ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 582 (1999) 211–217

Journal of Organometallic Chemistry

Synthesis of asymmetric β-hydroxy-cyclopentadienyl ligands and of their bidentate lanthanide complexes

Alexander Trifonov [1], Fabiola Ferri, Jacqueline Collin *

Laboratoire des Réactions Organiques Sélectives, URA 1497, ICMO, Université Paris-sud, F-91405 Orsay, France

Received 18 November 1998; received in revised form 8 January 1999

Abstract

The synthesis of novel asymmetric β-hydroxy-cyclopentadienyl ligands $C_5H_5CH_2CH(R^1)OH$ (R^1 = Me, CH_2OMe, Ph), obtained by the nucleophilic ring opening reaction of enantiopure epoxides by cyclopentadienyl anion is described. The metallation of these ligands by sodium or potassium metals or by butyl lithium leads to the formation of bis alkaline metals derivatives $[C_5H_4CH_2CH(R^1)O]M_2$ (M = Li, Na, K). Complexes (*S*)-$C_5H_4CH_2CH(Me)OLaI(THF)_2$ and (*S*)-$C_5H_4CH_2CH(Me)OSmI(THF)$ are synthesized from the bis potassium salt and lanthanum or samarium iodides in good yields. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ligand; Cyclopentadiene; Chirality; Lanthanum; Samarium

1. Introduction

The interest in cyclopentadienyl complexes of transition and lanthanide metals as catalysts for a large range of reactions has stimulated investigations into the effects of the cyclopentadienyl ligands on the structure of the complexes and on their catalytic properties. Modifications in the number and the bulkiness of the substituents of the cyclopentadienyl ligand allow the tuning of the steric and electronic properties of the complexes. For lanthanide based catalysts bulky ligands such as pentamethyl cyclopentadienyl or *ansa*-bispermethyl cyclopentadienyl ligand have been used by Marks et al. to synthesize various complexes [1,2]. All of them exhibit high activity for hydrogenation of olefins [3] or hydroamination/cyclization of amino alkenes or amino alkynes [4,5]. On the other hand Molander et al. have recently reported that for the cyclization/silylation of dienes catalysed by yttrium derivatives, complexes coordinated by smaller monosubstituted cyclopentadienyl ligands are more efficient than the corresponding permethyl analogues [6,7]. Following the pioneering work of Kagan et al. [8] on asymmetric hydrogenation catalysed by chiral cyclopentadienyl titanium derivatives, various complexes coordinated by chiral cyclopentadienyl ligands have been synthesized and evaluated as enantioselective catalysts [9,10].

Side chain functionalized cyclopentadienyl ligands allowing the formation of bidentate complexes by intramolecular coordination of a donor group to the metal atom have been more recently explored. Such cyclopentadienyl ligands substituted by an ether or an amino group have been employed for the synthesis of titanium [11–15] or lanthanide [16–21] complexes. The β-methoxyethyl cyclopentadienyl ligand has been used for the preparation of divalent or trivalent lanthanide complexes [16] which exhibit intramolecular coordination in most cases. This led us to examine the possibility of preparing complexes coordinated by asymmetric cyclopentadienyl ligands with a donor group on the side chain. In such compounds the intramolecular coordination should bring the stereogenic centre in close proximity to the metal, thus we hoped an increase of stereoselection in catalytic reactions. We have previously described the preparation of a cyclopentadienyl ligand with an asymmetric centre on which is fixed a

* Corresponding author. Tel.: +33-1-69-154740; fax: +33-1-69-154680.

E-mail address: jacollin@icmo.u-psud.fr (J. Collin)

[1] Present address: Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, ul. Tropinina 49, 603600, Nizny Novgorod, Russian Federation.

PII: S0022-328X(99)00037-6

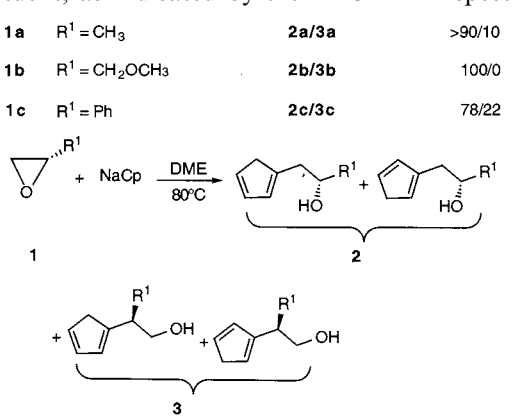
benzyl ether group, in the β-position of the ring [22]. This ligand was introduced in lanthanide iodo complexes which have been subsequently tested as catalysts. These compounds catalyse Diels–Alder reactions but with only modest enantioselectivities [23]. Other similar ligands with an ether or an amino group bearing a chiral centre attached in the β-position on a side chain of a cyclopentadienyl ring [24–26] have been synthesized. Some of them have been employed for the preparation of titanium or zirconium complexes [27–30] and also of some lanthanide metallocenes [31]. A cyclopentadienyl ligand derived from ephedrine, and β-alkoxy-cyclopentadienyl ligands prepared from enantiopure chiral alcohols have been used for the synthesis of the trichloro zirconium complex and of biscyclopentadienyl zirconium triflates, respectively [28–30]. Both complexes are efficient catalysts for Diels–Alder reactions but afford racemic adducts. This lack of enantioselectivity as well as the poor results obtained with biscyclopentadienyl lanthanide iodides for the same reactions could be explained by the decoordination of the donor atom in the enantiodetermining step. NMR studies of some of these complexes have indicated that dissociation–reassociation of the donor group of the side chain to the metal atom occurs in solution [23,30]. To create a rigid structure maintaining the asymmetric centre linked to the metal during catalytic reactions, we devised the preparation of asymmetric complexes with bidentate cyclopentadienyl alkoxy ligands. We now wish to report our first results on the synthesis of new asymmetric β-hydroxy-cyclopentadienyl ligands, and on their applications to the synthesis of bidentate cyclopentadienyl alkoxo lanthanide complexes.

2. Results and discussion

Most of the lanthanide, titanium or zirconium complexes coordinated by chiral cyclopentadienyl ligands with an ether group in the β-position show intramolecular coordination either in solution or in the solid state. Thus, a two-carbon chain between the cyclopentadienyl and the coordinating atom seems well suited to the preparation of bidentate complexes. In order to compare structure, properties and catalytic activity of complexes coordinated by similar cyclopentadienyl ligands bearing side chains of the same length, but bonded to metal atom by different coordination mode: a covalent metal–oxygen bond instead of the coordinative bond of the oxygen of the benzyl ether group, we envisaged the synthesis of asymmetric β-hydroxy-cyclopendadienes. Bidentate complexes of zirconium prepared from β-hydroxy-indenyl or β-hydroxy-cyclopentadienyl ligands have been previously described, [32,33] as well as cyclopentadienyl β-amido complexes of titanium and zirconium [34–36], but to the best of our knowledge no half sandwich-cyclopentadienyl alkoxo lanthanide complex has yet been reported.

2.1. Synthesis of the ligands

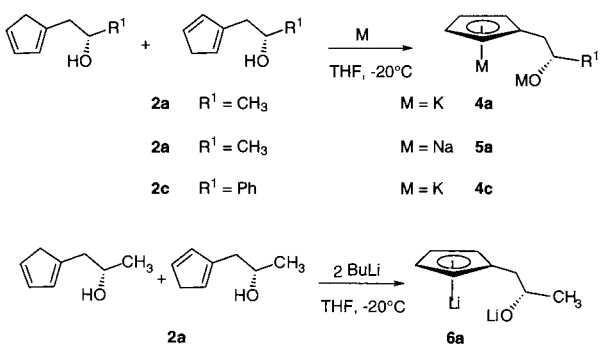
The preparation of racemic chiral β-hydroxy indenes, fluorenes or cyclopentadienes has been realized by the opening of epoxides by lithium or sodium salts of the cyclopentadienyl type [32,37–39]. In the case of monosubstituted epoxides, two regioisomers may be obtained, whether opening occurs at the more or at the less substituted side of the epoxide. The reaction of epoxystyrene with tetraphenyl cyclopentadienyl lithium salt leads to a mixture of both regioisomers in equal amounts [38] while the opening of propylene oxide with cyclopentadienyl sodium has been reported to occur selectively on the less substituted side [39]. We have studied the reactions of commercially available enantiopure epoxides by cyclopentadienyl sodium in refluxing dimethoxyethane using the procedure described. There is a selective opening on the less substituted side of the epoxide affording the secondary asymmetric β-hydroxy-cyclopentadienes **2** as the major products. Small amounts of primary alcohols **3** resulting from the opening on the more hindered side were observed for (*S*)-propylene oxide **1a** (**2a**/**3a** = 90/10) and (*S*)-phenyl oxirane (**2c**/**3c**: 78/22) while for (*S*)-glycidyl methyl ether **1b** the secondary alcohols **2b** are the sole product. The secondary and primary alcohols **2c** and **3c** could be separated by flash chromatography. All products **2** and **3** were isolated as a mixture of regioisomers corresponding to the position of double bonds relative to the substituent, as indicated by their ^{13}C-NMR spectra.



2.2. Preparation of bisalkaline salts of β-hydroxy-cyclopentadienes.

The β-hydroxy-cyclopentadienes **2** and **3** dimerize very rapidly as do cyclopentadiene or methylcyclopentadiene and cannot be stored for a long period even at low temperatures. Therefore, we examined different methods yielding salts which could allow an easier

storage of the compounds and furthermore which may be used to prepare complexes by reaction with various metal halides. We had previously synthesized asymmetric compounds from the reaction of lanthanides triiodides with an asymmetric potassium cyclopentadienyl salt [23]. Attempts to prepare in THF bispotassium salts of **2a**, using potassium hydride (as for 2-benzyloxypropyl cyclopentadiene), or sodium hydride, were unsuccessful and lead to brown oils insoluble in THF that we could not purify. Bispotassium or bissodium salts could be best prepared by reacting the β-hydroxycyclopentadienes with potassium or sodium metal in excess in THF. At the end of the reaction the excess of metal was removed, THF was evaporated and after treatment with hexane the bispotassium or sodium salts were isolated as a white powder in good yields. The reaction of cyclopentadiene **2a** with two equivalents of *n*-butyl lithium in THF afforded after the same treatment as above the bislithium salt **6a** as a white powder. The bisalkaline salts **4a**, **5a**, and **6a,** prepared from **2a** could be characterized by satisfactory elemental analysis. The structures were verified by ^{1}H-NMR for **4a** and **4c**.



2.3. Preparation and characterization of lanthanides complexes *7a* and *8a*

Recently, we investigated the efficiency of samarium diiodide as a precatalyst for various reactions catalysed by Lewis acids, such as Diels–Alder reactions [40], opening of epoxides by various nucleophiles [41], preparation of enoxysilanes [42], aldolization or Michael reactions [43] and tandem reactions [44]. For most of these reactions trivalent lanthanide iodides have exhibited similar catalytic activities and modifications in the nature of the lanthanide or the ligands influence the stereoselectivities of the reactions [45]. Therefore, one can envisage the preparation of complexes which are potentially interesting for enantioselective catalysis by substitution of one or two iodine atoms by asymmetric ligands. The reaction of bispotassium salt **4a** with lanthanum and samarium triiodides in a molar ratio 1:1 afforded complexes which were identified as **7a** and **8a** respectively. ^{1}H-NMR and elemental analysis of both compounds are in agreement with the structure depicted above having a bidentate ligand with an η^5-cyclopentadienyl bond and a covalent metal–oxygen bond. These complexes are to the best of our knowledge the first examples of lanthanide compounds coordinated by cyclopentadienyl, alkoxo and iodide ligands[2]. Several attempts to crystallize the complexes **7a** and **8a** afforded small crystals the quality of which did not permit an X-ray structure determination. Lanthanum complex **7a** is coordinated by two molecules of THF while the corresponding samarium compound **8a** has only one according to elemental analysis and ^{1}H-NMR. This can be explained by the smaller ion radius for the latter complex.

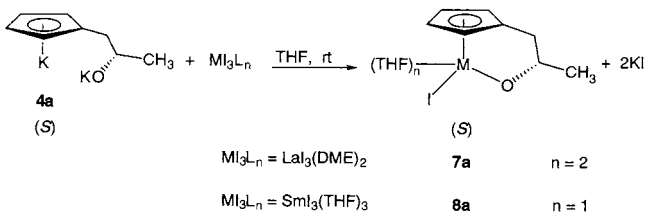


Table 1
NMR data of cyclopentadiene **2a** and derived lanthanide complexes

δ (ppm)	C_5H_4	CHO	CH_2	CH_3
2a $CDCl_3$	6.49–6.08 (3H) 2.5 (2H)	3.95	2.94 (2H)	1.23
4a d_8-THF	5.47 (2H) 5.39 (2H)	3.62	2.72 (1H) 2.22 (1H)	1.10
7a CD_2Cl_2	6.45 (1H) 6.32 (1H) 6.20 (2H)	4.93	2.90 (1H) 2.57 (1H)	1.50
8a CD_2Cl_2	10.0 (1H) 9.60 (1H) 9.18 (1H) 8.72 (1H)	4.77	3.42 (1H) 2.72 (1H)	1.40
$Cp'LaI_2(THF)_2$ CD_2Cl_2	6.53 (1H) 6.42 (1H) 6.27 (1H) 6.20 (1H)	4.22	2.78 (1H) 2.40 (1H)	1.40
$Cp'SmI_2(THF)_3$ C_6D_6	12.31 (1H) 10.80 (1H) 8.56 (1H) 7.89 (1H)	4.60	3.18 (1H) 2.84 (1H)	−0.06

[2] We previously tried to prepare a lanthanum complex with the same coordination sphere, from three different ligands [23], but the formation of this compound was immediately followed by dismutation to an equimolecular mixture of bis cyclopentadienyl iodo lanthanum and bis alkoxo iodo lanthanum.

^{1}H-NMR data for ligand **2a**, bispotassium salt **4a**, and complexes **7a** and **8a** are listed in Table 1. The ^{1}H-NMR data of lanthanum and samarium complexes coordinated by the asymmetric β-ether cyclopentadienyl ligand Cp′ (Cp′ = $C_5H_4CH_2CH(Me)OCH_2Ph$) are included for comparison. In the spectrum of **2a** two groups of signals are observed for the protons of the cyclopentadiene, vinylic protons (6.49–6.08 ppm, 3H) and allylic protons (2.50 ppm, 2H). On the contrary, in the spectra of other derivatives the integrations correspond to four cyclopentadienyl protons with two signals for **4a** [5.47 ppm (2H), 5.39 ppm (2H)], three signals for **7a** [6.45 ppm (1H), 6.32 ppm (1H), 6.20 ppm (2H)] and four signals for **8a** [10.0 ppm (1H), 9.60 ppm (1H), 9.18 ppm (1H), 8.72 ppm (1H)]. Close values are observed for the shifts of protons of the cyclopentadienyl ring of complexes **7a** and Cp′$LaI_2(THF)_2$ on the one hand, and of **8a** and Cp′$SmI_2(THF)_3$ on the other hand. The protons of the CH_2 group of the side chain are inequivalent in complexes **7a** and **8a**. The differences in the patterns of ^{1}H-NMR signals of starting β-hydroxy-cyclopentadiene and of those of its derived complexes reflect the bidentate coordination of cyclopentadienyl and alkoxy groups to the metal atom.

The isolation and characterization of the complexes **7a** and **8a** indicate that β-hydroxy-cyclopentadienyl ligands are well adapted for the formation of bidentate cyclopentadienyl alkoxocomplexes and that the two-carbon side chain has the required length for intramolecular coordination even with a large metal such as lanthanum.

3. Conclusions

New asymmetric cyclopentadienes bearing the chiral centre with an hydroxy group in the β-position on a side chain are easily prepared by the opening of enantiopure epoxides. During the course of this work the synthesis of ferrocenyl substituted β-hydroxy-cyclopentadienes with an asymmetric centre in β-position, and the transformation of the hydroxy groups by various functionalities has been described [46]. Otherwise we have investigated a steady method for the transformation of β-hydroxy-cyclopentadienes to various complexes by the intermediacy of bisalkaline salts, obtained either by reaction with potassium or sodium, or with *n*-butyl lithium. A bispotassium salt has been used for the preparation of bidentate lanthanide iodo complexes which are the first examples of asymmetric *ansa*-cyclopentadienyl alkoxo compounds. These new ligands allow the fixation of the asymmetric centre directly to the metal through a bidentate coordination with η^5-cyclopentadienyl bond and a covalent metal–oxygen bond. The complexes are currently being investigated as Lewis acid catalysts for enantioselective reactions.

4. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. THF, DME and ether were distilled from sodium/benzophenone ketyl and degassed immediately prior to use. Toluene, CH_2Cl_2 and benzene were distilled from CaH_2, and degassed before use. d_8-THF and d_8-toluene were distilled from sodium/benzophenone ketyl and degassed prior to use. Products were purified by flash chromatography on silica gel 60 (eluents given in brackets). Bruker AM 200 and AM 250 spectrometers, operating at 200 and 250 MHz for ^{1}H, 50.4 and 63 MHz for ^{13}C, were used for recording the NMR spectra. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane for spectra in $CDCl_3$. Infrared spectra were recorded as Nujol mulls using KBr plates on a Perkin–Elmer 883 spectrometer and are reported in cm^{-1}. GC analyses were performed with a 25 m BP 1 capillary column connected with a computing integrator. Mass spectra (MS) (70 eV) data were determined on a Ribermag R-10 GC/MS and high resolution mass spectra on a Varian 3400 GC-LC/MS. $SmI_3(THF)_3$ was obtained by reacting SmI_2 [47] and 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 in DME [48].

4.1. *2a: (2S)-1-Cyclopentadienyl-2-propanol (as a equimolar mixture of two regioisomers)*

A solution of NaCp (6.25 g, 71 mmol) in 25 ml of DME was heated at 80°C and a solution of (*S*)-(−)-propylene oxide (1.03 ml, 1.46 mmol) in 5 ml of DME was added dropwise. The reaction mixture was stirred overnight at the same temperature. The solution was cooled to r.t. and then hydrolysed by addition of a saturated solution of NH_4Cl (30 ml). After extraction with ether, the organic layer was dried over $MgSO_4$. Ether was removed under reduced pressure and the residue was Kugelrohr distilled (b.p. 44–48°C, 0.1 mmHg), yielding 1.20 g (68%) of colourless viscous oil. ^{1}H-NMR ($CDCl_3$, 250 MHz) δ ppm: 6.49–6.08 (m, 3H, C_5H_5), 4.08–3.82 and 3.55–3.66 (2m, 1H, C*H*); 3.03–2.86 (m, 2H, CH_2); 2.59–2.42 (m, 2H, CH_2); 1.80 (s, 1H, OH); 1.23 (dd, $J = 7.7$ Hz, $J = 2.2$ Hz, 3H, CH_3).^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ ppm: 146.05; 143.85; 135.02; 134.77; 132.74; 132.03; 129.54; 129.32; 67.92; 67.23; 44.15; 41.60; 41.01; 40.16; 23.29; 23.20. GC/MS (EI) m/z (intensity) M^+ (124, 13.8). IR ν cm^{-1}: 3372, 2966, 2926, 1603, 1457, 1366, 1120. Anal. Calc. for $C_8H_{12}O$: C 77.38; H 9.74; Found: C 77.38; H 9.77. $[\alpha]_D^{22} = +28.3°$ ($c = 1.302$ in CH_2Cl_2).

*4.2. **2b**: (2R)-3-Cyclopentadienyl-1-methoxy-2-propanol (as an equimolar mixture of two regioisomers)*

A solution of NaCp (12.5 g, 142 mmol) in 50 ml DME was heated at 80°C and a solution of (*S*)-glycidyl methyl ether (2.50 g, 28.4 mmol) in 10 ml DME was added dropwise. The reaction mixture was stirred overnight at the same temperature and treated as for **2a**, yielding 2.85 g of (2*R*)-3-cyclopentadienyl-1-methoxy-2-propanol (65%). ^{1}H-NMR ($CDCl_3$, 250 MHz) δ ppm: 6.49–6.07 (m, 3H, C_5H_5); 4.06–3.88 (m, 1H, C*H*); 3.46–3.21 (m, 2H, CH_2O); 3.39 (s, 3H, CH_3); 2.97 (dd, $J = 7.6$ Hz, $J = 1.3$ Hz, 2H, CH_2); 2.56 (t, 2H, $J = 7.3$ Hz, CH_2); 2.47 (s, 1H, OH). ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ ppm: 144.69; 142.52; 134.32; 133.55; 131.89; 131.02; 128.43; 128.18; 76.23; 76.08; 69.60; 69.08; 58.48; 43.39; 40.95; 34.29; 33.52. IR ν cm^{-1}: 3440, 3060, 2895, 1450, 1365, 1195, 1125, 965, 950, 900, 675. GC/MS (EI) m/z (intensity) M^+ (154, 7.0). HRMS (EI) Calc. for $C_9H_{14}O_2$: 154.0994; Found: 154.0987. $[\alpha]_D^{22} = -2.4°$ ($c = 1.278$ in CH_2Cl_2).

*4.3. **2c** + **3c**: (1R)-2-Cyclopentadienyl-1-phenyl-1-ethanol + (2S)-2-cyclopentadienyl-2-phenyl-1-ethanol (each as an equimolar mixture of two regioisomers)*

A solution of NaCp (9.15 g, 104 mmol) in DME (36 ml) was heated at 80°C and a solution of (*S*)-phenyloxirane (2.5 g, 20.8 mmol) in 10 ml DME was added dropwise. The mixture was treated as above to yield a mixture of (1*R*)-2-cyclopentadienyl-1-phenyl-1-ethanol and (2*S*)-2-cyclopentadienyl-2-phenyl-1-ethanol (ratio = 78:22). Chromatography on silica gel (cyclohexane/ether, 6/4) afforded 1.59 g of (1*R*)-2-cyclopentadienyl-1-phenyl-1-ethanol (41%) and 0.41 g of (2*S*)-2-cyclopentadienyl-2-phenyl-1-ethanol (11%).

*4.4. **2c**: (1R)-2-Cyclopentadienyl-1-phenyl-1-ethanol*

^{1}H-NMR ($CDCl_3$, 250 MHz) δ ppm: 7.42–7.23 (m, 5H, C_6H_5); 6.50–6.15 (m, 3H, C_5H_5); 4.90–4.78 (m, 1H, C*H*); 3.05–2.76 (m, 4H, 2 CH_2); 2.10 (t, OH, $J = 3.7$ Hz). ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ ppm: 145.41; 144.54; 144.48; 143.51; 134.91; 134.79; 132.73; 132.37; 130.22, 129.96; 127.93; 127.89; 127.80; 126.20; 74.28; 73.57; 44.23; 41.97; 41.29; 40.62. GC/MS (EI) m/z (intensity) M^+ (186, 1.2). HRMS (EI) Calc. for $C_{13}H_{14}O$: 186.1045; Found: 186.1058. IR ν cm^{-1}: 3400, 3060, 3030, 2880, 1700, 1600, 1495, 1455, 1365, 1050, 900, 460. $[\alpha]_D^{22} = +32.7°$ ($c = 1.402$ in CH_2Cl_2).

*4.5. **3c**: (2S)-2-Cyclopentadienyl-2-phenyl-1-ethanol*

^{1}H-NMR ($CDCl_3$, 250 MHz) δ ppm: 7.40–7.12 (m, 5H, Ph), 6.48–6.13 (m, 3H, C_5H_5), 4.12–3.87 (m, 3H, C*H* + CH_2OH), 3.07 (d, $J = 1.3$ Hz, 1H, CH_2), 3.0 (d, $J = 1.3$ Hz, 1H, CH_2), 1.53 (t, $J = 5.1$ Hz, 1H, OH). ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ ppm: 144.48; 144.27; 141.43; 139.21; 134.30; 133.75; 131.98; 128.62; 128.32; 128.14; 127.69; 127.33; 127.25; 125.70; 125.55; 66.01; 65.73; 49.92; 49.02; 37.94; 37.21. GC/MS (EI) m/z (intensity) M^+ (186, 11.8). HRMS (EI) Calc. for $C_{13}H_{14}O$: 186.1045; Found: 186.1041.

*4.6. **4a**: (2S)-1-Cyclopentadienyl-potassium-2-propanoxy-potassium*

To an excess of potassium in pieces (0.77 g, 19.74 mmol) in 20 ml THF was added a solution of (2*S*)-1-cyclopentadienyl-2-propanol (0.82 g, 6.60 mmol) in 5 ml THF at r.t. The reaction mixture was stirred overnight and the remaining potassium metal was separated by decantation. THF was evaporated under vacuum and the resulting oily residue was washed twice with hexane (20 ml) and dried under vacuum. (2*S*)-1-Cyclopentadienyl-potassium-2-propanoxy-potassium was obtained as off-white powder. Yield 0.84 g (64%). ^{1}H-NMR (d_8-THF, 250 MHz) δ ppm: 5.47 (m, 2H, C_5H_4); 5.39 (m, 2H, C_5H_4); 3.62 (m, 1H, C*H*); 2.72 (dd, $J = 14.7$ Hz, $J = 4$ Hz, 1H, CH_2); 2.22 (dd, $J = 9.7$ Hz, $J = 4$ Hz, 1H, CH_2); 1.10 (d, $J = 6.8$ Hz, 3H, CH_3). IR ν cm^{-1}: 2950, 2880, 1120, 910, 760. Anal. Calc. for $C_8H_{10}OK_2$: C 48.02; H 4.99; K 38.98; Found: C 48.48; H 5.37; K 38.20.

*4.7. **4c**: (1R)-2-cyclopentadienyl-potassium 1-phenyl-1-ethanoxy-potassium*

To an excess of potassium in pieces (0.436 g, 11.7 mmol) in THF (10 ml) at −78°C was added a solution of (1*R*)-2-cyclopentadienyl-1-phenyl-1-ethanol (0.46 g, 2.4 mmol) in 4 ml THF. The mixture was allowed to warm up and stirred overnight at r.t. The solvent was removed under vacuum. The resulting brown solid was washed twice with hexane to afford a pale yellow powder (0.58 g). Yield (95%). ^{1}H-NMR (d_8-THF, 200 MHz) δ ppm: 7.56–7.30 (m, 5H, Ph), 5.76 (m, 2H, C_5H_4); 5.63 (m, 2H, C_5H_4); 4.97 (m, 1H, C*H*); 3.10–2.80 (m, 2H, CH_2).

*4.8. **5a**: (2S)-1-Cyclopentadienyl-sodium-2-propanoxy-sodium*

To an excess of sodium in pieces (0.4 g, 17.4 mmol) in 20 ml of THF a solution of (2*S*)-1-cyclopentadienyl-2-propanol (1.1 g, 8.86 mmol) in 10 ml THF was added under stirring at r.t. and the reaction mixture was left overnight. THF was evaporated under vacuum and the resulting oily residue was washed twice with hexane (20 ml) and dried under vacuum. (2*S*)-1-Cyclopentadienyl-sodium-2-propanoxy-sodium was obtained as off-white powder. Yield 1.19 g, (82%). IR ν cm^{-1}: 2950, 2880,

1120, 910, 760. Anal. Calc. for $C_8H_{10}ONa_2$: C 57.16; H 5.94; Na 27.36. Found C 57.49; H 6.7; Na 27.00.

4.9. **6a**: (2S)-3-Cyclopentadienyl-lithium-2-propanoxy-lithium

To a solution of (2*S*)-1-cyclopentadienyl-2-propanol (0.64 g, 5.15 mmol) in 35 ml THF at −20°C, 9.64 ml of 1.07 M solution of *n*-BuLi was added under stirring. The reaction mixture was left at r.t. for 4 h. Solvents were evaporated under vacuum, and residue was dried under vacuum at 60°C. (2*S*)-1-Cyclopentadienyl-lithium-2-propanoxy-lithium was obtained as off-white powder in 81% yield (0.56 g). IR ν cm^{-1}: 2950, 2880, 1120, 910, 760. Anal. Calc. for $C_8H_{10}OLi_2$: C 70.60; H 7.34; Li 10.28. Found C 69.92; H 7.64; Li 9.60.

4.10. **7a**: (2S)-1-cyclopentadienyl-2-propanoxy lanthanum iodide bistetrahydrofuran

To a suspension of $LaI_3(DME)_2$ (0.36 g, 0.51 mmol) in 20 ml of THF was added solid $CpCH_2CH(Me)OK_2$ (0.10 g, 0.49 mmol) and the reaction mixture was stirred overnight at r.t. The white precipitate of KI was filtered, washed with hexane and dried under vacuum (0.48 g, 81%). THF was evaporated and the oily residue was extracted twice with hexane (10 ml). 0.22 g (79%) of (2*S*)-1-cyclopentadienyl-2-propanoxy lanthanum iodide bistetrahydrofuran as a colourless diamagnetic crystalline solid was obtained by slow addition of hexane to THF solution. ^{1}H-NMR (CD_2Cl_2, 250 MHz) δ ppm: 6.45 (m, 1H, C_5H_4), 6.32 (m, 1H, C_5H_4), 6.20 (m, 2H, C_5H_4), 4.93 (m, 1H, C*H*), 3.82 (m, 8H, CH_2O(THF)), 2.90 (m, 1H, CH_2), 2.57 (m, 1H, CH_2), 1.82 (m, 8H, CH_2 (THF)), 1.50 (d, $J = 7$ Hz, 3H, CH_3). ^{1}H-NMR (d_5-pyridine, 200 MHz) δ ppm: 6.72 (m, 1H, C_5H_4), 6.67 (m, 2H, C_5H_4), 6.50 (m, 1H, C_5H_4), 4.73 (m, 1H, C*H*), 3.68 (m, 8H, CH_2O(THF)), 3.05–2.70 (m, 2H, CH_2), 1.58 (m, 8H, CH_2 (THF)), 1.32 (d, $J = 6.5$ Hz, 3H, CH_3). IR ν cm^{-1}: 1300, 1120, 1070, 1020, 910, 860, 820, 760. Anal. Calc. for $C_{16}H_{26}O_3LaI$: C 36.12; H 4.88; La 26.11. Found C 36.47; H 5.01; La 26.24. $[\alpha]_D = 18.62°$, CH_2Cl_2.

4.11. **8a**: (2S)-1-cyclopentadienyl-2-propanoxy samarium iodide tetrahydrofuran

To a suspension of $SmI_3(THF)_3$ (1.30 g, 1.74 mmol) in 50 ml THF was added (2*S*)-1-cyclopentadienyl-potassium-2-propanoxy-potassium (0.35 g, 1.75 mmol). The reaction mixture was stirred for 16 h and the precipitate of KI (0.47 g, 81%) was separated by filtration. The solution was concentrated to 15 ml and hexane (20 ml) was added. On cooling to −20°C for 3 days yellow crystals formed and were separated by decantation, washed with hexane and dried in vacuo. 0.68 g (83%) of (2*S*)-1-cyclopentadienyl-2-propanoxy samarium iodide tetrahydrofuran was obtained. ^{1}H-NMR (CD_2Cl_2, 200 MHz) δ ppm: 10.0 (m, 1H, C_5H_4), 9.60 (m, 1H, C_5H_4), 9.18 (m, 1H, C_5H_4), 8.72 (m, 1H, C_5H_4), 4.77 (m, 1H, C*H*), 3.42 (m, 5H, CH_2O(THF) + CH_2), 2.72 (m, 1H, CH_2), 1.72 (m, 4H, CH_2 (THF)), 1.40 (s, 3H, CH_3). ^{1}H-NMR (d_5-pyridine, 250 MHz) δ ppm: 13.2 (m, 1H, C_5H_4), 10.22 (m, 1H, C_5H_4), 8.87 (m, 1H, C_5H_4), 5.45 (m, 1H, C*H*), 3.60 (m, 5H, CH_2O(THF) + CH_2), 3.13 (d, $J = 16$ Hz, 1H, CH_2), 1.60 (m, 7H, CH_2 (THF) + CH_3). IR ν cm^{-1}: 1380, 1300, 1110, 1010, 920, 790, 720, 480. Anal. Calc. for $C_{12}H_{18}O_2SmI$: C 30.57; H 3.85; Found C 30.02; H 4.03.

Acknowledgements

We are indebted to Professor H.B. Kagan and Professor J.C. Fiaud for fruitful discussions. We are grateful to Dr I. Santos and Dr P. Van de Weghe for discussions and help in the initial stage of this work. One of us (A.A.T.) acknowledges MENRT for a fellowship. We thank CNRS and JNICT for financial support.

References

[1] G. Jeske, H. Lauke, H. Mauerman, H.P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8091.
[2] G. Jeske, H. Lauke, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8103.
[3] G. Jeske, H. Lauke, H. Mauerman, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8111.
[4] M.R. Gagné, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 275.
[5] Y. Li, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 9295.
[6] G.A. Molander, E. Dowdy, H. Schumann, J. Org. Chem. 63 (1998) 3386.
[7] G.A. Molander, E. Dowdy, B.C. Noll, Organometallics 17 (1998) 3754.
[8] E. Cesarotti, H.B. Kagan, R. Goddard, C. Krûger, J. Organomet. Chem. 162 (1978) 297.
[9] R.L. Halterman, Chem. Rev. (1992) 965.
[10] M.A. Giardello, V.P. Conticello, L. Brard, M.R. Gagné, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10 241.
[11] H. Qichen, Q. Yanlong, L. Guisheng, T. Youqi, Trans. Met. Chem. 15 (1990) 483.
[12] P. Jutzi, U. Siemeling, J. Organomet. Chem. 500 (1995) 175.
[13] M.S. Blais, J.C.W. Chien, M.D. Rausch, Organometallics 17 (1998) 3775.
[14] W.A. Hermann, M.J.A. Morawietz, T. Priermeier, K. Mashima, J. Organomet. Chem. 486 (1995) 291.
[15] P. Jutzi, J. Kleimeier, J. Organomet. Chem. 486 (1995) 287.
[16] B. Wang, D. Deng, C. Qian, New J. Chem. 19 (1995) 515 and references therein.
[17] H. Schumann, F. Erbstein, K. Herrmann, J. Demtschuk, R. Weimann, J. Organomet. Chem. 562 (1998) 255.
[18] D. Deng, X. Zheng, C. Qian, J. Sun, A. Dormond, D. Baudry, M. Visseaux, J. Chem. Soc. Dalton Trans. (1994) 1665.
[19] W.A. Hermann, R. Anwander, F.C. Munck, W. Scherer, Chem. Ber. 126 (1993) 331.

[20] J.R. van den Hende, P.B. Hitchcock, M.F. Lappert, J. Organomet. Chem. 472 (1994) 79.
[21] R. Anwander, W.A. Hermann, W. Scherer, F.C. Munck, J. Organomet. Chem. 462 (1993) 163.
[22] P. Van de Weghe, C. Bied, J. Collin, J. Marçalo, I. Santos, J. Organomet. Chem. 475 (1994) 121.
[23] A.A. Trifonov, P. Van de Weghe, J. Collin, A. Domingos, I. Santos, J. Organomet. Chem. 527 (1997) 225.
[24] Q. Huang, Y. Qian, Synthesis (1987) 910.
[25] A.A.H. van der Zeijden, C. Mattheis, Synthesis (1996) 847.
[26] A.A.H. van der Zeijden, Tetrahedron Asymmetry 6 (1995) 913.
[27] Q. Huang, Y. Qian, Y. Tang, J. Organomet. Chem. 368 (1989) 277.
[28] A.A.H. van der Zeijden, J. Organomet. Chem. 518 (1996) 147.
[29] A.A.H. van der Zeijden, C. Mattheis, R. Fröhlich, Organometallics 16 (1997) 2651.
[30] A.A.H. van der Zeijden, C. Mattheis, J. Organomet. Chem. 555 (1998) 5.
[31] G.A. Molander, H. Schumann, E.C.E. Rosenthal, J. Demtschuk, Organometallics 15 (1996) 3817.
[32] B. Rieger, J. Organomet. Chem. 420 (1991) C17.
[33] J. Christoffers, R.G. Bergman, Angew. Chem. Int. Ed. 34 (1995) 2266.
[34] P.-J. Sinnema, L. van der Veen, A.L. Spek, N. Veldman, J.H. Teuben, Organometallics 16 (1997) 4245.
[35] C. Lensink, J. Organomet. Chem. 553 (1998) 387.
[36] P.-J. Sinnema, K. Liekelema, O.K.B. Staal, B. Hessen, J.H. Teuben, J. Mol. Catal. A 128 (1998) 143.
[37] B. Rieger, G. Jany, R. Fawzi, M. Steinmann, Organometallics 13 (1994) 647.
[38] B. Rieger, M. Steinmann, R. Fawzi, Chem. Ber. 125 (1992) 2373.
[39] H. Ohta, T. Kobori, T. Fujisawa, J. Org. Chem. 42 (1977) 1231.
[40] P. Van de Weghe, J. Collin, Tetrahedron Lett. 35 (1994) 2545.
[41] P. Van de Weghe, J. Collin, Tetrahedron Lett. 36 (1995) 1649.
[42] J. Hydrio, P. Van de Weghe, J. Collin, Synthesis (1996) 68.
[43] N. Giuseppone, P. Van de Weghe, M. Mellah, J. Collin, Tetrahedron 54 (1998) 13 129.
[44] N. Giuseppone, Y. Courtaux, J. Collin, Tetrahedron Lett. 39 (1998) 7845.
[45] J. Collin, N. Giuseppone, P. Van de Weghe, Coord. Chem. Rev. 178–180 (1998) 117.
[46] L. Schwink, P. Knochel, T. Eberle, J. Okuda, Organometallics (1998) 7.
[47] P. Girard, J.L. Namy, H.B. Kagan, J. Am. Chem. Soc. 102 (1980) 2693.
[48] C. Qian, P. Zheng, B. Wang, D. Deng, J. Sun, J. Organomet. Chem. 466 (1994) 101.