries. Data were collected at 294 K on an MSC/Rigaku RAXIS-IIC imaging plate using Mo- $K_\alpha$  radiation ( $0.71073 \text{ \AA}$ ) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABCOR program [8]. All structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically for all non-hydrogen atoms by full-matrix least squares, on  $F^2$  using the Siemens SHELXTL program package (PC version) [9]. All hydrogen atoms were geometrically fixed using the riding model. Three methylene groups (C33, C54 and C64) of the three THF molecules in **1** are disordered over two sets of positions with 0.6:0.4, 0.5:0.5 and 0.7:0.3 occupancies, respectively. Four methylene groups (C31, C41, C52 and C62) of the four THF molecules in **2** are disordered over two sets of positions with 0.5:0.5 occupancies. Further details are included in the supporting material.

#### 4. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 136846 for compound **1**, CCDC no. 136847 for compound **2**, and CCDC no. 136848 for compound **3**. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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