



## (*R*)-bis-Binaphthoxy iodo lanthanides as catalysts for Diels–Alder reactions

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### Abstract

[(*R*)-1,1'-bi-2,2'-Naphthoxy]LnI(THF)<sub>2</sub> (Ln: Yb, Sm, La) **5** have been prepared by reaction of the bispotassium salt of (*R*)-binaphthol with lanthanide triiodides, and characterized. They are active catalysts for Diels–Alder reactions although with low asymmetric inductions. The lanthanum iodo bisbinaphthoxide gives a slightly higher enantiomeric excess than the two other complexes.

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### 1. Introduction

1,1'-Binaphthol and substituted 1,1'-binaphthols have been employed as ligands for a wide range of metals including lanthanides, to prepare enantioselective catalysts [1]. With lanthanides, catalysts are either prepared in situ or isolated and characterized, and different modes of coordination of the binaphthol ligands can be found [2]. Shibasaki and coworkers have developed heterobimetallic derivatives with the binaphthol ligand coordinated both to the lanthanide and to an alkaline metal, which afford high asymmetric inductions for various reactions such as aldol, Michael, or Diels–Alder reactions [3,4]. Another type of complex was prepared by reacting lanthanum triisopropoxide with binaphthol, and used in situ as a catalyst for enan-

tioselective Michael reactions, epoxidation of enones, and for enantioselective borane reductions of ketones [5–7]. The catalyst is supposed to be the isopropoxy binaphthoxy lanthanum. Shibasaki realized enantioselective epoxidations of  $\alpha,\beta$ -unsaturated ketones with a catalyst prepared by the same method in the presence of Ph<sub>3</sub>As=O [8]. X-ray structure of the isolated complex shows two binaphthol ligands coordinated to lanthanum but the active species is supposed to be coordinated by only one bidentate binaphthoxide ligand. Qian prepared catalysts from ytterbium triisopropoxide and 6,6'-substituted binaphthols and studied the effect of substituents on the enantioselectivity of the epoxidation of  $\alpha,\beta$ -unsaturated ketones [9]. Enantioselective silylcyanations of aldehydes were achieved by catalysts obtained by the reaction of lanthanum tritertbutoxide with binaphthol or substituted binaphthol ligands for which a dimeric structure was proposed [10]. By contrast, the catalytic systems described by Kobayashi result from the addition of binaphthol type ligands to ytterbium or scandium

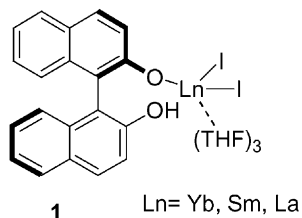
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triflates in the presence of a base, and are enantioselective catalysts for cycloaddition reactions [11–13]. These compounds, characterized in situ by  $^{13}\text{C}$  NMR and IR spectra, have no naphthoxy bonds between the metal and the oxygen atoms of the binaphthol ligands.

During our previous investigations, we have explored the activity of samarium diiodide, trivalent lanthanide iodides and mixed iodoalkoxides as Lewis acid catalysts [14,15]. We then examined the possibility to prepare heteroleptic lanthanide iodo binaphthoxides with naphthoxy lanthanide oxygen bonds, as a new family of enantioselective catalysts. By reacting the monopotassium salt of (*R*)-binaphthol with trivalent lanthanide iodides we have recently prepared and characterized (*R*)-binaphthoxy diiodo lanthanides **1** [16] which led to racemic products when used as catalysts for various reactions. We now describe the preparation of bidendate lanthanide iodo binaphthoxides **5** and their use as catalysts for Diels–Alder reactions. Some results with the samarium complex have been previously reported [17].



## 2. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove-box techniques. Tetrahydrofuran (THF) and hexane were distilled from sodium benzophenone ketyl and degassed immediately prior to use.  $\text{CH}_2\text{Cl}_2$  and  $\text{CDCl}_3$  were distilled from  $\text{CaH}_2$  and degassed immediately prior to use.  $\text{SmI}_2$  and  $\text{YbI}_3$  were prepared according to published methods [18,19].  $\text{SmI}_3(\text{THF})_3$  was obtained by reacting  $\text{SmI}_2$  with  $\text{I}_2$  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 [20]. Bruker AM 250, and Bruker DRX 400 NMR spectrometers, operating at 250, 300 and 400 MHz were used for recording the NMR spectra. Chemical shifts are reported in parts

per million (ppm) downfield from tetramethylsilane for spectra in  $\text{CDCl}_3$ . Infrared spectra were recorded as Nujol mulls using NaCl plates on a Perkin-Elmer 1000 FT-IR spectrometer and are reported in  $\text{cm}^{-1}$ . Carbon and hydrogen elemental analyses were performed on a Perkin-Elmer automatic analyzer. Optical rotations were measured with a Perkin-Elmer 341 Polarimeter.

### 2.1. [(*R*)-1,1'-(*bi*-2,2'-Naphthoxide)]-iodoytterbium-bis-tetrahydrofurane: **5a**

To a solution of (*R*)-1,1'-binaphthol (0.800 g, 2.80 mmol) in 10 ml THF under magnetic stirring was added potassium hydride (0.250 g, 6.25 mmol). After 0.5 h the suspension was added within 5 min to a suspension of  $\text{YbI}_3(\text{THF})_3$  (2.16 g, 2.80 mmol) in 10 ml THF. After 18 h the red-orange and homogeneous supernatant solution was separated from the KI formed and the solvent evaporated under vacuum, yielding an orange powder formulated as **5a** (1.80 g, 88% yield). IR ( $\text{cm}^{-1}$ ): 2963, 1616, 1591, 1502, 1465, 1424, 1364, 1332, 1261, 1239, 1100, 1055, 992, 955, 862, 817, 744, 667. Optical rotation  $[\alpha]_D^{20} = -221$  ( $c = 0.36$ ,  $\text{CH}_2\text{Cl}_2$ ). Anal. Calcd. for  $\text{C}_{28}\text{H}_{28}\text{IO}_4\text{Yb}$ : C, 46.17; H, 3.87. Found: C, 47.55; H, 4.12.

### 2.2. [(*R*)-1,1'-(*bi*-2,2'-Naphthoxide)]-iodosamarium-bis-tetrahydrofurane: **5b**

To a solution of (*R*)-1,1'-binaphthol (0.801 g, 2.80 mmol) in 10 ml THF under magnetic stirring was added potassium hydride (0.246 g, 6.16 mmol). After 0.5 h, the suspension was added within 5 min to a suspension of  $\text{SmI}_3(\text{THF})_3$  (2.09 g, 2.80 mmol) in 10 ml THF. The reaction mixture turned homogeneous and light-yellow with a white precipitate of KI. After 18 h the KI formed was filtrated and the supernatant solution evaporated under vacuum yielding a yellow powder formulated as **5b** (1.60 g, 81% yield).  $^1\text{H}$  NMR ( $\text{CHCl}_3$ , 250 MHz)  $\delta$ : 8.7–6.0 (m, 12H), 3.8 (l, 8H), 1.72 (l, 8H). IR ( $\text{cm}^{-1}$ ): 3050, 2973, 1616, 1590, 1500, 1463, 1424, 1351, 1328, 1261, 1236, 1144, 1072, 1015, 988, 954, 862, 812, 743, 666. Optical rotation  $[\alpha]_D^{20} = -448$  ( $c = 0.40$ ,  $\text{CH}_2\text{Cl}_2$ ). Calcd. for  $\text{C}_{28}\text{H}_{28}\text{IO}_4\text{Sm}$ : C, 47.65; H, 3.99. Found: C, 47.26; H, 3.35.

### 2.3. [(*R*)-2-(1,1'-(*bi*-2,2'-Naphthoxide)]-iodolanthane-bis-tetrahydrofuran: **5c**

To a solution of (*R*)-1,1'-binaphthol (0.572 g, 2.0 mmol) in 5 ml THF under magnetic stirring was added potassium hydride (0.170 g, 4.25 mmol). After 0.5 h the suspension was added within 5 min to a suspension of LaI<sub>3</sub>(DME)<sub>2</sub> (1.40 g, 2 mmol) in 10 ml THF. After 18 h the light-yellow supernatant was separated from the KI formed and vacuum dried, yielding a beige powder of **5c** (1.2 g, 85% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz) δ: 8.2–6.0 (l, 12H), 3.58 (l, 8H), 1.62 (l, 8H). IR (cm<sup>-1</sup>): 2960, 1618, 1592, 1498, 1420, 1372, 1330, 1260, 1235, 1096, 1052, 998, 952, 882, 814, 748, 668. Optical rotation [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -232 (*c* = 0.24, CH<sub>2</sub>Cl<sub>2</sub>). Anal. Calcd. for C<sub>28</sub>H<sub>28</sub>IO<sub>4</sub>La: C, 48.43; H, 4.06. Found: C, 48.15; H, 4.03.

### 2.4. General procedure for Diels–Alder reactions

To a solution of acyl oxazolidinone **6** or **7** (0.5 mmol) in 10 ml of dichloromethane were successively added molecular sieves 4 Å (50 mg) and complex **5** (0.05 mmol) in the glove-box. The reaction mixture was then cooled at the desired temperature outside of the glove-box and cyclopentadiene (1.5 mmol, 100 μl) was added. After stirring at the

same temperature the reaction mixture was hydrolyzed, extracted with dichloromethane and purified by preparative thin layer chromatography on silica gel (toluene/AcOEt, 60:40). The structure assignments, determination of enantiomeric excesses and absolute configurations of **8** and **9** were made by comparison with literature [11,21]. Enantiomeric excesses were measured by HPLC with Chiracel OD-H for *endo* **8** (hexane/*i*PrOH, 98:2; flow: 1 ml/min, retention times 34 and 35 min for *exo* enantiomers, and 40 and 44 min for *endo* enantiomers), and (*S,S*) Whelk-01 for *endo* **9** (hexane/*i*PrOH, 98:2; flow: 1 ml/min, retention times 37 and 39.5 min for *exo* enantiomers and 41.5 min (major) and 47 min for *endo* enantiomers).

## 3. Results

LnI<sub>3</sub>(THF)<sub>3</sub> (Ln: Yb, Sm) or LaI<sub>3</sub>(DME)<sub>2</sub> react in tetrahydrofuran with 1 eq. of the bispotassium-(*R*)-binaphthoxide **3** leading to the (*R*)-binaphthoxy iodo complexes **5a–5c**, respectively (Eq. (1)). The bispotassium salt **3** is prepared in situ by reacting two equivalents of potassium hydride with (*R*)-binaphthol in tetrahydrofuran. Compounds **5a–5c** are obtained in high yields and isolated as orange, yellow and beige powders, respectively. The <sup>1</sup>H NMR of **5b** and **5c**

Table 1  
Diels–Alder reactions catalyzed by (*R*)-1,1'-bi-2,2'-binaphthoxy iodo lanthanides (**5**)

Entry	R	Catalyst	Temperature (°C)	<i>t</i> (h) <sup>a</sup>	ee ( <i>endo</i> ) (%) <sup>b</sup>	Configuration
1	H	<b>5a</b>	20	1	6	2 <i>S</i>
2	H	<b>5a</b>	-25	10	11	2 <i>S</i>
3	H	<b>5a</b>	-78	48	20	2 <i>S</i>
4	H	<b>5b</b>	20	2	18	2 <i>S</i>
5	H	<b>5b</b>	-30	18	32	2 <i>S</i>
6	H	<b>5b</b>	-78	18	8	2 <i>S</i>
7	H	<b>5c</b>	20	2	20	2 <i>R</i>
8	H	<b>5c</b>	0	18	31	2 <i>R</i>
9	H	<b>5c</b>	-30	18	37	2 <i>R</i>
10	H	<b>5c</b>	-50	72	24	2 <i>R</i>
11	H	<b>5c</b>	-78	72	3 <sup>c</sup>	2 <i>R</i>
12	Me	<b>5a</b>	20	48	12	2 <i>R</i> , 3 <i>S</i>
13	Me	<b>5b</b>	20	6	15	2 <i>R</i> , 3 <i>S</i>
14	Me	<b>5b</b>	20	24 <sup>d</sup>	15	2 <i>R</i> , 3 <i>S</i>
15	Me	<b>5c</b>	20	36	3	- <sup>e</sup>

<sup>a</sup> Reaction time for 100% conversion.

<sup>b</sup> ee are measured by HPLC with Chiracel OD-H for **8** and with (*S,S*) Whelk-O1 for adduct **9**.

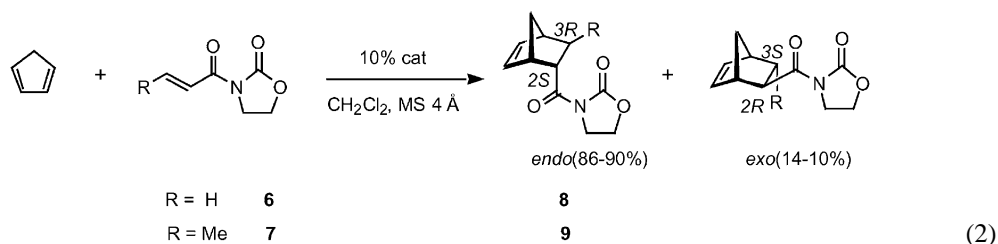
<sup>c</sup> 20% conversion is obtained.

<sup>d</sup> Reaction performed without molecular sieves.

<sup>e</sup> The low value of enantiomeric excess does not allow to assign the major configuration.

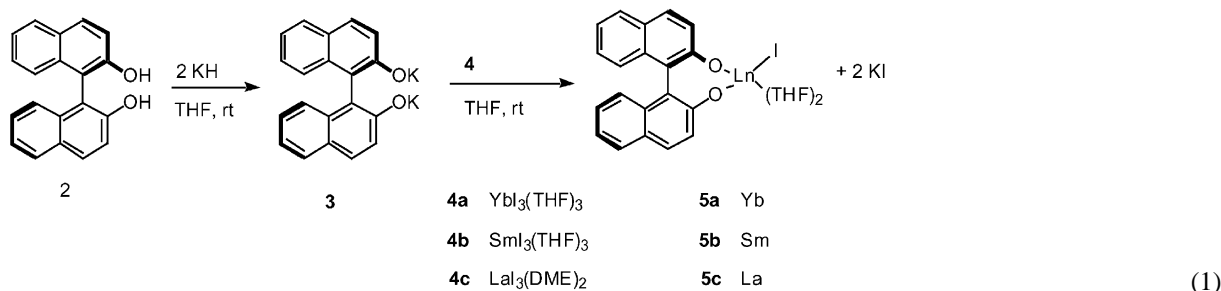
showed only a wide band for the signal of the aromatic protons and no signal corresponding to an hydroxy proton. Similarly the  $^{13}\text{C}$  NMR spectra of **5b** and **5c** show broad bands and no distinct peaks for aromatic carbons. For the three complexes **5a–5c** no hydroxy bond can be observed in the IR spectra. Integration

The lanthanide iodo (*R*)-binaphthoxides **5** catalyze the Diels–Alder additions of unsaturated acyl oxazolidinones **6** and **7** to cyclopentadiene in methylene chloride in the presence of molecular sieves, leading to the cycloadducts **8** and **9** with the *endo* products as the major diastereomers (Eq. (2)). The results are gathered in the Table 1.



and/or elemental analysis are consistent with the formulation of complexes **5** with two molecules of THF. The  $^1\text{H}$  NMR spectra of samarium and lanthanum complexes **5b** and **5c** differ from those of the corresponding (*R*)-binaphthoxide diiodo complexes previously reported which showed well-resolved spectra [16]. An  $^1\text{H}$  NMR study of heterobimetallic lanthanide complexes has also shown well-resolved spectra for the aromatic protons [22]. In contrast  $^{13}\text{C}$  NMR spectra of the catalyst prepared from lanthanum isopropoxide and binol by Shibasaki were complex. This observation together with asymmetric amplification in catalytic reactions was explained by the presence of oligomers [8]. The differences in the spectra of the various catalysts can be explained by different modes of coordination of binaphthol ligands. Until now we have not yet obtained crystals of good quality for X-ray diffraction studies to confirm the structure of our complexes. Yet it appears that the use of bispotassium salt of binaphthol allows the isolation of bidentate binaphthoxide lanthanide complexes while the binaphthol lithium or sodium salts in the presence of lanthanum chloride were unreactive even in refluxing THF [3].

At room temperature (*R*)-binaphthoxy iodo lanthanide complexes **5a–5c** catalyze the cycloaddition of *N*-acryloyl-oxazolidinone **6** to cyclopentadiene in 100% conversion with short reaction times but with only small enantiomeric excesses (entries 1, 4 and 7). Performing the reaction at low temperatures allows to increase the enantiomeric excess of the *endo* product. For ytterbium iodo (*R*)-binaphthoxide the maximum enantiomeric excess (20%) is obtained at the lower temperature (entry 3). The samarium compound **5b** gives slightly better results than ytterbium with a value of ee of 32% at  $-30^\circ\text{C}$ . At this temperature, the samarium iodo (*R*)-binaphthoxide furnishes higher asymmetric induction than at room temperature or at lower temperature. Similarly, the lanthanum compound **5c** furnishes higher enantioselectivities at 0 and  $-30^\circ\text{C}$  (entries 8 and 9) than at room temperature (entry 7) or low temperatures (entries 10 and 11). A similar variation of enantiomeric excess with temperature has already been observed in another reaction catalyzed by complex **5c** [23]. The configuration of the major enantiomer of *endo* isomer



is 2*S* for adducts provided by reaction catalyzed by ytterbium and samarium complexes while the lanthanum compound yields to the other configuration. The (*R*)-binaphthoxy iodo lanthanide complexes **5a–5c** catalyze also the cycloaddition of *N*-crotonyl-oxazolidinone **7** to cyclopentadiene, but for this reaction the enantiomeric excesses are low for all three compounds and the reaction times are longer than for the unsubstituted unsaturated acyl oxazolidinone **6** (entries 12–15). Because of their low rates at room temperature these reactions were not studied at lower temperatures. We checked that the presence of molecular sieves allows to increase the rate of the reaction without changing enantioselectivity (entries 13 and 14). The obtention of asymmetric inductions, yet small, with iodobinaphthoxy complexes **5** is also indicative of the bidentate coordination of the ligand since we precedently obtained racemic products with the monodentate diiodobinaphthoxy lanthanides of type **1**.

#### 4. Conclusion

We have prepared a new family of lanthanide iodo binaphthoxide complexes with a bidentate binaphthol ligand from lanthanide iodides and the bispotassium salt of binaphthol. These derivatives are active catalysts for Diels–Alder reactions but with low enantioselectivities. The lanthanum complex shows a special behaviour as enantiomeric excesses of the Diels–Alder reactions first increase and then decrease when temperature decrease, with a maximum value at  $-30^{\circ}\text{C}$ . Interestingly, the opposite configurations can be obtained for the major enantiomer of *endo* adduct with the same ligand by using either samarium or lanthanum complex. These complexes are currently investigated as Lewis acids catalysts in our laboratory and afford good asymmetric inductions for other reactions [23].

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