

## Synthesis of lanthanide complexes coordinated by an asymmetric cyclopentadienyl ligand

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### Abstract

The synthesis and characterization of bis- and monocyclopentadienyl lanthanide iodides [(*S*)-Cp']<sub>2</sub>LnI (Ln = Sm, **3**; Ln = La, **4**) and (*S*)-Cp'LnI<sub>2</sub>(THF)<sub>*n*</sub> (Ln = Sm, *n* = 3, **5**; Ln = La, *n* = 2, **6**) coordinated by an asymmetric cyclopentadienyl ligand (Cp' = C<sub>5</sub>H<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)OCH<sub>2</sub>Ph) have been carried out. Variable-temperature NMR study of compounds **3** and **4** reveals a fluxional process in solution. The X-ray crystal structure analysis of **3** shows a bent metallocene structure with intramolecular coordination to the oxygen atoms of the side chains of both cyclopentadienyl ligands. For monocyclopentadienyl complexes, intramolecular coordination is observed only for the lanthanum complex **6**. All compounds exhibit activity for the catalysis of Diels–Alder reactions.

**Keywords:** Samarium; Lanthanum; Cyclopentadienyl; Chirality

### 1. Introduction

Lanthanides have been studied extensively during recent years, both for their applications in organic synthesis as reagents or catalysts, and for the preparation of new organometallic complexes [1,2].

The potential of lanthanides in asymmetric catalysis has been demonstrated only recently. Marks and coworkers have synthesized lanthanide complexes coordinated by an asymmetric ansa-biscyclopentadienyl ligand which introduces two types of chirality in the molecule after complexation: planar chirality due to the 1,3-disubstitution on one cyclopentadienyl ring, and also the chirality due to the substituent on the cyclopentadienyl ligand [3]. Several compounds of this family, such as amides and hydrocarbyls, have been investigated as precatalysts for olefin hydrogenation or hydrosilylation, and for hydroamination/cyclization of aminoalkenes, and high enantiomeric excesses have been obtained in some cases. Binaphthol has been successfully employed as an asymmetric ancillary ligand at-

tached to lanthanide metals in Lewis-acid-catalysed reactions [4–6]. Kobayashi and coworkers have described the catalysis of Diels–Alder reactions by chiral ytterbium or scandium triflates coordinated by (*R*)-(+)-binaphthol [4]. Shibasaki and coworkers [6–8] and others [9] have prepared several asymmetric lanthanum catalysts with binaphthol or binaphthoxide ligands which give good enantioselection in nitroaldolization, Michael and hydrophosphonylation reactions. Lanthanide triflates (Yb, Eu, La) coordinated by a chiral sulfonamide catalyse Mukaiyama-type aldol reactions with only moderate yields and enantiomeric excesses [10]. Asymmetric Meerwein–Ponndorf-type reactions catalysed by lanthanides have also been investigated [11,12]: a samarium compound prepared from SmI<sub>3</sub> and dilithium aminodiolate gave a high enantiomeric excess in the reduction of acetophenone by isopropanol [11,12].

Our recent investigations have been directed towards the use of lanthanide derivatives as Lewis acid catalysts and we have demonstrated the efficiency of both SmI<sub>2</sub> and other lanthanide iodides for the catalysis of various reactions such as Mukaiyama-type aldolizations, Michael additions, Diels–Alder reactions and ring opening of epoxides by various nucleophiles [13]. We subsequently decided to explore the potential of lanthanide

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iodides coordinated by chiral ligands as asymmetric catalysts. With the aim of designing new chiral ligands suited for lanthanides, we focused on cyclopentadienyl ligands with a pendant ether function. Qian and coworkers [14–23] and others [24,25] have synthesized numerous divalent and trivalent lanthanide derivatives of various classes coordinated by the 2-methoxyethylcyclopentadienyl ( $C_5H_4CH_2CH_2OMe = Cp^0$ ) ligand. Most of the compounds are bis- or tri-cyclopentadienyl complexes, and one or two oxygen atoms of the ligands are intramolecularly coordinated to the Ln centre. Some divalent and trivalent lanthanide complexes with cyclopentadienyl ligands containing nitrogen atoms on the side chain, which coordinate by intramolecular bonds to lanthanide metals, have also been described [26,27]. We envisaged to prepare complexes coordinated by a cyclopentadienyl ligand containing both a chiral centre and a Lewis base on the side chain. It was hoped that such a bidentate ligand would stabilize the complex through intramolecular chelation and hence prevent solvent coordination to the metal. It should, moreover, bring the stereogenic centre into close proximity with the lanthanide atom for better control of asymmetric induction during catalysis.

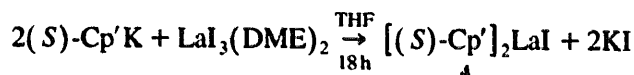
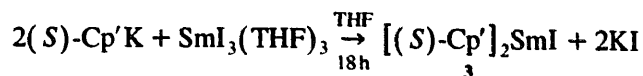
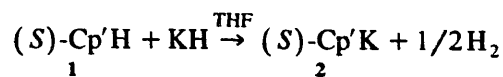
We have already published the synthesis of (*S*)-(2-benzyloxypropyl) cyclopentadiene **1**, as a mixture of two regioisomers, which is readily performed in four steps from (*S*)-ethyl lactate [28]. After several trials to obtain a cyclopentadienyl salt (*S*)-Cp'M (M = alkali metal) with good and reproducible yields (*S*)-Cp'K **2** was synthesized by the reaction of (*S*)-(2-benzyloxypropyl) cyclopentadiene with potassium hydride in THF, and the preparation of a biscyclopentadienyl samarium complex [(*S*)-Cp']<sub>2</sub>SmI was described [28]. We report now the X-ray structural analysis of this complex, the synthesis and characterization of the monocyclopentadienyl samarium iodide and the related mono- and bis-cyclopentadienyl lanthanum compounds and their use as catalysts in Diels–Alder reactions. We also describe the X-ray structural analysis of LaI<sub>3</sub>(THF)<sub>4</sub> obtained as a by-product during our studies.

## 2. Results and discussion

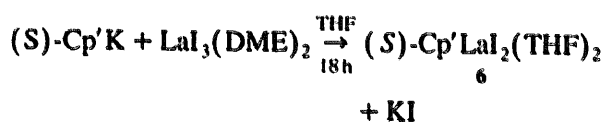
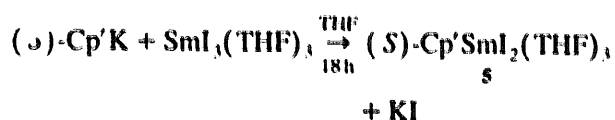
### 2.1. Synthesis of lanthanide iodide complexes coordinated with the asymmetric ligand: (*S*)-Cp'H = (*S*)-C<sub>5</sub>H<sub>5</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)OCH<sub>2</sub>Ph

The starting lanthanide iodides were prepared by literature procedures, i.e. the reaction of lanthanum powder with iodine in DME for LaI<sub>3</sub>(DME)<sub>2</sub> [29] and the reaction of SmI<sub>2</sub>(THF)<sub>2</sub> with iodine in THF for SmI<sub>3</sub>(THF)<sub>3</sub>. Biscyclopentadienyl samarium and lanthanum iodides were prepared by the reaction of two equivalents of (*S*)-Cp'K with the corresponding tri-

iodides in THF at room temperature and yielded the complexes [(*S*)-Cp']<sub>2</sub>LnI (**3**: Ln = Sm, **4**: Ln = La), isolated as yellow (**3**) or colourless (**4**) crystals. **3** and **4** were fully characterized by FTIR/MS [28], <sup>1</sup>H, <sup>13</sup>C, and for **4** <sup>139</sup>La NMR, and elemental analysis.



Monocyclopentadienyl complexes of samarium **5** and lanthanum **6** were obtained by reacting SmI<sub>3</sub>(THF)<sub>3</sub> and LaI<sub>3</sub>(DME)<sub>2</sub> in THF at room temperature with (*S*)-Cp'K **2**, in the molar ratio 1:1, and were fully characterized by <sup>1</sup>H, <sup>13</sup>C, and for **6** <sup>139</sup>La NMR and elemental analysis. For **3** and **5**, X-ray diffraction studies have been carried out. It has been established that the samarium complex **5** is coordinated by three THF molecules while there are only two for the lanthanum analogue **6**. (Recrystallization of **5** from THF–hexane mixture gave single crystals. The data were collected at  $-150 \pm 0.5^\circ\text{C}$  on an Enraf–Nonius CAD-4 diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a graphite monochromator: FW = 833.78; space group *P*41(76);  $a = b = 11.560(1) \text{ \AA}$ ,  $c = 22.746(2) \text{ \AA}$ ;  $V = 3039.59(79) \text{ \AA}^3$ ;  $Z = 4$ ;  $D_{\text{calc}} = 1.822 \text{ g cm}^{-3}$ ;  $\mu = 39.8 \text{ cm}^{-1}$ ;  $F(000) = 1612$ ; number of observed reflections, 4344; final  $R = 0.063$ ;  $R_w = 0.71$ .)

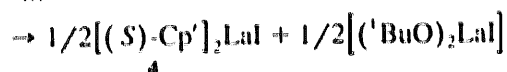
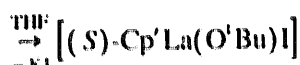
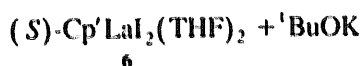


Complexes **3–6** are highly soluble in THF and DME, moderately soluble in diethyl ether and aromatic solvents, and insoluble in aliphatic hydrocarbons and are extremely air- and moisture-sensitive. All these compounds are stable in toluene as well as in methylene chloride, as no change of their <sup>1</sup>H NMR spectra could be detected after several days at room temperature. This observation is of particular interest for the screening of the activity of these complexes in catalysis: lanthanide(III) iodides and SmI<sub>2</sub> give better activities as Lewis-acid-type catalysts in methylene chloride than in other solvents such as toluene [13].

Solvent-free lanthanide compounds are supposed to give high catalytic activity due to an unsaturated coordination sphere. An efficient method to prepare THF-free

$\text{Cp}^* \text{LaI}_2$  consisting in the treatment of  $\text{Cp}^* \text{LaI}_2(\text{THF})_3$  with  $\text{Me}_3\text{SiI}$  has been reported [30]. An attempt to obtain the THF-free  $\text{Cp}^* \text{LaI}_2$  using the above method resulted in the cleavage of the ether bond and in the loss of the benzylic group. The treatment of **6** with hot toluene removes all the THF molecules from the coordination sphere of the lanthanum atom and leads to the formation of a product which probably has an oligomeric structure  $[(S)\text{-Cp}^* \text{LaI}_2]_x$ , **7** and is soluble only in donor solvents. Complex **7** can be reversibly converted to **6** by treatment with THF. The first results in catalysis obtained with compound **7** were deceptive (see below) and we did not go further in its characterization.

Lanthanide compounds coordinated by three different ligands, such as cyclopentadienyl, alkoxide and iodide are as yet unknown. In order to synthesize the cyclopentadienyl alkoxide iodide lanthanum complex,  $(S)\text{-Cp}^* \text{LaI-O}^t\text{Bu}$  which could possibly have interesting properties for catalysis, the reaction of **6** with  ${}^t\text{BuOK}$  was carried out. Instead of the desired product being formed, however, this reaction resulted in the formation of **4** (72% yield) and of a second lanthanum-containing product which, presumably, was the mixed lanthanum alkoxyiodide  $\text{LaI}(\text{O}^t\text{Bu})_2$ . This result can be explained by the disproportionation reaction of complex  $[(S)\text{-Cp}^* \text{La}(\text{O}^t\text{Bu})]$ , which is formed as an intermediate, since such reactions have been reported for unsubstituted cyclopentadienyl organolanthanum compounds [31].



## 2.2. Solid-state structure of bis[(*S*)-(2-benzyloxypropyl)cyclopentadienyl] samarium iodide [(*S*)-Cp']<sub>2</sub>SmI: **3**

X-ray structural characterization of the chiral compound  $[(S)\text{-Cp}']_2\text{SmI}$  **3** confirms the *S* configuration and reveals the expected bent-metallocene structure similar to those previously reported for the achiral  $\text{Cp}^*_2\text{LnI}$  ( $\text{Cp}^* = \text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4$ ,  $\text{Ln} = \text{La}, \text{Sm}, \text{Yb}, \text{Y}$ ) [14,19–21].

As shown in Fig. 1, the structure is monomeric and the samarium ion is pentacoordinated by the two cyclopentadienyl rings, one iodide and the two oxygen atoms of the two (*S*)-Cp' ligands in an approximately trigonal bipyramidal geometry, with the two oxygen atoms in apical positions. The formal coordination number of the samarium is nine. The ligand arrangement around the central metal atom is very close to the structure of the recently published analogous  $\text{Cp}^*_2\text{SmI}$  [21].

Table 1 shows selected bond distances and angles and Table 2 fractional atomic coordinates for **3**. Considering that the cyclopentadienyl ring occupies a single coordination site, the values of the bond angles around the samarium, in particular  $\text{O}(1)\text{-Sm-O}(2)$   $159.4(4)^\circ$  and  $\text{Cp}(1)\text{-Sm-Cp}(2)$   $123.7^\circ$ , compared with  $180^\circ$  and  $120^\circ$  for a regular trigonal bipyramid (TBP), lead to the description of the geometry as approximately TBP. Similar TBP structures have also been found in the compounds  $\text{Cp}^*_2\text{LnI}$  ( $\text{Ln} = \text{La}, \text{Sm}, \text{Yb}, \text{Y}$ ) [14,15,19–21].

Of great interest is the geometry involving the metal centre and the formation of two intramolecular bonds from the oxygen atoms of the two cyclopentadienyl ligands to samarium, which form two chelated five-membered rings. These two rings,  $\text{Sm-O}(1)\text{-C}(7)\text{-C}(6)\text{-C}(5)\text{-O}(1)$  and  $\text{Sm-O}(2)\text{-C}(23)\text{-C}(22)\text{-C}(21)\text{-O}(2)$ , are

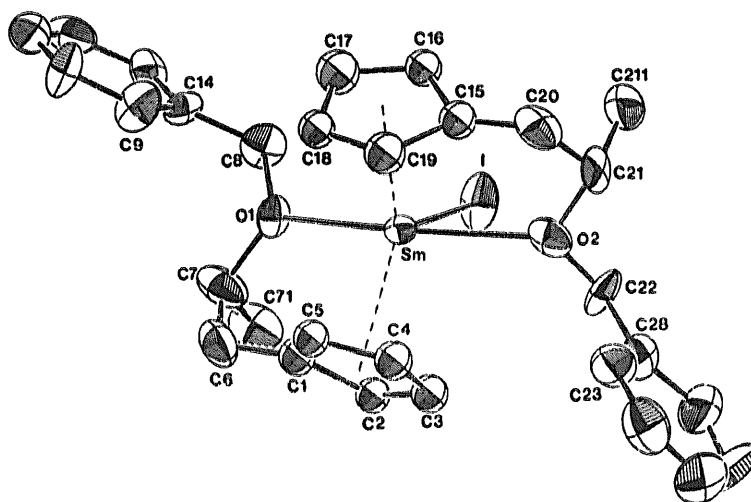


Fig. 1. ORTEP plot of  $[(S)\text{-Cp}']_2\text{SmI}$  **3**.

**Table 1**  
Selected bond distances (Å) and angles (deg) for [(S)-Cp']<sub>2</sub>SmI: 3

Sm–I	3.088(5)	O(1)–C(7)	1.47(3)
Sm–O(1)	2.563(15)	O(1)–C(8)	1.45(2)
Sm–O(2)	2.575(20)	C(7)–C(6)	1.51(4)
Sm–C(1)	2.67(2)	C(6)–C(1)	1.49(3)
Sm–C(2)	2.76(2)	C(7)–C(71)	1.50(3)
Sm–C(3)	2.76(2)	C(8)–C(14)	1.47(3)
Sm–C(4)	2.71(2)	O(2)–C(21)	1.49(3)
Sm–C(5)	2.67(2)	O(2)–C(22)	1.41(2)
Sm–C(15)	2.76(2)	C(21)–C(20)	1.49(4)
Sm–C(16)	2.74(2)	C(20)–C(15)	1.40(3)
Sm–C(17)	2.82(2)	C(21)–C(211)	1.59(4)
Sm–C(18)	2.68(2)	C(22)–C(28)	1.53(3)
Sm–C(19)	2.68(2)	av.(C–C) <sub>Cp</sub>	1.42(5)
Sm–Cp(1) <sup>a</sup>	2.43	av.(C–C) <sub>Ph</sub>	1.38(4)
Sm–Cp(2) <sup>a</sup>	2.45		
O(1)–Sm–O(2)	159.4(4)	Sm–O(1)–C(7)	125(2)
O(1)–Sm–I	80.1(4)	Sm–C(1)–C(6)	117(1)
O(2)–Sm–I	79.4(4)	O(1)–C(7)–C(6)	106(2)
O(1)–Sm–Cp(1)	90.1	Sm–O(1)–C(8)	120(1)
O(1)–Sm–Cp(2)	100.5	O(1)–C(8)–C(14)	111(2)
O(2)–Sm–Cp(1)	99.0	C(8)–O(1)–C(7)	112(2)
O(2)–Sm–Cp(2)	89.8	Sm–O(2)–C(21)	125(1)
I–Sm–Cp(1)	119.0	Sm–C(15)–C(20)	116(2)
I–Sm–Cp(2)	117.3	O(2)–C(21)–C(20)	107(2)
Cp(1)–Sm–Cp(2)	123.7	Sm–O(2)–C(22)	121(1)
O(1)–Sm–C(1)	62.6(6)	O(2)–C(22)–C(28)	113(2)
O(2)–Sm–C(15)	62.0(7)	C(22)–O(2)–C(21)	111(2)

<sup>a</sup> Cp(1) is the centroid of the C(1)–C(5) ring and Cp(2) is the centroid of the C(15)–C(19) ring.

C(6)–Cp(1) and Sm–O(2). C(21)–C(20)–Cp(2), are not rigorously planar but slightly puckered. Considering the two planes Sm–O(1)–Cp(1) and Sm–O(2)–Cp(2), the distances of C(6), C(7) and C(20), C(21) atoms to the corresponding plane are 0.319 and –0.307 Å and 0.200, –0.306 Å respectively.

The Sm–I, the average Sm–O and the average Sm–C(ring) distances and angles around the samarium are compared in Table 3 to analogous distances and angles in the reported compounds Cp<sub>2</sub>LnI, Cp<sub>2</sub>SmI(THF) and Cp<sub>2</sub>SmI(η<sup>2</sup>-tetrazole) [19,20,32,33]. The average Sm–C(ring) distance is 2.73(5) Å and the cyclopentadienyl rings are tilted in a bent metallocene arrangement with a centroid–Sm–centroid angle of 123.7°. This angle is comparable with the values 124.5°, 127.1° and 125.6° found in the monomeric Cp<sub>2</sub>LnI (Ln = La, Yb, Y) structures as well as to those in Cp<sub>2</sub>LnCl (Ln = Dy, Yb) [16] and is very close to that in Cp<sub>2</sub>SmI (123.8°). However, it is much smaller than the angle 137(1)° found in Cp<sub>2</sub>SmI(THF) and Cp<sub>2</sub>SmI(η<sup>2</sup>-tetrazole), and reflects the greater steric demand of the two cyclopentadienyls with their additional pendant functional groups, due to the intramolecular Sm–O bonds and consequent formation of the two chelate five-membered rings.

Bond length comparison of the Sm–I and Sm–C(ring) distances with the related Cp<sub>2</sub>LnI (Ln = La, Yb, Y) compounds are in accordance with the general decrease-

ing trend of bond distances as the ionic radius of the metal decreases (Table 3). The similarity of the structures can also be seen in the values of the four angles (ring centroid)–metal–(ring centroid), (ring centroid)–metal–halide, (ring centroid)–metal–oxygen and halide–metal–oxygen given in Table 3.

The Sm–I distance in **3** is slightly shorter than in Cp<sub>2</sub>SmI, whereas the Sm–O bond lengths are longer. Taking into account the differences in the ionic radii of the Sm and the other Ln elements, the larger Sm–O distance in complex **3** compared with the corresponding distances in Cp<sub>2</sub>LnI and to the Ln–O distances in Cp<sub>2</sub>LnI, can be explained by the steric bulk of the benzyl group relative to the size of the methyl group.

Bond length comparison of the Sm–I bond with the corresponding distance in Cp<sub>2</sub>SmI(THF) shows a bond length difference consistent with a smaller effective radius of Sm<sup>3+</sup>, as its formal coordination number is lowered from nine in [(S)-Cp']<sub>2</sub>SmI to eight in Cp<sub>2</sub>SmI(THF). This distance compares well with the value found in the nine-coordinate complex Cp<sub>2</sub>SmI(η<sup>2</sup>-tetrazole).

### 2.3. Solid-state structure of tetra-tetrahydrofuran tri-iodolanthanum LaI<sub>3</sub>(THF)<sub>4</sub>: **8**

The X-ray structure determination of a crystal obtained in the crystallization process of (S)-Cp'LaI<sub>2</sub>(THF)<sub>2</sub> revealed the structure of the LaI<sub>3</sub>(THF)<sub>4</sub> compound **8**, which is monomeric, with an approxi-

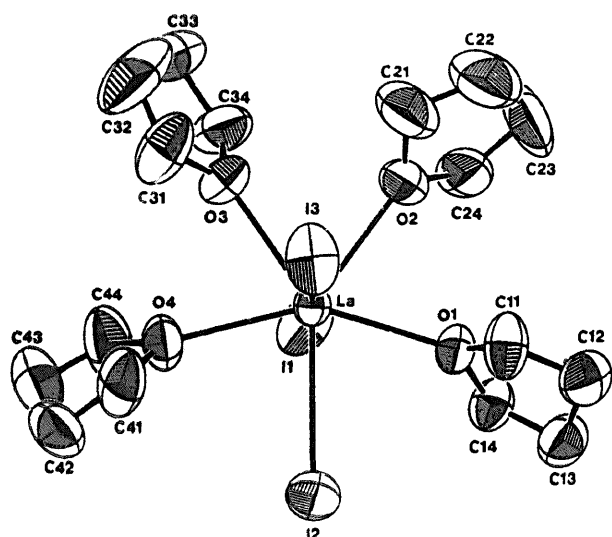
**Table 2**  
Fractional atomic coordinates (× 10<sup>4</sup>) for [(S)-Cp']<sub>2</sub>SmI

	x	y	z
Sm	–2263(1)	–1123.3(7)	–3765.3(2)
I	–3722(2)	602(1)	–4089.8(4)
O(1)	–1152(15)	–1255(10)	–4311(3)
O(2)	–3772(15)	–459(11)	–3312(4)
C(6)	1212(24)	–1274(17)	–4113(6)
C(7)	315(25)	–972(17)	–4389(8)
C(71)	385(29)	88(17)	–4457(7)
C(8)	–2057(25)	–1269(16)	–4586(5)
C(9)	–1087(29)	–2942(17)	–4707(6)
C(10)	–759(30)	–3645(16)	–4912(5)
C(11)	–970(26)	–3465(21)	–5244(7)
C(12)	–1486(26)	–2629(22)	–5334(7)
C(13)	–1858(23)	–1911(15)	–5122(5)
C(14)	–1652(23)	–2057(15)	–4800(4)
C(20)	–4980(27)	–1958(17)	–3240(7)
C(21)	–5123(24)	–897(19)	–3199(5)
C(211)	–6367(27)	–504(25)	–3416(7)
C(22)	–3658(28)	511(15)	–3217(5)
C(23)	–2618(28)	–155(19)	–2706(6)
C(24)	–2097(34)	–19(24)	–2409(7)
C(25)	–2031(33)	842(26)	–2282(6)
C(26)	–2544(47)	1624(24)	–2447(9)
C(27)	–3126(34)	1521(23)	–2742(9)
C(28)	–3124(26)	626(18)	–2882(5)

Table 3  
Structural parameters for biscyclopentadienyl iodine lanthanide complexes

Compound <sup>a</sup>	Ln-I (Å)	Av. Ln-O (Å)	Av. Ln-C (Å)	Centroid-Ln- centroid (deg)	O(1)-Ln-O(2) (deg)	Centroid-Ln-I (deg)	Centroid-Ln-O (deg)	I-Ln-O (deg)	Ref.
Cp <sub>2</sub> Lal	3.206(3)	2.584(1)	2.81(3)	124.5	158.8(4)	123.3 112.1	88.1 88.2	80.7(3) 78.3(3) 79.0	[19] [21] 77.3
Cp <sub>2</sub> SmI	3.119(1)	2.519(8) 2.528(8)	2.72(3)	123.8	156.2(3)				this work
Cp <sub>2</sub> SmI 3	3.088(5)	2.569(8)	2.73(5)	123.7	159.4(4)	119.0 117.3	90.1 100.5 99.0 89.8	80.1(4) 79.4(4)	
Cp <sub>2</sub> Yl	3.057(4)	2.48(1)	2.68(3)	125.6	154.2(6)	121.1 113.3	92.7 92.6	78.1(5) 76.3(5)	[21]
Cp <sub>2</sub> Ybl	3.049(1)	2.45(2)	2.62(3)	127.1	152.6(4)	119.9 113.0	92.1 100.2 99.3 92.7	76.7(3) 76.0(3)	[20]
Cp <sub>2</sub> SmI(THF) <sup>b</sup>	3.043(2) 3.053(2)	2.45(1) 2.45(1)	2.725(1)	136(1) 137(1)	—	106.2(2) 106.1(2) 104.7(2)	105.7(4) 104.2(4) 104.4(4)	88.8(3) 90.5(3)	[32]
Cp <sub>2</sub> SmI(η <sup>2</sup> -tetrazole)	3.100(2)	—	2.73(2)	137	—	106.4(2) 106.6 104.3	104.6(4)		[33]

<sup>a</sup> Cp<sup>0</sup> = MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>; Cp<sup>+</sup> = C<sub>5</sub>Me<sub>5</sub>; Ln = La, Y, Yb. <sup>b</sup> There are two independent molecules in the asymmetric unit.

Fig. 2. ORTEP plot of  $\text{LaI}_3(\text{THF})_4$  **8**.

mately pentagonal bipyramidal coordination geometry around the central metal atom, as shown in Fig. 2. Selected bond lengths and angles are listed in Table 4 and fractional atomic coordinates in Table 5. Two iodide ligands occupy axial positions with an average La–I distance of 3.135(4) Å, while the third iodide ligand lies in the equatorial plane with a La–I distance of 3.190(4) Å. All the oxygen atoms of the THF ligands lie in the equatorial plane with an average La–O distance of 2.54(3) Å. The axial I(1)–La–I(3) angle is 171.4(1)°. The  $\text{LaI}_3(\text{THF})_4$  compound is isostructural with the analogous  $\text{UI}_3(\text{THF})_4$  [34]. Noteworthy is the difference on the molecular geometry about the La atom in  $\text{LaI}_3(\text{THF})_4$  compared with  $\text{LaI}_3(\text{PrOH})_4$ , whose solid-state structure was published recently [35] and has revealed a capped trigonal prismatic geometry. Thus, in **8** the La–I and the La–O distances are respectively shorter and longer than the corresponding distances in the isopropanol adduct. The molecular geometry of **8**,

Table 4  
Selected bond lengths (Å) and angles (deg) for **8**,  $\text{LaI}_3(\text{THF})_4$ 

La–I(1)	3.129(4)	La–O(2)	2.576(8)
La–I(2)	3.190(4)	La–O(3)	2.550(8)
La–I(3)	3.142(4)	La–O(4)	2.535(8)
La–O(1)	2.515(7)		
I(1)–La–I(2)	94.9(1)	O(3)–La–I(2)	145.8(1)
I(1)–La–I(3)	171.4(1)	O(3)–La–I(3)	84.6(2)
I(2)–La–I(3)	93.4(1)	O(3)–La–O(1)	140.7(2)
O(1)–La–I(1)	87.2(2)	O(3)–La–O(2)	71.5(3)
O(1)–La–I(2)	73.5(2)	O(4)–La–I(1)	89.4(2)
O(1)–La–I(3)	97.2(2)	O(4)–La–I(2)	76.0(2)
O(1)–La–O(2)	69.5(3)	O(4)–La–I(3)	90.6(2)
O(2)–La–I(1)	89.1(2)	O(4)–La–O(1)	148.9(2)
O(2)–La–I(2)	142.5(1)	O(4)–La–O(2)	141.4(2)
O(2)–La–I(3)	85.6(2)	O(4)–La–O(3)	69.9(3)
O(3)–La–I(1)	87.3(2)		

Table 5  
Fractional atomic coordinates ( $\times 10^4$ ) for  $\text{LaI}_3(\text{THF})_4$  **8**

	x	y	z
La	1520.1(5)	1938.4(2)	2114.1(2)
I(1)	–749.4(7)	1704.8(4)	3459.5(3)
I(2)	1641.1(8)	193.1(4)	1637.3(4)
I(3)	3883.5(7)	2414.1(4)	874.7(3)
O(1)	–707(5)	1708(3)	1121(3)
O(2)	162(7)	3192(3)	1736(3)
O(3)	2747(6)	2990(3)	2977(3)
O(4)	3655(6)	1406(3)	3041(3)
C(11)	–546(10)	1818(6)	279(4)
C(12)	–2059(11)	1614(5)	–121(4)
C(13)	–2567(11)	999(5)	382(5)
C(14)	–2027(8)	1235(5)	1210(4)
C(21)	804(13)	3869(6)	1462(7)
C(22)	–275(20)	4247(8)	965(8)
C(23)	–1765(18)	3911(9)	1092(9)
C(24)	–1444(12)	3339(6)	1754(7)
C(31)	4326(11)	3219(7)	3021(7)
C(32)	4441(17)	3842(10)	3541(9)
C(33)	3016(15)	4056(7)	3816(9)
C(34)	1977(11)	3437(5)	3544(6)
C(41)	5002(10)	1003(7)	2809(6)
C(42)	5388(12)	476(6)	3484(8)
C(43)	4844(14)	873(7)	4186(7)
C(44)	3586(13)	1315(7)	3881(5)

on the whole, is closer to a number of similarly characterized complexes of the type  $\text{LnCl}_3(\text{THF})_4$  (Ln = Sm [36], Eu [37], Nd [38]) rather than to  $\text{LaI}_3(\text{PrOH})_4$ . A similar seven-coordinated pentagonal bipyramidal geometry has been observed in the structure of  $\text{SmI}_2(\text{THF})_4$  [39], in which the iodine ligands are in axial positions. To the best of our knowledge, the structure of  $\text{LaI}_3(\text{THF})_4$  is the first example of a THF adduct of an Ln(III) iodide.

#### 2.4. $^1\text{H}$ NMR studies

The  $^1\text{H}$  NMR data obtained for compounds **3**–**6** are presented in Table 6. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of complexes  $[(S)\text{-Cp}']_2\text{LnI}$  **3** and **4** reveal the presence of only one diastereomer. Either the minor isomer  $[(S)\text{-Cp}'][(R)\text{-Cp}']\text{LnI}$  is formed in a very low amount, or has been separated during the recrystallization of the complexes, or both isomers have the same spectra. The variable-temperature studies of complexes **3** and **4** in  $d_8$ -toluene, as well as in  $d_2$ -methylene chloride, reveal fluxional behaviour for both compounds.

The variable-temperature  $^1\text{H}$  NMR of the lanthanum complex  $[(S)\text{-Cp}']_2\text{LaI}$  **4**, in  $\text{CD}_2\text{Cl}_2$ , is shown in Fig. 3 for the temperature range 298–223 K. At room temperature (Fig. 3, spectrum a) we observed a doublet at 1.56 ppm for the methyl group, a doublet of doublets at 2.58 and 2.80 ppm for the diastereotopic  $\text{CH}_2$  protons near the cyclopentadienyl ring, a multiplet at 4.40 ppm for the proton on the tertiary carbon, two doublets at

4.81 and 5.30 ppm for the benzylic protons, two multiplets at 6.07 and 6.36 ppm for the protons of the cyclopentadienyl rings and a multiplet at 7.40–7.55 ppm corresponding to five aromatic protons. The spectrum obtained at 223 K (Fig. 3, spectrum d) presents two doublets of equal intensity for the methyl groups and seven resonances (due to the accidental overlap of two protons) of relative intensity 1:1:1:1:1:2:1 for the protons of the cyclopentadienyl rings. The splitting observed at 223 K indicates the non-equivalence of the two cyclopentadienyl ligands. The splitting of the resonances due to the diastereotopic CH<sub>2</sub> protons adjacent to the cyclopentadienyl ring and to the CH<sub>2</sub> protons of the benzyl group was not observed.

For the previously described compound **3**, variable-temperature <sup>1</sup>H NMR experiments were also undertaken and it exhibited similar behaviour to that of **4**. The magnetic equivalence of the two cyclopentadienyl ligands is not observed in the static spectrum obtained at 223 K in CD<sub>2</sub>Cl<sub>2</sub>. At this temperature two resonances of equal intensity for the methyl groups at 3.20 and 0.01 ppm appear, and seven resonances, significantly shifted from the diamagnetic position, for the protons of the cyclopentadienyl rings (see Section 4).

So far, no solid-state structure of **4** has been determined, but a structure analogous to [(*S*)-Cp']<sub>2</sub>SmI **3** is expected, despite the differences in the ionic radius of La and Sm. These compounds, owing to the intramolecular coordination of the oxygen of the side chain, are pentacoordinated, and in solution they present stereochemical non-rigidity, which is normal for five-coordinated compounds [40]. The static spectra are in accordance with the solid-state structure which indicates non-equivalence for the two cyclopentadienyl ligands. The exchange process is responsible for the magnetic equivalence observed at room temperature, while decreasing the temperature slows down the exchange resulting in decoalescence. This exchange process can be explained either by a Berry pseudorotation or by decoordination–reassociation of the ether group of the side chain.

Using the Eyring equation, and based on the behaviour of the resonances of the methyl groups, the activation energies for the fluxional process at the coalescence temperature  $\Delta G_{T_c}^{\ddagger}$  ( $T_c$  is the coalescence temperature) were calculated for **3** and **4** [41]:

$$\Delta G_{T_c}^{\ddagger} = 19.113T_c[9.983 + \log(T_c/\delta v)] \text{ (J mol}^{-1}\text{)}$$

$\delta v = \nu_A - \nu_B$  (extrapolated at the coalescence temperature).

$$T_c = 263 \text{ K; } \delta v = 738 \text{ Hz; } \Delta G_{T_c}^{\ddagger} = 50 \pm 2 \text{ kJ mol}^{-1}$$

$$T_c = 253 \text{ K; } \delta v = 33.5 \text{ Hz; } \Delta G_{T_c}^{\ddagger} = 52 \pm 2 \text{ kJ mol}^{-1}$$

The activation energies  $\Delta G_{T_c}^{\ddagger}$  of the interconversion processes are similar for both complexes. Temperature-dependent intramolecular exchange processes have recently been described for several lanthanide complexes possessing ligands with versatile coordination modes ([SmCp<sub>2</sub><sup>o</sup>](THF)[Co(CO)<sub>4</sub>] [42], {Y( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)[N(SiMe<sub>2</sub>-CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>, YCl[N(SiMe<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>]<sub>2</sub> [43], Y[OSi<sup>t</sup>BuAr<sub>2</sub>][N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, Y[OSi<sup>t</sup>BuAr<sub>2</sub>]-[OC<sub>6</sub>H<sub>3</sub>Bu<sub>2</sub>-2,6]<sub>2</sub> (Ar = C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>) [44], Y[OSi<sup>t</sup>Bu<sub>2</sub>[(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>]<sub>3</sub>] [45]) and were explained either by Berry pseudorotation or by decoordination–reassociation of a Lewis base of a pendant chain on a metal centre.

Despite the bad quality of the crystal obtained for **5**, it was clear that in this compound the Sm was six-coordinated by three oxygen atoms of the THF, by the cyclopentadienyl and by two iodides, with no intramolecular coordination to the oxygen of the side chain. The <sup>1</sup>H NMR spectrum of this complex was in accordance with the solid-state structure, and variable-temperature <sup>1</sup>H NMR studies indicated static behaviour for **5**.

Compound **6** exhibits <sup>1</sup>H NMR behaviour similar to **5**, with no temperature dependence being observed. However, for **6**, elemental analysis, as well as the relative intensity of the resonances are consistent with the formula (*S*)-Cp'LaI<sub>2</sub>(THF)<sub>2</sub>. Considering the larger size of lanthanum compared with samarium, the number

Table 6  
<sup>1</sup>H NMR shifts of complexes

Compound	Solvent	$\delta$ -CH <sub>3</sub>	$\delta$ -CH <sub>2</sub> -	$\delta$ -CH-	$\delta$ -OCH <sub>2</sub> -	$\delta$ -C <sub>5</sub> H <sub>4</sub>
<b>2</b>	THF	1.14	2.82	3.68	4.53	5.47
<b>3</b>	C <sub>6</sub> D <sub>6</sub>	0.48	1.77; 1.87	3.58	6.21	7.08; 8.47; 10.41; 13.56
<b>3</b>	CD <sub>2</sub> Cl <sub>2</sub>	1.18	2.20; 2.70	4.18	6.40	6.10; 7.80; 9.50; 13.0
<b>4</b>	C <sub>7</sub> D <sub>8</sub>	1.40	2.40; 2.78	4.22	4.78; 5.49	6.20; 6.27; 6.42; 6.53
<b>4</b>	CD <sub>2</sub> Cl <sub>2</sub>	1.52	2.71	4.40	4.80; 5.27	6.07; 6.33
<b>5</b> <sup>a</sup>	C <sub>6</sub> D <sub>6</sub>	-0.06	2.84; 3.18	4.60	6.95	8.56; 10.80; 11.67; 12.31
<b>6</b> <sup>b</sup>	CD <sub>2</sub> Cl <sub>2</sub>	1.51	2.72	4.52	5.12; 5.34	6.32; 6.63

$\delta$ , ppm, 293 K: <sup>a</sup> THF,  $\delta$ -CH<sub>2</sub>- 1.73,  $\delta$ -OCH<sub>2</sub>- 4.08; <sup>b</sup> THF,  $\delta$ -CH<sub>2</sub>- 1.88,  $\delta$ -OCH<sub>2</sub>- 3.98.

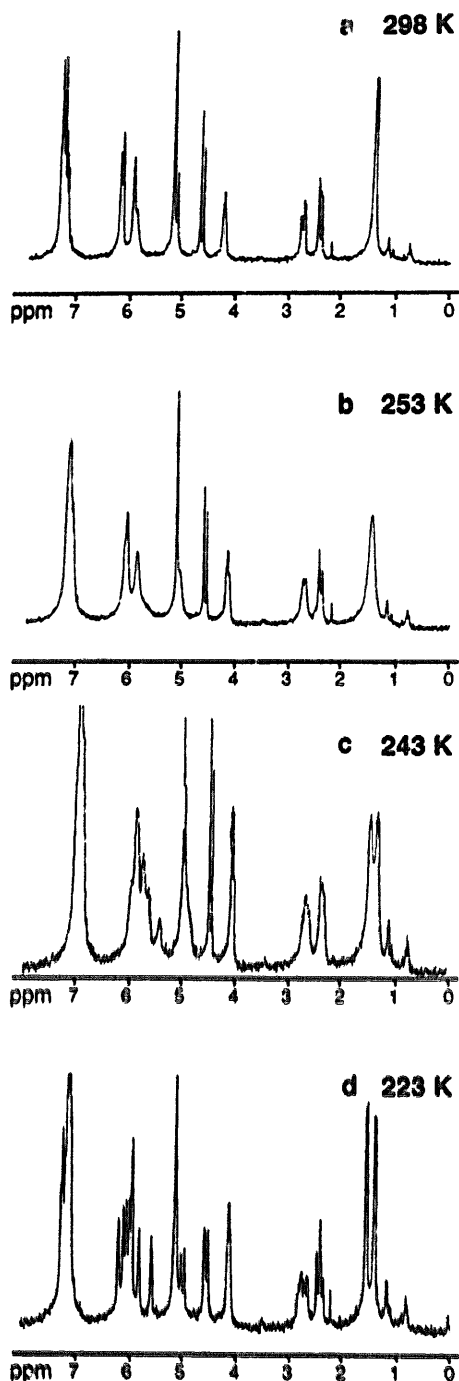


Fig. 3.  $^1\text{H}$  NMR study of  $[(S)\text{-Cp}']_2\text{LaI}$  **4** at: (a) 298 K; (b) 253 K; (c) 243 K; (d) 223 K.

of THF molecules found in complex **6** suggests an intramolecular coordination of the oxygen side chain to the metal. This coordination certainly justifies the displacement of the resonances due to the  $\text{CH}_3$ ,  $\text{OCH}_2\text{C}_6\text{H}_5$ , and  $\text{OCH}$  groups to lower field than those of the corresponding potassium salt (the same effect is similarly observed on the signals of **4**, see Table 6).

Table 7  
 $^{139}\text{La}$  NMR shifts

Complex	$\delta^{139}\text{La}$ (ppm 293 K)	$\nu_{1/2}$ (Hz)	Solvent	Ref.
$[(S)\text{-Cp}']_2\text{LaI}$ <b>4</b>	338	5653	$\text{CH}_2\text{Cl}_2$	
$(S)\text{-Cp}'\text{LaI}_2(\text{THF})_2$ <b>6</b>	770	2548	THF	
$\text{Cp}_2\text{LaI}(\text{THF})$	-90	165	THF	[46]
$\text{CpLaI}_2(\text{THF})_3$	406	815	THF	[46]

### 2.5. $^{139}\text{La}$ NMR spectroscopy for the characterization of organolanthanum complexes **4** and **6**

Up until now, comparatively few  $^{139}\text{La}$  NMR studies have been reported [27,31,46,47].  $^{139}\text{La}$  NMR spectroscopy, however, turns out to be a useful technique for the characterization of organolanthanum complexes because of the high selectivity of  $^{139}\text{La}$  resonance due to the symmetry and to the electric field gradient of the environment of the metal atom.

Single resonances have been observed for analytically pure samples of **4** and **6** at  $\delta$  338 ppm and  $\delta$  770 ppm respectively (Table 7). The signals of both complexes are shifted compared with those of  $\text{CpLaI}_2(\text{THF})_3$  and  $\text{Cp}_2\text{LaI}(\text{THF})$  [31], though their relative positions remain. Thus, for bicyclopentadienyl complexes  $\text{Cp}_2\text{LaI}(\text{THF})$  and  $[(S)\text{-Cp}']_2\text{LaI}$ , the  $^{139}\text{La}$  peaks are shifted upfield relative to the peaks of monocyclopentadienyl derivatives. Noteworthy is that the resonance for **4** is considerably broader than those of the related complexes with an unsubstituted cyclopentadienyl ligand, and it is consistent with the dynamic behaviour of this complex in solution.

### 2.6. Catalysis

Asymmetric Diels–Alder reactions catalysed by chiral Lewis acids are now well documented [48], and results concerning ytterbium and scandium triflates have been reported [4,5]. We found that  $\text{SmI}_2(\text{THF})_2$  is an efficient catalyst for Diels–Alder reactions and began the screening of the catalytic activity of complexes **3–6**

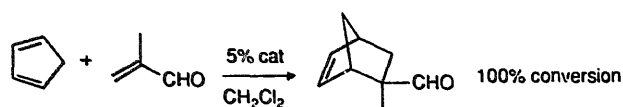
Table 8  
Catalysis of a Diels–Alder reaction

Entry	Catalyst <sup>a</sup>	<i>t</i>	Exo/endo <sup>b</sup>	<i>e.e.</i> (%) <sup>c</sup>
1	<b>3</b>	24h	92/8	11 ( <i>R</i> )
2	<b>3</b>	4d <sup>d</sup>	93/7 <sup>d</sup>	5 ( <i>R</i> )
3	<b>4</b>	3h	90/10	3 ( <i>R</i> )
4	<b>5</b>	18h	88/12	0
5	<b>6</b>	3h	90/10	13 ( <i>S</i> )
6	<b>7</b>	18h	92/8%	0

<sup>a</sup> All reactions are performed in  $\text{CH}_2\text{Cl}_2$  at room temperature except where stated. <sup>b</sup> Determined by  $^1\text{H}$  NMR and GLC for a quantitative conversion. <sup>c</sup> Determined by optical rotation  $[\alpha]_D$  and  $^1\text{H}$  NMR with  $\text{Eu}(\text{hfc})_3$ . <sup>d</sup> Reaction temperature:  $-30^\circ\text{C}$ .



for this reaction. The cycloaddition of methacrolein and cyclopentadiene was selected as a test reaction (Table 8).



All complexes are efficient catalysts when used in methylene dichloride, as total conversion is attained within 24 h. The rate of the reaction, however, is considerably reduced in toluene or THF. Selectivity in the *exo* isomer is high, and similar to that obtained with  $\text{SmI}_2(\text{THF})_2$ , and does not vary noticeably with the different catalysts. The enantiomeric excesses are modest with all catalysts, and lowering of the reaction temperature does not lead to better asymmetric induction (entries 1, 2, Table 8). Nevertheless, the complexes 3, 4 and 6, which exhibit intramolecular coordination of the cyclopentadienyl ligand, give significant asymmetric induction in the Diels–Alder reaction, while no induction is observed with complex 5 where the asymmetric centre is far away from samarium (entry 4). The use of complexes 3 and 6 coordinated by the same ligand leads respectively to the two enantiomers *R* and *S* preferentially (entries 1, 5). These first observations show the potential of chelated asymmetric ligands with the chiral centre maintained close to the metal by coordination with a donor atom. The use of these compounds for the catalysis of other reactions is currently under investigation.

### 3. Conclusions

The first examples of organolanthanide compounds coordinated by an asymmetric cyclopentadienyl ligand with an ether group on the chiral centre have been synthesized. These compounds, which are stable in solution, are active catalysts for Diels–Alder reactions, albeit with low enantiomeric excesses. The structural studies indicate intramolecular coordination of the oxygen for the biscyclopentadienyl compounds and for the monocyclopentadienyl lanthanum iodide 6. No chelation is observed for the monocyclopentadienyl samarium iodide, while intramolecular coordination has been reported for the parent monocyclopentadienyl compound coordinated by  $\text{Cp}^o$  ( $\text{Cp}^o = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe}$ ) [14,21]. These results show that small steric effects can have a dramatic influence on the structure of the complex. Taking into account that in our first experiments asymmetric induction was connected with intramolec-

ular coordination, such bidentate cyclopentadienyl ligands represent a new family of ligands which could be of interest for asymmetric catalysis.

### 4. Experimental section

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove box techniques. THF, toluene and hexane (including  $d_8$ -THF and  $d_8$ -toluene) were distilled from sodium benzophenone ketyl and degassed immediately prior to use. Methylene dichloride was distilled from  $\text{CaH}_2$  and degassed immediately prior to use.  $\text{SmI}_2$  was prepared according to the published method [49].  $\text{SmI}_3(\text{THF})_3$  was obtained by reacting  $\text{SmI}_2$  and  $\text{I}_2$  in THF in the molar ratio 1/0.5 at room temperature.  $\text{LaI}_3(\text{DME})_2$  was prepared from La powder and iodine [29]. (*S*)-2-(Benzyloxypropyl)cyclopentadiene was synthesized by the method previously described [28].

Bruker AM 200, AM 250 and AM 400 NMR spectrometers, operating at 200 and 250 MHz for  $^1\text{H}$  and 50.4 and 63 MHz for  $^{13}\text{C}$  and at 400 MHz for  $^{139}\text{La}$  were used for the NMR spectra. Chemical shifts are reported in parts per million downfield from tetramethylsilane for spectra in  $\text{CDCl}_3$ , relative to  $\text{C}_7\text{D}_7\text{H}$ , 2.09 ppm, for spectra in  $d_8$ -toluene or relative to  $\text{C}_4\text{D}_7\text{HO}$ , 1.72 ppm, for spectra in  $d_8$ -THF. Infrared spectra were recorded as Nujol mulls using CsI plates on a Perkin–Elmer 883 spectrometer and are reported in wavenumbers. GC analyses were performed with a 25 m BP 1 capillary column connected with a computing integrator. Carbon and hydrogen analyses were performed on a Perkin–Elmer automatic analyser.

#### 4.1. Preparation of (*S*)-(2-benzyloxypropyl) cyclopentadienyl potassium: 2

A solution of 1 (0.462 g, 2.37 mmol) in 20 ml THF was added to a suspension of KH (0.095 g, 2.37 mmol) in 10 ml THF at  $-20^\circ\text{C}$ . After 0.5 h, the mixture was warmed to room temperature, filtrated and THF was removed under reduced pressure to give a brown oil. After addition of hexane, a pale yellow powder was obtained (0.385 g, 70% yield).

$^1\text{H}$  NMR ( $d_8$ -THF)  $\delta$  (ppm): 1.20 (d, 3H,  $J = 7$  Hz); 2.50–2.80 (m, 2H); 3.51 (m, 1H); 4.50 (m, 2H); 5.40 (m, 4H); 7.25 (m, 5H).  $^{13}\text{C}$  NMR (THF- $d_8$ )  $\delta$  (ppm): 20.45 ( $\text{CH}_3$ ); 36.81 ( $\text{CH}_2$ -Cp); 63.19 ( $\text{CH}_2$ -Ph); 77.51 ( $\text{CH-O}$ ); 104.13 and 105.74 ( $\text{C}_5\text{H}_4$ ); 115.40 ( $\text{C}_5\text{H}_4$ ); 127.55, 127.85 and 128.77 (Ph). IR  $\text{cm}^{-1}$ : 1193, 1145, 1048, 940, 794, 760, 737, 700, 570, 490, 440, 315. MS:LD  $m/z$ : 291.01 ( $\text{M} + \text{K}$ , 8.67). Anal. Found: C, 69.97; H, 7.16.  $\text{C}_{15}\text{H}_{17}\text{KO}$ . Calc.: C, 71.43; H, 6.75%.

#### 4.2. Synthesis of bis[(S)-(2-benzyloxypropyl)cyclopentadienyl] samarium iodide: 3

To a suspension of  $\text{SmI}_3(\text{THF})_3$  (0.373 g, 0.5 mmol) in 10 ml THF was added a solution of (S)-Cp'K (0.252 g, 1 mmol) in 5 ml THF. At the end of the addition the solution has turned yellow with a white precipitate of KI which was filtrated (0.136 g). The solution was concentrated under vacuum and toluene was added. After filtration and evaporation of toluene, the oil was precipitated by addition of hexane to give a pale yellow powder (0.228 g, 65% yield).

$^1\text{H NMR}$  ( $d_8$ -toluene)  $\delta$  (ppm): 25 °C: 0.61 (br s, 3H,  $\text{CH}_3$ ); 1.71 (d, 1H,  $J = 17\text{ Hz}$ ); 2.11 (d, 1H,  $J = 17\text{ Hz}$ ); 3.89 (m, 1H); 6.12 (m, 2H); 6.24 (br s, 1H); 7.01–7.08 (m, 5H); 7.76 (br s, 1H); 10.11 (br s, 1H); 13.11 (br s, 1H). 35 °C: 0.64 (br s, 3H,  $\text{CH}_3$ ); 1.83 (d, 1H,  $J = 16\text{ Hz}$ ); 2.06 (d, 1H,  $J = 16\text{ Hz}$ ); 3.86 (m, 1H); 6.15 (2H); 6.66 (s, 1H,  $\text{C}_5\text{H}_4$ ); 6.86–7.15 (m, 5H, Ph); 8.06 (s, 1H,  $\text{C}_5\text{H}_4$ ); 10.33 (s, 1H,  $\text{C}_5\text{H}_4$ ); 13.36 (s, 1H,  $\text{C}_5\text{H}_4$ ).

$^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm): 25 °C: 1.18 (br s, 3H,  $\text{CH}_3$ ); 2.20 (d, 1H,  $J = 14\text{ Hz}$ ); 2.70 (d, 1H,  $J = 14\text{ Hz}$ ); 4.18 (m, 1H); 6.10 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 6.40 (d,  $J = 3\text{ Hz}$ , 2H,  $\text{OCH}_2$ ); 7.0–7.15 (m, 5H); 7.80 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 9.50 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 13.0 (br s, 1H,  $\text{C}_5\text{H}_4$ ).

$^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm): –50 °C: 0.08 (s, 3H,  $\text{CH}_3$ ); 1.62 (d, 1H,  $J = 14\text{ Hz}$ ); 2.65 (d, 1H,  $J = 14\text{ Hz}$ ); 3.23 (s, 3H,  $\text{CH}_3$ ); 4.06 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 4.18 (br s, 2H,  $\text{OCH}_2$ ); 4.33 (m, 1H); 4.87 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 5.55 (br s, 2H,  $\text{OCH}_2$ ); 6.67 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 6.80–7.30 (m, 5H); 7.40 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 7.62 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 13.21 (br s, 1H,  $\text{C}_5\text{H}_4$ ); 14.38 (br s, 1H,  $\text{C}_5\text{H}_4$ ).

$^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm): 19.20; 42.54; 72.35; 81.32; 102.04; 110.08; 126.45; 127.88; 128.39; 129.32; 135.28.

IR  $\text{cm}^{-1}$ : 1204; 1035; 1020; 917; 840; 792; 772; 742; 697; 625; 452; 380; 333. MS: (FW for Sm: 154), LD/positive:  $m/z$ : 580 (56.0)  $\text{Cp}'_2\text{Sm}$ ; 494 (21.9)  $\text{Cp}'\text{SmI}$ ; 489 (19.3)  $\text{Cp}'(\text{Cp}'-\text{CH}_2\text{Ph})\text{Sm}$ ; 367 (11.0)  $\text{Cp}'\text{Sm}$ ; 281 (37.3)  $\text{SmI}$ . LD/negative:  $m/z$ : 616 (92.0)  $\text{Cp}'(\text{Cp}'-\text{CH}_2\text{Ph})\text{SmI}$ ; 525 (26.7)  $(\text{Cp}'-\text{CH}_2\text{Ph})_2\text{Sm}^+$ ; 398 (46.3)  $(\text{Cp}'-\text{CH}_2\text{Ph})_2\text{Sm}$ . Anal. Found: C, 52.73; H, 5.09.  $\text{C}_{30}\text{H}_{34}\text{IO}_2\text{Sm}$ . Calc.: C, 51.2; H, 4.84%.

#### 4.3. Synthesis of bis[(S)-(2-benzyloxypropyl)cyclopentadienyl] lanthanum iodide: 4

A solution of (S)-Cp'K (0.36 g, 1.42 mmol) in 25 ml THF was added slowly to a suspension of  $\text{LaI}_3(\text{DME})_2$  (0.5 g, 0.71 mmol) in 30 ml THF at room temperature. The reaction mixture was stirred for 18 h, and the precipitate of KI was separated by filtration. The solution was evaporated to dryness, the white solid was extracted with toluene and recrystallized from a mixture of toluene–hexane. White crystals were washed with

cold hexane and dried in vacuo at room temperature: (0.44 g, 88% yield).

$^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm): 1.56 (d,  $J = 5\text{ Hz}$ , 3H,  $\text{CH}_3$ ); 2.58 (d,  $J = 14\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 2.80 (dd,  $J = 14\text{ Hz}$ ,  $J = 6\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 4.40 (m, 1H, CH); 4.81 (d,  $J = 15\text{ Hz}$ , 1H,  $\text{OCH}_2$ ); 5.30 (d,  $J = 15\text{ Hz}$ , 1H,  $\text{OCH}_2$ ); 6.07 (m, 2H,  $\text{C}_5\text{H}_4$ ), 6.36 (m, 2H,  $\text{C}_5\text{H}_4$ ); 7.40–7.55 (m, 5H, Ph).  $^1\text{H NMR}$  (toluene- $d_8$ )  $\delta$  (ppm) 1.40 (br s, 3H,  $\text{CH}_3$ ); 2.40 (dd,  $J = 7\text{ Hz}$ ,  $J = 2\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 2.78 (dd,  $J = 9\text{ Hz}$ ,  $J = 5\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 4.22 (m, 1H, CH); 4.78 (d,  $J = 10\text{ Hz}$ , 1H,  $\text{OCH}_2$ ); 5.49 (d,  $J = 10\text{ Hz}$ , 1H,  $\text{OCH}_2$ ); 6.20 (s, 1H,  $\text{C}_5\text{H}_4$ ), 6.27 (s, 1H,  $\text{C}_5\text{H}_4$ ); 6.42 (s, 1H,  $\text{C}_5\text{H}_4$ ); 6.53 (s, 1H,  $\text{C}_5\text{H}_4$ ); 7.40–7.55 (m, 5H, Ph).

$^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm): 19.29; 35.70; 72.09; 81.84; 112.79; 115.39; 127.74; 128.67; 129.10; 130.85; 136.61.

$^{139}\text{La}$   $\delta$  (ppm): 338.

IR  $\text{cm}^{-1}$ : 2924, 1461, 1373, 1204, 1115, 1034, 1022, 915, 836, 786, 767, 743, 729, 698, 553, 451. Anal. Found: C, 51.56; H, 5.13; La, 20.20.  $\text{C}_{30}\text{H}_{34}\text{IO}_2\text{La}$ . Calc.: C, 52.05; H, 4.91; La, 20.06%.  $[\alpha]_D -17.9$  ( $c$  0.615;  $\text{CH}_2\text{Cl}_2$ ).

#### 4.4. Synthesis of [(S)-(2-benzyloxypropyl)cyclopentadienyl] tris-tetrahydrofurane diiodosamarium: 5

A solution of (S)-Cp'K (0.32 g, 1.27 mmol) in 15 ml THF was added to a suspension of  $\text{SmI}_3(\text{THF})_3$  (0.95 g, 1.27 mmol) in 50 ml THF at room temperature. The reaction mixture was stirred for 18 h, and the precipitate of KI was separated by filtration. The solution was evaporated to dryness, the yellow solid residue was extracted with toluene and recrystallized from THF–hexane mixture at –20 °C. The crystals were washed with cold hexane and dried in vacuo (0.79 g, 75% yield).

$^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm): –0.06 (d,  $J = 5\text{ Hz}$ , 3H,  $\text{CH}_3$ ); 1.73 (s, 12H,  $\text{CH}_2$  (THF)); 2.84 (d,  $J = 11\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 3.18 (d,  $J = 11\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 4.08 (s, 12H,  $\text{OCH}_2$  (THF)); 4.60 (m, 1H, CH); 6.95 (s, 2H,  $\text{OCH}_2$ ); 7.06–7.60 (m, 5H, Ph); 7.89 (s, 1H,  $\text{C}_5\text{H}_4$ ); 8.56 (s, 1H,  $\text{C}_5\text{H}_4$ ); 10.80 (s, 1H,  $\text{C}_5\text{H}_4$ ); 12.31 (s, 1H,  $\text{C}_5\text{H}_4$ ).

$^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm): 18.99; 25.50; 41.11; 71.17; 72.04; 83.99; 105.6; 106.3; 111.41; 114.0.

IR  $\text{cm}^{-1}$ : 3190, 1480, 1380, 1210, 1075, 1010, 990, 920, 870, 790, 750, 720, 700, 625, 452, 380. Anal. Found: C, 38.66; H, 4.52; Sm, 18.32.  $\text{C}_{27}\text{H}_{41}\text{I}_2\text{O}_4\text{Sm}$ . Calc.: C, 38.90; H, 4.91; Sm, 18.04%.

#### 4.5. Synthesis of [(S)-(2-benzyloxypropyl)cyclopentadienyl] bistetrahydrofurane diiodo lanthanum: 6

A solution of (S)-Cp'K (0.21 g, 0.82 mmol) in 15 ml THF was added to a suspension of  $\text{LaI}_3(\text{DME})_2$  (0.58 g, 0.82 mmol) in 50 ml THF at room temperature. The reaction mixture was stirred for 18 h, and the precipitate

of KI (0.13 g, 96%) was separated by filtration. The pale-yellow solution was evaporated to dryness, the solid off-white residue was extracted with toluene and recrystallized from a mixture of THF–hexane at  $-20^{\circ}\text{C}$ . The colourless crystals were washed with cold hexane and dried in vacuo (0.51 g, 81% yield).

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm), at  $20^{\circ}\text{C}$ : 1.51 (d,  $J = 10\text{ Hz}$ , 3H,  $\text{CH}_3$ ); 1.88 (m, 8H,  $\text{CH}_2$  (THF)); 2.61 (dd,  $J = 16\text{ Hz}$ ,  $J = 3\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 2.88 (dd,  $J = 12\text{ Hz}$ ,  $J = 6\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 3.98 (s, 8H,  $\text{OCH}_2$  (THF)); 4.52 (m, 1H,  $\text{CH}$ ); 5.12 (d,  $J = 12\text{ Hz}$ , 1H,  $\text{OCH}_2$ ); 5.34 (d,  $J = 12\text{ Hz}$ , 1H,  $\text{OCH}_2$ ); 6.32 (s, 2H,  $\text{C}_5\text{H}_4$ ); 6.63 (s, 2H,  $\text{C}_5\text{H}_4$ ); 7.38 (m, 5H, *Ph*).

$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm): 20.85; 25.76; 34.8; 64.45; 71.0; 83.88; 115.09; 115.59; 117.59; 117.75; 119.09; 128.97; 129.06; 129.15.

$^{139}\text{La}$   $\delta$  (ppm): 770.

IR  $\text{cm}^{-1}$ : 3190, 1480, 1380, 1210, 1075, 1010, 985, 865, 770, 695, 459, 390. Anal. Found: C, 36.32; H, 4.39; La, 18.27.  $\text{C}_{23}\text{H}_{33}\text{I}_2\text{LaO}_3$ . Calc.: C, 36.82; H, 4.43; La, 18.51%.

#### 4.6. Synthesis of [(*S*)-(2-benzyloxypropyl)cyclopentadienyl] diiodo lanthanum: 7

A solution of (*S*)- $\text{Cp}'\text{LaI}_2(\text{THF})_2$  (0.15 g, 0.20 mmol) in 30 ml toluene was heated at  $60^{\circ}\text{C}$  for 30 min. After about 20 min the formation of a white precipitate was observed. Toluene was evaporated in vacuo, 10 ml of toluene was added and the procedure was repeated. The resulting white powder was washed with hexane and dried in vacuo at room temperature (0.11 g, 91% yield).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6\text{N}$ )  $\delta$  (ppm), at  $20^{\circ}\text{C}$ : 1.11 (d,  $J = 10\text{ Hz}$ , 3H,  $\text{CH}_3$ ); 2.82 (dd,  $J = 16\text{ Hz}$ ,  $J = 3\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 3.08 (dd,  $J = 12\text{ Hz}$ ,  $J = 4\text{ Hz}$ , 1H,  $\text{CH}_2$ ); 3.72 (m, 1H,  $\text{CH}$ ); 4.52 (s, 2H,  $\text{OCH}_2$ ); 6.75 (s, 4H,  $\text{C}_5\text{H}_4$ ); 7.35 (m, 5H, *Ph*).

IR  $\text{cm}^{-1}$ : 1193, 1145, 1048, 940, 794, 760, 737, 700, 570, 490, 440, 315.

#### 4.7. Reaction of (*S*)- $\text{Cp}'\text{LaI}_2(\text{THF})_2$ with $^t\text{BuOK}$

To a solution of (*S*)- $\text{Cp}'\text{LaI}_2(\text{THF})_2$  (0.95 g, 1.26 mmol) in 30 ml THF, a solution of  $^t\text{BuOK}$  (0.14 g, 1.25 mmol) in 15 ml THF was added. The reaction mixture was stirred for 18 h, and the precipitate of KI (0.2 g, 100%) was separated. The solution was evaporated to dryness and a pale beige residue was extracted with toluene (10 ml). Hexane (20 ml) was added to the toluene solution and the mixture was cooled to  $-20^{\circ}\text{C}$  for several days. Colourless crystals of  $\text{Cp}'_2\text{LaI}$  (0.3 g, 72% yield) were isolated.

#### 4.8. Typical experiment for catalytic reactions

To a solution of **3** (0.070 g, 0.1 mmol), in 5 ml  $\text{CH}_2\text{Cl}_2$  was added cyclopentadiene (0.300 ml, 4 mmol)

and methacrolein (0.163 ml, 2 mmol). The reaction mixture was stirred for 20 h at room temperature. After hydrolysis and extraction with ether, the crude product was obtained as an orange oil. The cycloadduct was isolated as white crystals after sublimation (0.218 g, 80% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm), *exo/endo* 90/10: 9.70 (s, 9/10H, *exo*); 9.40 (s, 1/10H, *endo*); 6.30 (m, 9/10H, *exo*); 6.15 (m, 2/10H, *endo*); 6.05 (m, 9/10H, *exo*); 2.80 (m, 2H, *exo + endo*); 2.20 (dd, 2 and 7 Hz, 1H, *exo + endo*); 1.35 (d, 2 Hz, 2H, *exo + endo*); 1.00 (s, 3H, *exo + endo*); 0.75 (d, 7 Hz, 1H, *exo + endo*).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm), *exo/endo* 90/10: 205.73; 139.37; 138.51; 134.00; 133.38; 132.91; 48.86; 48.26; 47.42; 43.05; 42.67; 34.39; 19.85.  $[\alpha]_D - 2.16$  (*c* 0.695; EtOH); *e.e.* = 11% (*R*).

#### 4.9. X-ray crystallographic analysis

X-ray data were collected from a light yellow crystal of **3**, obtained by diffusion of *n*-hexane into a saturated solution of the compound in toluene and from a colourless thick plate-shaped crystal of **8** obtained by recrystallization from THF. A crystal of **3** was mounted in a thin-walled glass capillary and a crystal of **8** in a quartz capillary, in an argon-filled glove box.

The data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer, with graphite-monochromated Mo-K $\alpha$  radiation, using a  $\omega$ - $2\theta$  scan mode. For **3**, an Enraf–Nonius Turbo CAD-4 diffractometer, equipped with a rotating anode (50 kV, 80 mA)

Table 9  
Crystallographic data

	<b>3</b>	<b>8</b>
Formula	$\text{C}_{30}\text{H}_{34}\text{O}_2\text{I}_2\text{Sm}$	$\text{C}_{16}\text{H}_{12}\text{O}_4\text{I}_2\text{La}$
Mol wt	703.86	808.05
Cryst syst	Orthorhombic	Monoclinic
Space group	$\text{C}222_1$	$\text{P}2_1/\text{c}$
$a$ (Å)	9.415(1)	8.776(2)
$b$ (Å)	13.869(1)	17.675(2)
$c$ (Å)	42.732(2)	16.736(4)
$\beta$ (deg)		93.74(1)
$V$ (Å <sup>3</sup> )	5580(1)	2591(1)
$Z$	8	4
$D_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )	1.676	2.071
Linear abs coeff ( $\text{Mo K}\alpha$ ) ( $\text{cm}^{-1}$ )	30.44	49.01
$2\theta$ range (deg)	3.0–54.0	3.0–52.0
Decay cor: min., max.	1.00001, 1.01455	1.00000, 1.01032
Range in abs cor factors	0.8378, 0.9999	0.7965, 0.9998
No. of reflections ( $F_o > 3\sigma(F_o)$ )	3151	4322
No of params refined	261	218
Weighting scheme used, $w = (\sigma^2(F_o) + gF_o^2)^{-1}$ , $g$	0.000695	0.00005
Final $R$ , $R_w$	0.064, 0.086	0.048, 0.043

was utilized. The unit cell dimensions were determined and refined from 25 reflections with  $23.0 < 2\theta < 32.0^\circ$  for **3**, and  $20.0 < 2\theta < 30.0^\circ$  for **8**. Crystal data, data collection and refinement parameters are given in Table 9. Data were corrected for Lorentz-polarization effects, for linear decay and for absorption by empirical corrections based on  $\psi$  scans, using the Enraf–Nonius program. The structure was solved by Patterson [50] and Fourier methods and refined by full-matrix least squares procedures [51]. For **8**, all non-hydrogen atoms were refined anisotropically; for **3**, all but the cyclopentadienyl carbon atoms were refined anisotropically. The contributions of the hydrogen atoms were introduced in calculated positions, constrained to ride on their carbon atoms with group  $U_{iso}$  values assigned. For **3**, the structure was refined for both enantiomers: the one chosen has the lower  $R$  factor (the other enantiomer ( $R$ ) had  $R$  values of  $R = 0.068$  and  $R_w = 0.090$ ). For **8**, two strong low-angle reflections which were thought to be affected by extinction were omitted from the data.

In the final difference Fourier map, the highest peak was  $2.0e\text{\AA}^{-3}$  for **3** near the Sm atom, and for **8**  $1.6e\text{\AA}^{-3}$ ,  $1.01\text{\AA}$  from I(2) atom. Atomic scattering factors and anomalous dispersion terms were taken from *International Tables for X-ray Crystallography* (Table 9) [52].

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