(R)-Binaphthoxy diiodide lanthanides

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Abstract

The synthesis and characterization of novel enantiopure binaphthoxy-diiodo lanthanides [(R)-2-(1-naphthol)-1'-naphthoxide)LnI$_2$(THF)$_3$] (Ln = Sm (**4a**), Yb (**4b**), La (**4c**)) are described. These complexes have been prepared by reacting the mono potassium salt of (R)-binaphthol with the corresponding lanthanide triiodides and were characterized by elemental analysis, IR and NMR spectroscopies. Recrystallization of **4c** from THF–hexane led to monocrystals of [(R)-2-(1-naphthol)-1'-naphthoxide)]-diiodolanthane-tetrakistetrahydrofurane] (**4c***). Complex **4c*** crystallizes in the orthorhombic space group, $P2_12_12_1$ with cell parameters $a = 13.086(1)$ Å, $b = 15.496(1)$ Å, $c = 18.854(1)$ Å, $V = 3823.2(6)$ Å^3, and $Z = 4$. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

During the last few years, applications of lanthanides in catalysis have developed very rapidly. Besides lanthanide triflates, which are very powerful catalysts for a wide range of reactions [1,2], lanthanide alkoxides and iodides [3–6] are also efficient, especially for carbon–carbon bond-forming reactions. Asymmetric induction has been observed in reactions catalyzed by lanthanide complexes containing different types of chiral ligands, such as bis sulfonamides [7,8], β-diketonates [9], ferrocenes [10], bis cyclopentadienyl [11] or binaphthol type ligands [12–15]. Highly enantioselective catalysts have been prepared by the groups of Shibazaki and Kobayashi from lanthanides and binaphthol or substituted binaphthols, with different modes of coordination of the ligands in the two systems [12–15]. The former are heterobimetallic derivatives, while the latter have not been structurally characterized.

Previously, we have investigated the activity of lanthanide iodoalkoxides, prepared in situ, as Lewis acid catalysts or for Meerwein–Ponndorf reductions [6,16–22]. For the latter, enantioselective reactions have been reported [23]. Due to the coordination versatility of the binaphthol, we decided to prepare and characterize iodo binaphthoxide lanthanide complexes in order to get a better insight of the role of the coordination mode in catalytic processes.

In this paper we report the synthesis and characterization of mono (R)-binaphthoxide diiodo lanthanide complexes which are, to the best of our knowledge, the first examples of enantiopure mixed iodoalkoxides.
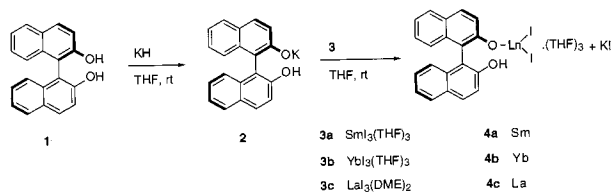
2. Results

LnI$_3$(THF)$_3$ (Ln = Sm, Yb) or LaI$_3$(DME)$_2$ react in tetrahydrofuran with one equivalent of the monopotassium (R)-binaphthoxide leading to the mono (R)-binaphthoxide diiodo complexes **4a**, **4b** and **4c,** respectively (Eq. (1)). As described in Section 4, the monopotassium (R)-binaphthoxide is prepared in situ by reacting one equivalent of potassium hydride with (R)-binaphthol in tetrahydrofuran. Compounds **4a**, **4b** and **4c** are obtained in very high yield and isolated as yellow, orange and beige powders, respectively. ^{1}H-NMR integration and/or elemental analysis are consistent with the formulation of complexes **4** with three

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(1)

Table 1
Selected bond lengths (Å) and angles (°) for **4c***

Bond lengths			
La–I(1)	3.235(2)	La–O(3)	2.528(14)
La–I(2)	3.268(2)	La–O(4)	2.567(13)
La–O(1)	2.190(11)	La–O(5)	2.56(2)
O(1)–C(1)	1.34(2)	La–O(6)	2.582(13)
O(2)–C(22)	1.33(2)		

Bond angles			
I(1)–La–I(2)	84.12(5)	O(3)–La–O(6)	148.6(4)
O(1)–La–I(2)	172.1(4)	O(4)–La–I(1)	139.4(4)
O(1)–La–I(1)	94.0(3)	O(4)–La–I(2)	86.8(3)
O(1)–La–O(3)	81.4(5)	O(4)–La–O(5)	71.7(5)
O(1)–La–O(4)	99.5(5)	O(4)–La–O(6)	68.6(5)
O(1)–La–O(5)	91.6(4)	O(5)–La–I(1)	146.3(4)
O(1)–La–O(6)	83.9(5)	O(5)–La–I(2)	85.8(3)
O(3)–La–I(1)	78.5(3)	O(5)–La–O(6)	138.6(5)
O(3)–La–I(2)	90.7(3)	O(6)–La–I(1)	75.1(4)
O(3)–La–O(4)	141.3(5)	O(6)–La–I(2)	102.9(3)
O(3)–La–O(5)	69.6(5)	La–O(1)–C(1)	157.4(11)

molecules of THF. The presence of the OH group was confirmed in the IR spectra (between 3420 and 3430 cm^{-1}). The ^{1}H-NMR spectra for **4a** and **4c** are relatively well resolved, but for **4b** the resonances are too broad to be of diagnostic value, which is certainly related with the paramagnetic influence of the metal center [24]. For complexes **4a** and **4c** the proton of the hydroxyl group appears at 5.46 and 5.13 ppm, respectively. The ^{1}H-NMR spectrum of **4a** presents five resonances of relative intensity 2:2:4:2:2 for the protons of the naphthoxide ligand and two resonances integrating for 12 protons each for the THF solvent coordinated to the metal. For **4c**, the splitting of the protons due to the naphthoxide ligand is relatively different as one resonance integrates for six protons and the other three integrate for two protons each. For **4a** the chemical shifts of the resonances are not significantly shifted from the diamagnetic region. The small dipolar effect observed for **4a** is certainly related to the nature of the ligand and to the coordination geometry around the metal center, and has also been previously observed for other Sm complexes, namely with aryloxides stabilizing ligands [25–27].

A large variety of aryloxide lanthanide complexes have been described [28] and the most popular synthetic routes are halide metathesis or protonolytic exchange with trisilylamides or with trialkyl lanthanides. In these cases most of the complexes isolated are homoleptic lanthanide alkoxides. We must refer to the fact that heteroleptic lanthanium alkoxides have been obtained by mild protonolysis of [La{CH(SiMe$_3$)$_2$}$_3$] with 3,3′-substituted binaphthol or diphenol, and for one of those, [La{CH(SiMe$_3$)$_2$}{1,1′-(2-OC$_6$H$_2^t$Bu$_2$-3,5)$_2$}-(THF)$_3$], the characterization includes X-ray crystallographic analysis [29]. Halide metathesis using anhydrous lanthanide chlorides and dilithium or disodium binaphthoxide does not afford the expected products [15,30]. The reaction does not proceed even at reflux temperature, and only in the presence of water does the exchange occur, yielding an heterobimetallic compound. Our process indicates that the use of iodides instead of chlorides allows the preparation of lanthanide binaphthoxides without alkali salts in the coordination sphere, and these compounds open access to a new family of mixed iodo alkoxides which are potential enantioselective catalysts.

Recrystallisation of compound **4c** from THF–hexane gave single crystals suitable for X-ray diffraction analysis. The X-ray analysis of the crystal indicates the formation of [(R)-2-(1-naphthol)-1′-naphthoxide)]-di-iodolanthane-(tetrahydrofurane)$_4$] (**4c***). Selected bond lengths and angles are listed in Table 1. An ORTEP view of the molecular structure of **4c*** is presented in Fig. 1. The complex is monomeric and the binaphtholate ligand is monodentate bonding. The lanthanum atom is seven-coordinate and displays approximately pentagonal bipyramidal geometry. The I(2) and the O(1) atoms of the binaphtholate ligand are in the axial positions (I(2)–La–O(1), 172.1(4)°), while the other iodide and all the oxygen atoms of the THF ligands lie in the equato-
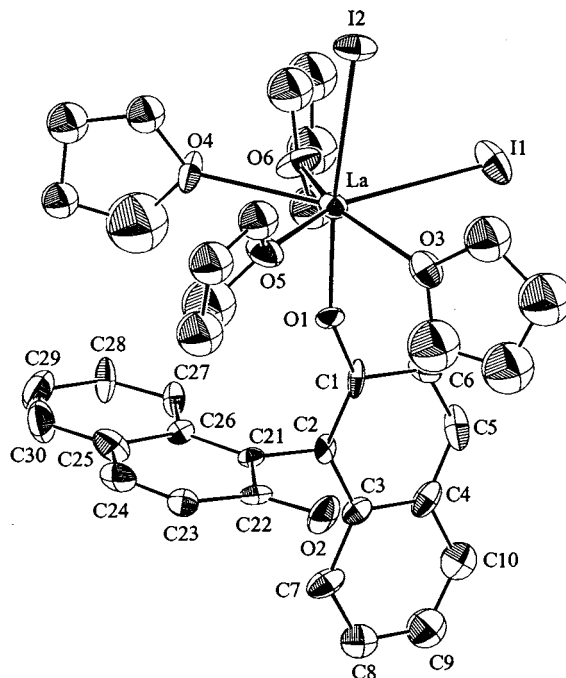

Fig. 1. An ORTEP view of the molecular structure of **4c***.

rial plane. Distortions from the regular geometry can be observed in the equatorial O–La–I and O–La–O angles which vary in the range 68.6(5)–78.5(3)°, far from the idealized 72°.

The La–I bond distances are 3.235(2)Å and 3.268(2) Å, the longest being the one *trans* to the binaphtholate ligand. The La–I distances (av. 3.252(2) Å) are longer than the values of 3.154(4) Å and 3.206(1) Å in the seven-coordinate $LaI_3(THF)_4$ [31] and $LaI_3(^iPrOH)_4$ [32] complexes.

In the binaphtholate ligand the La–O distance and the La–O(1)–C(1) angle are 2.190(11) Å and 157.4(11)°, respectively. Bond-length comparison with other related complexes is difficult since, to our knowledge, this is the first structural characterization of a lanthanide binaphtholate compound. However, the La–O distance and the La–O–C bond angle in the binaphtholate ligand are slightly shorter and greater than the value 2.216(7) Å and the associate La–O–C angle of 132.9(7)° in the octahedral $[La\{CH(SiMe_3)_2\}\{1,1'-(2-OC_6H_2^tBu_2-3,5)_2\}-(THF)_3]$ [29], where the authors suggest some π-bonding from the O to La (in this chelating bis-phenoxide the other La–O distance is 2.271(9) Å and the associate La–O–C angle 113.6(7)°). This short La–O bond distance of 2.190(11) Å and the La–O–C angle of 157.4(11)° in **4c*** can then provide some evidence of π-bonding between the La and O atoms.

In the related $[Me_2Si(3'Bu-C_5H_3)_2ZrCl(binaphtholate)]$ complex [33], where the coordination of the binaphtholate ligand is also monodentate, the Zr–O–C angle is 154.6(2)°, comparable to the value found for La–O–C in **4c***. The torsion angle between the naphthol ring planes is 74.8° in **4c***, comparable to the value 75.8° found for the above-mentioned Zr complex.

The La–O(THF) distance (av. 2.56(2) Å) is comparable with the value 2.54(3) Å in $[LaI_3(THF)_4]$ which also presents a pentagonal bipyramidal geometry. However, it is shorter than the value La–O(THF) of 2.678(10) Å in $[La\{CH(SiMe_3)_2\}\{1,1'-(2-OC_6H_2^tBu_2-3,5)_2\}(THF)_3]$ [29], due to greater steric congestion around the metal center from the presence of the chelating bis-phenoxide.

3. Conclusions

We have described the first examples of diiodocomplexes of Sm, Yb and La stabilized with a mono (*R*)-binaphthoxide. The characterization of the solids obtained is consistent with the presence of three molecules of THF and with the monodentate coordination of the binaphthol. For La, recrystallization of **4c** from THF–hexane has shown that it is possible to stabilize complex **4c*** with four molecules of THF and with a mono (*R*)-binaphthoxide. These complexes are the first examples of lanthanide complexes with a

monodentate ligand and **4c*** is the first complex of this family structurally characterized.

4. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. THF and hexane were distilled from sodium benzophenone ketyl and degassed immediately prior to use. CD_2Cl_2 and $CDCl_3$ were distilled from CaH_2 and degassed immediately prior to use. SmI_2 and YbI_2 were prepared according to published methods [34]. $SmI_3(THF)_3$ and $YbI_3(THF)_3$ were respectively obtained by reacting SmI_2 and YbI_2 with I_2 in THF in the molar ratio 1/0.5 at room temperature. $LaI_3(DME)_2$ was prepared from La powder and iodine [35]. Brucker AM 250, Varian Unity 300 and Bruker DRX 400 NMR spectrometers, operating at 250, 300 and 400 MHz were used for the NMR spectra. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane for spectra in $CDCl_3$, relative to CH_2Cl_2, 5.32, for spectra in CD_2Cl_2. Infrared spectra were recorded as Nujol mulls using NaCl plates on a Perkin–Elmer 1000 FT-IR spectrometer and are reported in cm^{-1}. Carbon hydrogen and iodine elemental analyses were performed on a Perkin–Elmer automatic analyzer.

4.1. [(R)-2-(1-Naphthol)-1'-naphthoxide)]diiodosamarium-tris-tetrahydrofurane (**4a**)

To a solution of (*R*)-1-1'-binaphthol (0.286 g, 1.00 mmol) in 10 ml THF under magnetic stirring was added potassium hydride (0.040 g, 1.00 mmol). After 0.5 h the suspension was added within 5 min to a suspension of $SmI_3(THF)_3$ (0.745 g, 1.00 mmol) in 15 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 **4a** (0.74 g, 88% yield). ^1H-NMR (CD_2Cl_2, 400 MHz, δ ppm): 7.98 (d, 2H, J = 8.9 Hz); 7.90 (d, 2H, J = 8.0 Hz); 7.37 (m, 4H); 7.30 (dt, 2H, J = 8.1 Hz, J = 1.2 Hz); 7.15 (d, 2H, J = 8.3 Hz); 5.46 (s, 1H, OH); 3.94 (br s, 12H); 1.89 (br s, 12H). IR (cm^{-1}): 3432, 1618, 1596, 1511, 1469, 1439, 1383, 1348, 1318, 1272, 1219, 1182, 1148, 1048, 951, 932, 823, 814, 762, 748, 664. Anal. Calc. for $C_{32}H_{34}I_2O_5Sm$: C 42.57; H 3.80. Found: C 42.79; H 4.09.

4.2. [(R)-2-(1-Naphthol)-1'-naphthoxide)]diiodoytterbium-tris-tetrahydrofurane (**4b**)

To a solution of (*R*)-1-1'-binaphthol (0.397 g, 1.39 mmol) in 15 ml THF under magnetic stirring was

added potassium hydride (0.056 g, 1.39 mmol). After 0.5 h the suspension was added within 5 min to a suspension of $YbI_3(THF)_3$ (1.025 g, 1.39 mmol) in 20 ml THF. After 18 h the red–orange and homogeneous supernatant solution was separated from the KI formed and vacuum dried, yielding an orange powder of **4b** (1.20 g, 92% yield). IR (cm^{-1}): 3431, 1615, 1595, 1510, 1468, 1383, 1318, 1272, 1256, 1219, 1181, 1147, 814, 748. Anal. Calc. for $C_{32}H_{34}I_2O_5Yb$: C 41.53; H 3.70; I 27.43. Found: C 41.66; H 4.07; I 26.95.

4.3. [(R)-2-(1-Naphthol)-1′-naphthoxide)]-diiodolanthane-tris-tetrahydrofurane (4c)

To a solution of (R)-1-1′-binaphthol (0.084 g, 0.29 mmol) in 5 ml THF under magnetic stirring was added potassium hydride (0.012 g, 0.29 mmol). After 0.5 h the suspension was added within 5 min to a suspension of $LaI_3(DME)_2$ (0.203 g, 0.29 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 **4c** (0.217 g, 84% yield). ^{1}H-NMR (CDCl$_3$, 250 MHz, δ ppm): 7.96 (d, 2H, $J = 8.9$ Hz); 7.87 (d, 2H, $J = 7.6$ Hz); 7.35–7.24 (m, 6H); 7.13 (d, 2H, $J = 8.2$ Hz); 5.13 (s, 1H, OH); 3.71 (br s, 12H); 1.81 (br s, 12H)]. IR (cm^{-1}): 3420, 1610, 1590, 1505, 1460, 1380, 1340, 1310, 1270, 1260, 1220, 1170, 1145, 1010, 820, 810, 790, 748, 660, 640. Anal. Calc. for $C_{32}H_{34}I_2O_5La$: C 43.12; H 3.84. Found: C 42.95; H 4.24.

5. X-ray crystallographic analysis

A light yellow crystal of **4c***, of approximate dimensions $0.36 \times 0.27 \times 0.27$ mm, obtained by diffusion of n-hexane into a saturated solution of **4c** in THF, was mounted in thin-walled glass capillary in an argon-filled glove box. Data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo–K$_\alpha$ radiation, using an ω–2θ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $14.7 < 2\theta > 27.5°$. A summary of the crystallographic data is given in Table 2. Data were corrected for Lorentz-polarization effects, for linear decay (-23.3%) and for absorption by empirical corrections based on ψ-scans.[36] The structure was solved by Patterson methods [37] and subsequent difference Fourier techniques and refined by full-matrix least-squares procedures on F^2 using SHELXL-93. All but the THF carbon atoms were refined anisotropically. The THF carbon atoms show large thermal parameters and attempts to refine anisotropically gave several atoms in splitting positions. Isor restraints were applied to a few atoms which got 'nonpositive-definite'. The contribu-

Table 2
Crystallographic data for **4c***

Formula	$C_{36}H_{45}I_2O_6La$
Formula weight	966.43
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	13.086(1)
b (Å)	15.496(1)
c (Å)	18.854(1)
V (Å^3)	3823.2(6)
Z	4
$\rho_{calc.}$ (g cm^{-3})	1.679
R_1 ^{a}	0.0805
wR_2 ^{b}	0.1032

^{a} $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$.
^{b} $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. The values were calculated for data with $I > 2\sigma(I)$.

tions of the hydrogen atoms were included in calculated positions. A final difference Fourier synthesis showed no significant features. Atomic scattering factors and anomalous dispersion terms were taken as in Ref. [38].

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