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Optically active cyclopentadienyl and indenyl ligands obtained from lactic acid esters

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Abstract

Asymmetric cyclopentadienes and indenes are easily prepared by nucleophilic attack of LiCp or LiInd on tosylate or triflate of ethyl (*S*)-(−) lactate. The selectivity of the reaction depends on the nature of the leaving group. This is particularly true in the case of the reaction of LiCp with sulfonates of ethyl (*S*)-(−) lactate. Indeed, only the monosubstituted cyclopentadiene lactate **2** is obtained from the triflate **6**, whereas from the tosylate **1**, besides **2** (20%) a 1,3-disubstituted cyclopentadiene lactate **3** is isolated (16.5%). From cyclopentadiene and indene lactate **2** and **7**, optically active β-hydroxycyclopentadiene **10** and β-hydroxyindene **11** are obtained by reduction with $LiAlH_4$. Two rhodium(I) complexes **14** and **15** have been synthesized from (*R*,*S*)-2-(cyclopentadienyl)*N*,*N*-dimethylpropanamide **12** and (*S*)-2-(cyclopentadiene)propan-1-ol **10**, respectively. The molecular structure of these complexes has been determined. Analytical and preparative chiral HPLC have been used to determine the optical purity of the ligands and to isolate enantiopure cyclopentadienyl complexes from racemic or enantiomerically enriched rhodium(I) complexes.

Keywords: Chiral cyclopentadienyl rhodium(I) complexes; Ethyl (*S*)-(−) lactate; Cyclopentadiene and indene lactate; Chirality; Chiral HPLC; X-ray diffraction

1. Introduction

In addition to the ansa complexes which constitute a new generation of group IV bent metallocenes suitable as olefin polymerization catalysts, a resurgence of research has started rather recently in order to produce new optically active cyclopentadienyl ligands.

As part of our interest in the synthesis of optically active cyclopentadienyl ligands, we have recently reported the preparation of differently substituted chiral cyclopentadienes and indenes [1–4] from various natural products.

From methyl(−)-pinane-3-carboxylate [1,5], using the Bercaw's method [6], we could obtain optically active cyclopentadienes (Scheme 1).

This method was also successfully applied to (*S*)-(+)-naproxene and 2-bromo-butene [7] (Scheme 2).

Optically active cyclopentadienyl ligands, bearing a pendant arm in order to reach bidentate coordination providing a rigid structure that is suited for transfer of asymmetry, are of great interest in enantioselective catalysis. For this reason we decided to investigate the behaviour of α-hydroxyesters such as acid lactic esters.

2. Results and discussion

From ethyl (*S*)-(−) lactate, two synthetic routes to optically active cyclopentadienes can be envisioned as shown in Scheme 3.

Preliminary experiments have shown that, under Bercaw's conditions (route (a)), the reaction between ethyl

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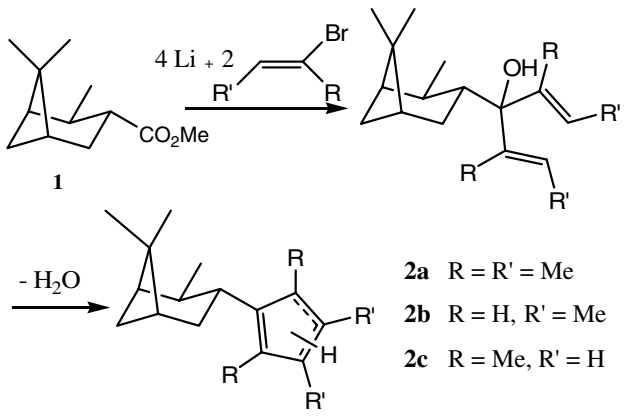
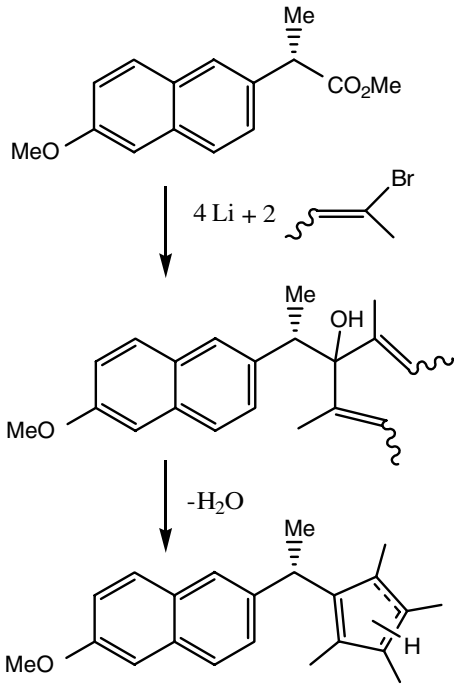


Scheme 1.



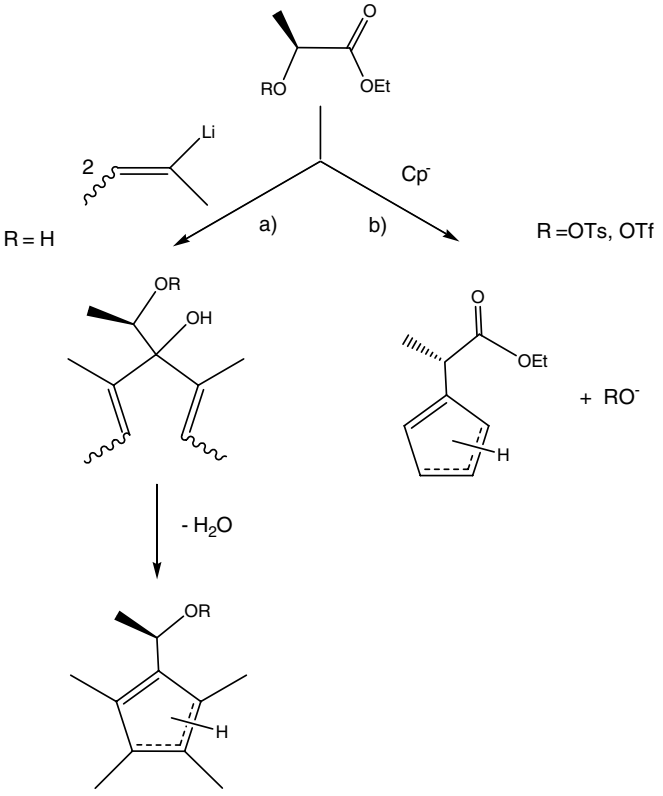
Scheme 2.

lactate and two equivalents of the lithium derivative of 2-bromobutene afforded the isomeric dienic alcohols in good yields. However, the formation of the cyclopentadienes by dehydration with different dehydration agents did not work at all, the isomeric tertiary alcohols being recovered unchanged, together with untractable products.

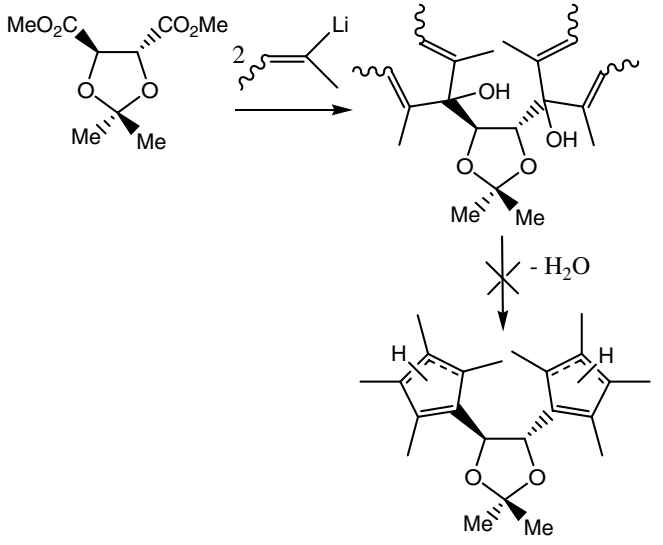
Ethyl lactate, protected as the phenoxy derivative, afforded a similar result.

The same reactivity was also observed with the dimethyl ketal-protected tartrate (Scheme 4).

So far, we do not have any definitive explanation for the failure of the dehydration process. The presence of an oxygen atom in α position with respect to the hydroxyl group could be at the origin of the observed lack of reactivity. Indeed, one can assume that the carbocation formed in the first step of the dehydration process could be stabilized



Scheme 3.

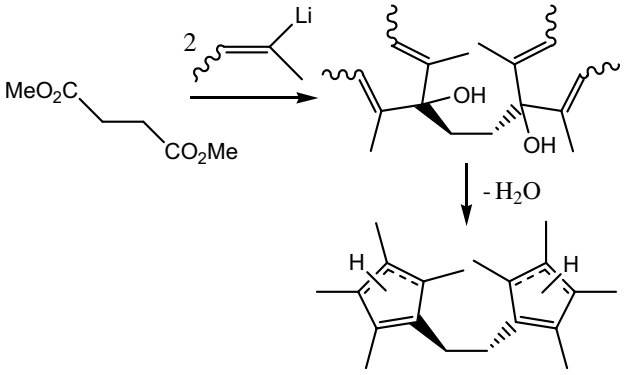


Scheme 4.

by the oxygen atom in α position, thus preventing the electrocyclization to occur.

This hypothesis find some support in the reaction of dimethyl succinate which afforded the corresponding dicyclopentadiene in good yields, as described by Brintzinger [8] (Scheme 5).

The other synthetic route (b), consists in a substitution reaction of S_N2 type of cyclopentadienide anions on sulfonates derivatives of ethyl lactate.



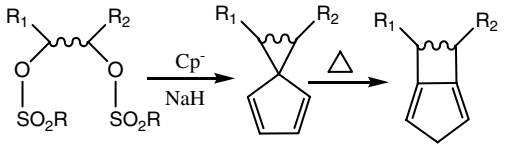
Scheme 5.

This synthetic route has been described in the literature [9] with different substrates but, to our knowledge, not in the case of acid lactic esters.

When the tosylate of ethyl (*S*)-(−) lactate **1** was reacted with LiCp, the cyclopentadiene lactate **2** was obtained as a mixture of two isomers ((*S*)-ethyl 2-(cyclopenta-1,3-dienyl)propanoate and (*S*)-ethyl 2-(cyclopenta-1,4-dienyl)propanoate), as shown in Scheme 6.

Besides this compound, an other unexpected lactate 1,3-disubstituted cyclopentadiene **3** (16.5% yield) was also isolated as a mixture of two isomers diethyl (2*S*,2′*S*)-2,2′-cyclopenta-1,3-diene-1,3-diyldipropanoate and diethyl (2*S*,2′*S*)-2,2′-cyclopenta-1,3-diene-1,4-diyldipropanoate.

To our knowledge, this is the second example of such a behaviour in a substitution reaction between a sulfonate monoester and a cyclopentadienide anion. Indeed, as we mentioned elsewhere [3], in the case of glucose-substituted cyclopentadienes and indenes, generally the reaction of sulfonate monoesters with cyclopentadienide or indenide anions produces only the expected monosubstituted products [2,4,10,11]. This is in the particular case of sulfonate diesters that disubstitution products are very often observed as the result of a sequential inter- and intramolecular reactions as shown in Scheme 7.



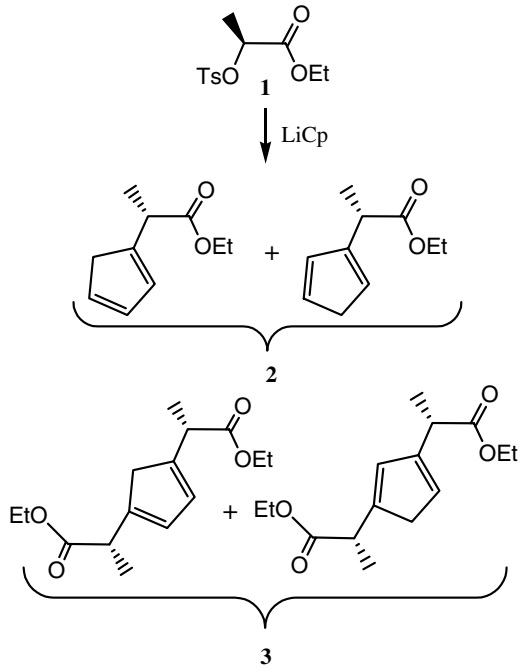
Scheme 7.

The result of this reaction is mostly the formation of annulated compounds resulting of thermal sigmatropic rearrangements of intermediate spiroannulated cyclopentadienes [12–14] or indenes [15] intermediates.

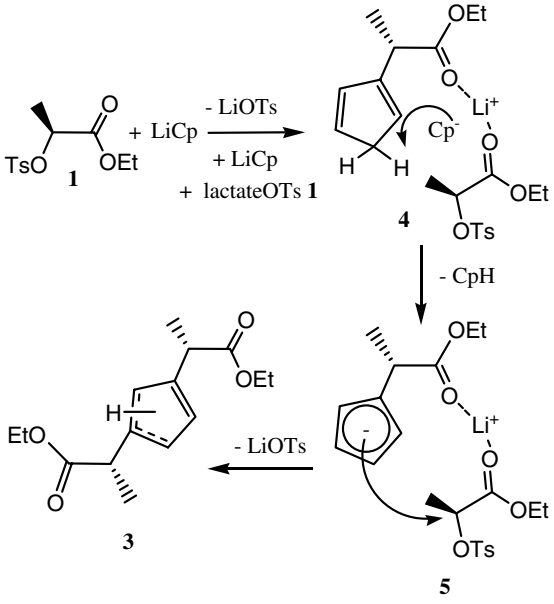
It is, of course, possible to synthesize di- and even polysubstituted cyclopentadienes from monosulfonate esters or alkyl halides by intermolecular reactions. However, in these cases, the reaction proceeds by successive steps with a base necessary for the deprotonation of cyclopentadienes intermediates [16,17].

As we proposed earlier [3], for allose-derived cyclopentadiene and indene, the formation of **3** could be tentatively rationalized by a nucleophilic attack of LiCp on **1** with formation of the monosubstituted cyclopentadiene **2**. Intramolecular complexation of one molecule of LiCp with the oxygen atom of either the carbonyl or the ethoxy group of the ester function could occur giving a termolecular structure **4**. The complexation of lithium with the oxygen of a carbonyl group has been described and can explain the stereoselectivity of different reactions [18,19].

In the case of lactate esters, the cyclopentadienide anion would abstract a proton to the already bound



Scheme 6.



Scheme 8.

cyclopentadiene to give a lactate-substituted cyclopentadienide **5** which, in turn, could attack the complexed tosylate lactate affording the disubstituted cyclopentadiene **3** (Scheme 8).

When the triflate **6** of ethyl lactate was reacted with LiCp, under the same conditions as those used with the tosylate, the monosubstituted cyclypentadiene **2** was found as the sole product. In this case the yield of 54% is better than with the tosylate.

Because of the presence of isomers it is not easy to determine the optical purity of cyclopentadiene lactate. However, after deprotonation and formation of transition metal complexes as a single compound, the optical purity was determined by chiral HPLC and found to be 90%. A very similar value was obtained starting either from the triflate **6** or the tosylate lactate **1**.

3. Obtention of indene lactate

When the tosylate of ethyl lactate **1** was reacted in THF at low temperature with lithium indenide, indene lactate **7** ((*S*)-ethyl 2-(1*H*-inden-3-yl)propanoate) was obtained as a sole isomer with a yield of 57% and an optical purity measured by chiral HPLC as *S*:*R* 97.5:2.5 (Scheme 9).

Starting from triflate **6** of ethyl lactate, it was observed that, sometimes besides compound **7**, the other possible isomer **8** ((*S*)-ethyl 2-(1*H*-inden-1-yl)propanoate) was formed with a *de* of 50%. Thermodynamically less stable than **7**, this compound isomerizes thermally or by deprotonation and reprotonation to give **7** with an optical purity of the same value as that of directly formed **7** (*S*:*R* 97.5:2.5) (Scheme 10).

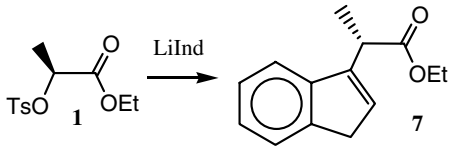
A third compound can be isolated by liquid chromatography and identified by NMR as a disubstituted indene **9** (diethyl (2*S*,2′*S*)-2,2′-(1*H*-indene-1,3-diyl)dipropanoate). In **9** a new stereogenic center is created and, on the ground of ^{1}H and ^{13}C NMR study in different solvents, it is possible to assume that **9** is formed with a very high diastereoselectivity.

It is worthy to note that the same results are obtained with the tosylate or the triflate of isopropyl (*S*)-(−) lactate but, in these cases, the yields are slightly higher than with ethyl (*S*)-(−) lactate sulfonates. This could be due to a higher steric hindrance close to the ester carbonyl group, decreasing undesired nucleophilic attack on this group.

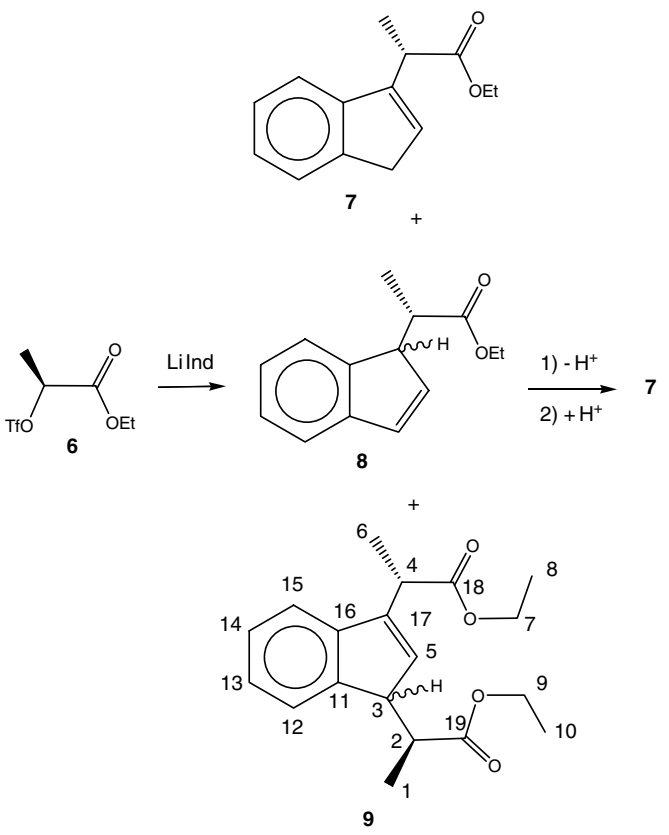
With $LiAlH_4$, cyclopentadiene and indene lactate **2** and **7** are readily converted into the corresponding alcohols, **10** ((*S*)-2-(cyclopenta-1,3-dienyl)propan-1-ol and (*S*)-2-(cyclopenta-1,4-dienyl)propan-1-ol) and **11** ((*S*)-2-(1*H*-inden-3-yl)propan-1-ol) in high yields, as shown in Scheme 11.

The optical purity of **11**, formed as a single isomer, is almost identical as the starting ester, according to chiral HPLC analysis.

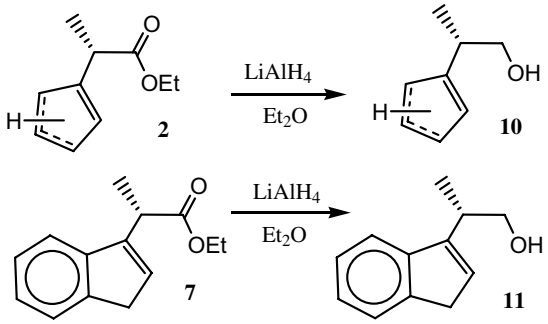
These chiral β-hydroxy cyclopentadienes are isomers of those obtained by attack of chiral propylene oxide with sodium cyclopentadienide [20].



Scheme 9.



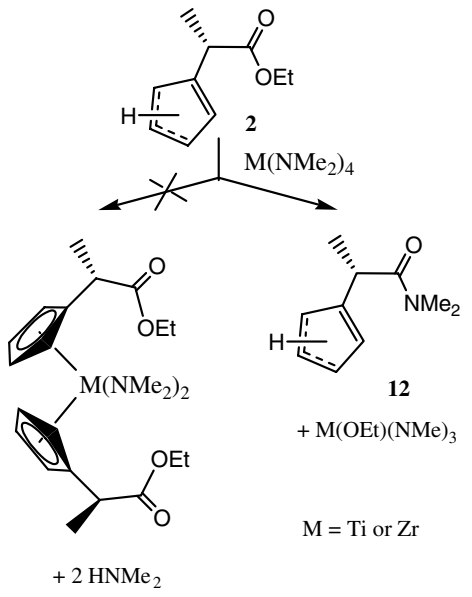
Scheme 10.



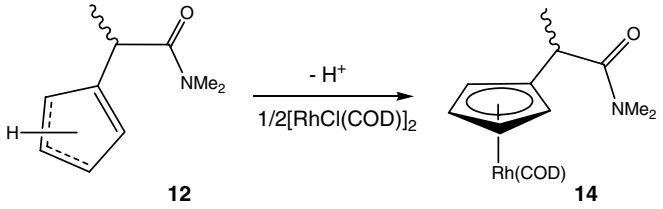
Scheme 11.

4. Syntheses of complexes

Attempts to obtain group IV transition metal complexes from cyclopentadiene and indene lactate by salt elimination reactions were unsuccessful.



Scheme 12.



Scheme 13.

We thought it could be possible to obtain titanium or zirconium complexes by the well-established amine elimination route [21]. In the case of cyclopentadiene and indene ethyl lactate **2** and **7**, with either $Ti(NMe_2)_4$ or $Zr(NMe_2)_4$, instead of the hope-for complexes, we observed almost quantitatively the transformation of the ester function to an amide function, as shown in Scheme 12 from cyclopentadiene lactate **2**.

A similar result was obtained from indenyl ethyl lactate **7** to give **13** quantitatively:

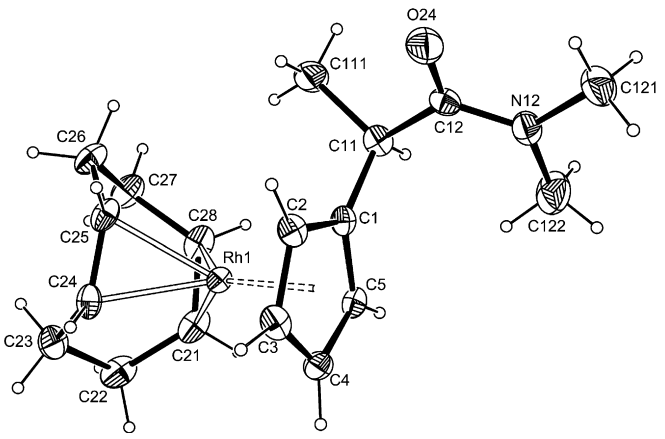
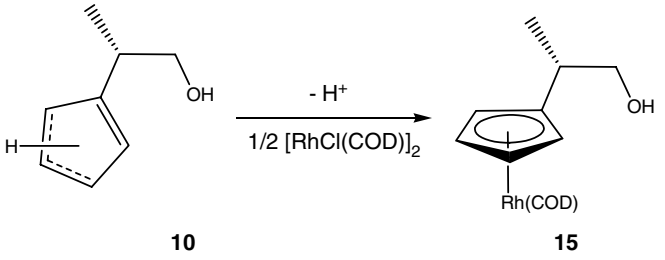


Fig. 1. ORTEP view of compound **14.**



Scheme 14.

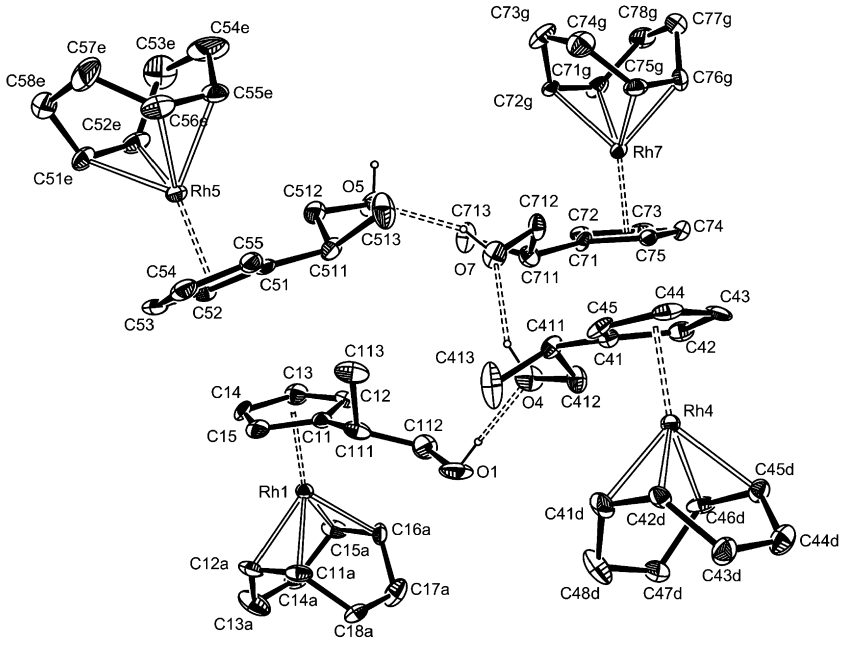
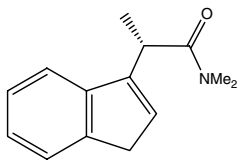


Fig. 2. ORTEP view of compound **15**.



13

From racemic 2-(cyclopentadienyl)-*N*,*N*-dimethylpropanamide **12**, a cycloocta-1,5-diene rhodium(I) complex **14** was prepared in the racemic version (see Scheme 13).

The X-ray structure of this complex is shown in Fig. 1.

From the racemic complex **14**, it was possible to obtain both enantiomers in a pure form by preparative chiral HPLC in a multimilligram scale (see Section 5).

The preparation of an optically active cycloocta-1,5-diene rhodium(I) complex **15** was achieved from cyclopentadiene alcohol **10** as shown in Scheme 14. The optical purity of **15** was shown to be *S*:*R* 95:5 by chiral HPLC.

It was observed that the X-ray analysis was impossible to carry out on crystals obtained from the mixture containing 95% of the major enantiomer. However, preparative chiral HPLC allowed the obtention of the pure major enantiomer, the crystals of which were suitable for an X-ray determination.

The X-ray structure of this complex is shown in Fig. 2.

In compound **15**, there are eight molecules in the asymmetric unit. All eight complexes have the same absolute configuration and are nearly identical. They are interconnected as shown in Fig. 2 by O–H···O hydrogen bonds which links four complexes then forming a pseudo tetramer structure. The other four complexes form also a tetrameric structure. Furthermore each tetramer is linked by O–H···O hydrogen bonds to symmetry related tetramers building columns of complexes which develop parallel to the *b* axis.

From the molecular structure, the *S* absolute configuration found for the cyclopentadienyl ligand, confirms that the initial nucleophilic attack on the starting sulfonates **1** and **6** occurs *via* a S_N2 substitution.

5. Experimental

General comments. All reactions were carried out under an atmosphere of argon. The solvents were dried by the appropriate procedure [22] and distilled under nitrogen before use. Standard Schlenk techniques and conventional glass vessels were employed. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-200 and Bruker Avance DRX-500 spectrometers, chemical shifts are referenced to internal solvent resonances and reported relative to TMS. Elemental analyses were carried out by the Spectropole-Service d'Analyse Elémentaire-Faculté de St Jérôme. Optical rotations were determined on a Perkin–Elmer Model 241 MC digital polarimeter operating at 25 °C using a 1 dm cell length. Tosylate **1** [23], triflate **6** [24] of ethyl(S)-(−)lactate and $Zr(NMe_2)_4$ [21] were prepared according to literature methods. $Ti(NMe_2)_4$ was purchased from Strem Chemicals.

Chiral HPLC: The chiral HPLC analyses were performed on a screening unit composed of Merck D-7000 system manager, Merck-Lachrom L-7100 pump, Merck-Lachrom L-7360 oven which may accommodate 12 columns alimented by a Valco 12 positions valve, Merck-Lachrom L-7400 UV detector and on-line chiroptical detector: Jasco OR-1590 polarimeter or Jasco CD-1595 circular dichroism detector. The sign given by the chiroptical detectors is the sign of the enantiomer in the solvent used for the analyse [25]. Retention times R_t in min, retention factors $k_i = (R_{t_i} - R_{t_0})/R_{t_0}$ and enantioselectivity factor $\alpha = k_2/k_1$ are given. R_{t_0} was determined by injection of tri-tertio-butyl benzene. *N*-hexane and 2-PrOH are HPLC grade from SDS (Peypin, France), the solvents for chromatography experiments, are degassed and filtered on Millipore membrane 0.45 μm before use. The semi-preparative separation were performed with Merck-Hitachi LiChrograph L-6000 pump, Merck-Hitachi L-4000 UV detector and Merck D-7000 system manager. The chiral stationary phases used are cellulose tris(3,5-dimethylphenylcarbamate) Chiralcel OD-H (250 × 4.6 mm) and Chiralcel OD (250 × 10 mm), amylose tris(3,5-dimethylphenylcarbamate) Chiralpak AD (250 × 4.6 mm) and (250 × 10 mm), and cellulose tris(4-methylbenzoate) Chiralcel OJ (250 × 4.6 mm), all available from Chiral Technologies Europe (Illkirch, France).

*5.1. Synthesis of cyclopentadiene lactate ((S)-ethyl 2-(cyclopenta-1,3-dienyl)propanoate and (S)-ethyl 2-(cyclopenta-1,4-dienyl)propanoate) **2** from tosylate of ethyl (S)-(−)lactate (ethyl (S)-2-[[(4-methylphenyl) sulfonyl]oxy]propanoate) **1***

A solution of LiCp (5 g, 70 mmol), prepared from freshly cracked dicyclopentadiene and *n*-BuLi (2.5 M in hexane), in 100 ml THF was slowly added over 2 h to a solution of 19 g (69.8 mmol) of tosylate of ethyl lactate **1** in THF (200 ml) cooled at −78 °C. The solution was stirred overnight at room temperature. After evaporation of THF under vacuum, addition of a saturated aqueous solution of NaCl extraction of the organic compounds was made with Et_2O (5 × 50 ml). The combined extracts were dried over $MgSO_4$ and Et_2O was eliminated under vacuum leaving the crude product as an oily brown residue (11.5 g). Purification on a silica gel column, followed by distillation under reduced pressure, afforded **2** (2.52 g, 20% yield) and **3** (1.67 g, 16.5% yield). The Rf of **2** and **3** are 0.58 and 0.23, respectively (hexane/Et_2O 80/20).

*5.2. Synthesis of cyclopentadiene lactate ((S)-ethyl 2-(cyclopenta-1,3-dienyl)propanoate and (S)-ethyl 2-(cyclopenta-1,4-dienyl)propanoate) 2 from triflate of ethyl (S)-(−) lactate (ethyl (S)-2-[[(trifluoromethyl) sulfonyl]oxy]propanoate) **6***

In the same conditions as those described above from tosylate of ethyl lactate **1**, 6.86 g of triflate of ethyl lactate **6** afforded, after purification on a silica column, 2.44 g of **2** (54% yield).

5.3. Cyclopentadiene ethyl lactate **2**

^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.54, 6.43, 6.33, 6.17 (m, 3H, CH Cp), 4.15 (q, 2H, CH_2CH$_3$), 4.13 (q, 2H, CH_2CH$_3$), 3.58 (q, 1H, CHCH$_3$), 3.55 (q, 1H, CHCH$_3$), 2.98 (m, 4H, CH$_2$ Cp), 1.40 (d, 3H, CHCH_3), 1.25 (t, 3H, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 173.7 (C=O), 146.0 (Cquat Cp), 145.5 (Cquat Cp), 134.0, 133.2, 132.1, 128.2, 127.5, 126.1 (CH Cp), 60.6 (*C*H$_2$CH$_3$), 42.0 (CH$_2$ Cp), 41.4 (*C*HCH$_3$), 41.3 (CH$_2$ Cp), 40.6 (*C*HCH$_3$), 17.5 (CH*C*H$_3$), 16.7 (CH*C*H$_3$), 14.5 (CH$_2$*C*H$_3$), 14.3 (CH$_2$*C*H$_3$). Anal. Calc. for $C_{10}H_{14}O_2$: C, 72.23; H, 8.42. Found: C, 72.45; H, 8.36%.

5.4. Disubstituted cyclopentadiene ethyl lactate (diethyl (2S,2′S)-2,2′-cyclopenta-1,3-diene-1,3-diyldipropanoate and diethyl (2S,2′S)-2,2′-cyclopenta-1,3-diene-1,4-diyldipropanoate) **3**

^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.54–6.04 (m, 2H, CH C_5H_4), 4.13 (m, 4H, CH_2CH$_3$), 3.77 (q, 1H, CHCH$_3$), 3.46 (q, 1H, CHCH$_3$), 2.99 (m, 4H, CH$_2$ Cp), 1.37 (m, 6H, CHCH_3), 1.23 (6H, m, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): d 173.0 (C=O), 147.0 (Cquat Cp), 146.0 (Cquat Cp), 134.0, 133.5, 132.3, 132.0 (CH Cp), 60.3 (*C*H$_2$CH$_3$), 42.1 (CH$_2$ Cp), 41.5 (*C*HCH$_3$), 41.3 (CH$_2$ Cp), 40.6 (*C*HCH$_3$), 17.6 (CH*C*H$_3$), 16.9 (CH*C*H$_3$), 14.5 (CH$_2$*C*H$_3$), 14.1 (CH$_2$*C*H$_3$). Anal. Calc. for $C_{15}H_{22}O_4$: C, 67.76; H, 8.31. Found: C, 68.20; H, 8.56%.

5.5. Synthesis of indene lactate ((S)-ethyl 2-(1H -inden-3-yl)propanoate) 7 from tosylate of ethyl (S)-(−) lactate **1**

A solution of LiInd (4.4 g, 36 mmol), prepared from Indene and BuLi (2.5 M in hexane) in hexane, in 100 ml THF was slowly added over 2 h to a solution of 10 g (360 mmol) of tosylate of ethyl lactate **1** in THF (200 ml) cooled at −78 °C. The solution was stirred overnight at room temperature. After evaporation of THF under vacuum, addition of a saturated aqueous solution of NaCl extraction of the organic compounds was made with Et_2O (5 × 50 ml). The combined extracts were dried over $MgSO_4$ and Et_2O was eliminated under vacuum leaving the crude product as an oily brown residue. Purification on a silica gel column afforded 4.5 g of **7** (56.5% yield). The Rf of **7** is 0.43 (hexane/Et_2O 80/2).

Chiral HPLC: Chiralcel OJ (250 × 4.6 mm), hexane/isopropanol (90/10) as mobile phase, flow-rate = 1 ml/mn, 25 °C, detection by UV at 254 nm and polarimeter, $R_t(S,+) = 7.48$, $R_t(R,-) = 11.90$, $k(S) = 1.45$, $k(R) = 2.90$, $\alpha = 2.00$ and Rs = 6.17.

5.6. Synthesis of indene lactate ((S)-ethyl 2-(1H -inden-3-yl)propanoate) 7 from triflate of ethyl lactate **6**

In the same conditions as those described above, 4.9 g (19.6 mmol) of triflate of ethyl lactate **6** afforded, after purification on a silica gel column, 1.9 g of **7** (45% yield), 0.34 g of **8** (8% yield) and 0.06 g of **9** (2% yield). The Rf of **8** and **9** are 0.47 and 0.40, respectively (hexane/Et_2O 80/2). The optical purity found for **7** was 95% by chiral HPLC. The same value was found from **8** after protonation and reprotonation.

5.7. Indene ethyl lactate ((S)-ethyl 2-(1H -inden-3-yl) propanoate) 7

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.47–7.22 (m, 4H, CH arom), 6.40 (m, 1H, CH indene), 4.16 (q, 7.2, 2H, CH_2CH$_3$), 3.81 (qdd, 7.1, 1.5, 0.9, 1H, CHCH$_3$), 3.37 (bs, 2H, CH$_2$ indene), 1.55 (d, 7.1, 3H, CHCH_3), 1.23 (t, 7.2, 3H, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 174.3 (C=O), 144.4 (Cquat arom), 144.0 (Cquat arom), 143.2 (Cquat indene), 129.4 (CH indene), 126.1, 124.8, 123.9, 119.5 (CH arom), 60.9 (*C*H$_2$CH$_3$), 39.1 (*C*HCH$_3$), 37.9 (CH$_2$ indene), 16.6 (CH*C*H$_3$), 14.1 (CH$_2$*C*H$_3$). Anal. Calc. for $C_{14}H_{16}O_2$: C, 77.74; H, 7.45. Found: C, 77.03; H, 7.64%. For the (*S*)-enantiomer, $[\alpha]_D^{25} = +25.6$ ($CHCl_3$, $c = 6.75$).

5.8. Indene ethyl lactate ((S)-ethyl 2-(1H-inden-1-yl) propanoate) **8**

Only the NMR data of the major diastereoisomer will be given.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.30 (m,4 H, CH arom), 6.86 (dd, 1 H, CH-sp^{2}indene), 6.49 (dd, 1 H, CH-sp^{2}indene), 4.25 (q, 2 H, CH$_2$–O), 3.88 (m, 1 H, CH-sp^3 indene), 2.99 (q, 1 H, C*H*–CH$_3$), 1.32 (t, 3 H, CH_3–CH$_2$), 0.84 (d, 3 H, CH_3–CH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 175.7 (C=O), 145.4 and 144.8 (Cquat arom), 136.2 and 132.7 (CH-sp^2 indene), 127.0, 125.0, 122.7 and 121.2 (CH arom), 60.7 (CH$_2$–O), 52.0 (CH-sp^3 indene), 40.9 (*C*H–CH$_3$), 12.4 (*C*H$_3$–CH), 12.2 (*C*H$_3$–CH$_2$).

5.9. Disubstituted indene ethyl lactate (diethyl (2S,2′S)-2,2′-(1H-indene-1,3-diyl)dipropanoate) **9**

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (ddc, 7.4, 1H, CH arom), 7.33 (ddc, 7.8, CH arom), 7.26 (tc, 7.4, 1H, CH arom), 7.18 (ddd, 7.3, 1.1, 1H, CH arom), 6.31 (dd, 1.95, 1.2, 1H, CH indene), 4.24 (q, 7.1, 2H, CH_2-9), 4.13 (qd, 7.1, 1.1, 2H, CH_2-7), 3.86 (mc, 1H, C*H*-3), 3.76 (qt, 7.0, 1.2, 1H, C*H*-4), 2.98 (qd, 7.0, 5.0, 1H, C*H*-2), 1.52 (d, 7.1, 3H, CH_3-6), 1.31 (t, 7.1, 3H, CH_3-10), 1.18 (t, 7.1, 3H, CH_3-8), 0.78 (d, 7.0, 3H, CH_3-1). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.7 (C-19), 174.0 (C-18), 146.1 (C-11), 144.1 (C-16), 144.1 (C-17), 131.4 (C-5), 126.9 (C-14), 125.3 (C-13), 122.8 (C-12), 119.6 (C-15), 60.8 (C-7), 60.7 (C-9), 50.5 (C-3), 41.4 (C-2), 39.1 (C-4), 16.5 (C-6), 14.4 (C-10), 14.2 (C-8), 11.7 (C-1). Anal. Calc. for $C_{19}H_{24}O_4$: C, 72.12; H, 7.63. Found: C, 72.36; H, 7.45%. $[\alpha]_{546}^{25} = -58.6$ (CH_2Cl_2, $c = 0.365$).

5.10. Synthesis of cyclopentadiene alcohol ((S)-2-(cyclopenta-1,3-dienyl)propan-1-ol and (S)-2-(cyclopenta-1,4-dienyl)propan-1-ol) **10**

To a suspension of 0.96 g (25.4 mmol) $LiAlH_4$ in 100 ml of dry Et_2O cooled at 0 °C, a solution of 4.6 g (27.7 mmol) of cyclopentadiene lactate **2** in 100 ml Et_2O was slowly added via canula. After 4 h stirring at room temperature and monitoring by TLC (hexane/Et_2O 70/30) water was carefully added. Extraction of the aqueous phase with Et_2O and drying on $MgSO_4$ of the combined organic fractions afforded 3.4 g of crude **10**. Purification on a silica gel column yielded 2.8 g of pure **10** (81.4% yield).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.53–6.14 (m, 3H, CH Cp), 3.61 (m, 2H, CH_2OH), 2.99 (m, 1H, CH_2 Cp), 2.92 (m, 1H, CH_2 Cp), 2.80 (m, 1H, CHCH$_3$), 1.38 (m, 1H, OH),1.18 (d, 7.0, 1,5 H, CHCH_3), 1.17 (d, 7.0, 1,5 H, CHCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 150.97 and 148.69 (Cquat Cp), 133.98, 132.83, 131.94, 131.00, 126.85, 126.44 (CH Cp), 67.41 and 66.69 (CH_2OH), 41.23 and 40.97 (CH_2 Cp), 37.68 and 36.87 (CHCH$_3$), 17.01 and 16.12 (CHCH$_3$). Anal. Calc. for $C_8H_{12}O$: C, 77.37; H, 9.73. Found: C, 77.12; H, 9.52%.

5.11. Synthesis of indene alcohol ((S)-2-(1H-inden-3-yl)-propan-1-ol) **11**

In the same conditions as those described for the preparation of **10**, 0.87 g (23 mmol) of $LiAlH_4$ with 4.85 g of **7** afforded 3.8 g (97.2% yield) of **11** after purification by column chromatography on silica gel.

Chiral HPLC: Chiralcel OD-H (250 × 4.6 mm), hexane/isopropanol (90/10) as mobile phase, flow-rate = 1 ml/mn, 25 °C, detection by UV at 254 nm and polarimeter, $R_t(S, +) = 6.45$, $R_t(R, -) = 8.39$, $k(S) = 1.12$, $k(R) = 1.75$, $\alpha = 1.57$ and Rs = 4.87.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.51–7.19 (m, 4H, CH arom), 6.32 (m, 1H, CH indene), 3.81 (m, 2H, CH_2OH), 3.37 (bs, 2H, CH_2 indene), 3.11 (qd, 1H, CHCH$_3$), 1.48 (bs, 1H, OH), 1.33 (d, 6.9, 3H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 146.2 (Cquat arom), 144.7 (Cquat arom), 144.6 (Cquat indene), 128.2 (CH indene), 126.1, 124.0, 123.9 and 119.3 (CH arom), 66.6 (CH_2OH), 37.9 (CH_2 indene), 35.3 (CHCH$_3$), 16.4 (CHCH$_3$). Anal. Calc. for $C_{12}H_{14}O$: C, 82.72; H, 8.09. Found: C, 82.57; H, 8.01%. Interestingly, we observed that the sign of the rotation was dependent on the nature of the solvent [25]. For the (*S*)-enantiomer, $[\alpha]_D^{25} = -4.5$ ($CHCl_3$, $c = 0.6$); +15.2 (ethanol, $c = 0.6$); +14.5 (hexane/isopropanol 9/1, $c = 0.6$).

5.12. (R,S)-2-(Cyclopenta-1,3-dienyl)-N,N-dimethylpropanamide and (R,S)-2-(cyclopenta-1,4-dienyl)-N,N-dimethylpropanamide **12**

A solution of racemic **2** (0.3 g, 1.8 mmol) in 15 ml toluene cooled at −10 °C was slowly added to 0.485 g (1.8 mmol) of $Zr(NMe_2)_4$ in 15 ml toluene kept at −10 °C. The resulting red solution was stirred at room temperature during 24 h. Elimination of $Zr(NMe_2)_3(OEt)$ by filtration at −20 °C, followed by chromatography of the filtrate on silica gel, afforded **12** as an oily yellow liquid (0.26 g, 87.5% yield).

^{1}H NMR (C_6D_6, 200 MHz): δ 6.65–5.92 (m, 3H, CH Cp), 3.45 and 3.44 (qd, 1H, CHCH$_3$), 2.86 and 2.69 (m, 2H, CH_2 Cp), 2.66, 2.63, 2.31 and 2.26 (s, 6H, CH_3N), 1.47 and 1.38 (d, 3H, CH_3CH). Anal. Calc. for $C_{10}H_{15}NO$: C, 72.70; H, 9.14; N, 8.48. Found: C, 72.60; H, 9.25; N, 8.41%.

5.13. (η^4-Cycloocta-1,5-diene)(R,S)-2-(cyclopentadienyl)-N,N-dimethylpropanamide rhodium(I) **14**

At −50 °C, 0.15 g (9 mmol) of **12** in 20 ml of THF was reacted with 0.20 g (8.5 mmol) NaH. After 2 h stirring the solution was slowly added at 0 °C to a solution of 0.197 g (0.4 mmol) of $[RhCl(COD)]_2$ in 20 ml THF. The solution was stirred at room temperature for 24 h and at reflux during 2 h. After evaporation of THF the product was purified on a silica gel column to give 0.162 g of **14**. Crystallization from hexane/Et_2O afforded yellow crystals suitable for X-ray analysis.

Chiral HPLC: Chiralpak AD (250 × 4.6 mm), hexane/isopropanol (90/10) as mobile phase, flow-rate = 1 ml/mn, 25 °C, detection by UV at 254 nm and circular dichroism at 254 nm, $R_t(+) = 6.63$, $R_t(-) = 8.77$, $k(+) = 1.14$, $k(-) = 1.83$, $\alpha = 1.60$ and Rs = 3.48.

Preparative chiral HPLC: Ten successive injections of 500 μl of a 5 mg/ml solution of racemic **12** were done on Chiralpak AD (250 × 10 mm), with hexane/isopropanol (90/10) as mobile phase, flow-rate = 4.5 ml/mn, detection by UV at 254 nm. The (+)-enantiomer was collected between 6 and 8 min and the (−)-enantiomer between 9 and 11 min. About 12 mg of each enantiomer with an enantiomeric excess higher than 99% were recovered.

For the first eluted enantiomer, $[\alpha]_D^{25} = +30.6$ ($c = 0.74$; $CHCl_3$). For the second enantiomer $[\alpha]_D^{25} = +30.4$ ($c = 0.74$; $CHCl_3$).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.17, 5.02, 5.00, 4.90 (m, 4H, CH Cp), 3.91 (s br, 2H, COD, CH=CH), 3.82 (s br, 2H, COD, CH=CH), 3.71 (q, 1H, CHCH$_3$), 3.13 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 2.17-1.89 (m, ×2, 4H ×2, COD CH_2), 1.49 (d, 6.9, 3H, CHCH_3). ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ 174.2 (C=O), 108.6 (d, 3.3, Cquat Cp), 85.8 (d, 3.88, 2 CH Cp), 85.6 (d, 3.42, *C*H Cp), 85.55 (d, 4.16, *C*H Cp), 85.53 (d, 3.9, *C*H Cp), 63.7 (d, 14.4, CH=CH cod), 63.3 (d, 14.2, CH=CH cod), 37.7 (N–CH_3), 35.9 (N–CH_3), 35.1 (CHCH$_3$), 32.6 and 32.3 (CH_2 cod), 20.6 (CH_3CH). Anal. Calc. for $C_{18}H_{26}NORh$: C, 57.60; H, 6.97; N, 3.73. Found: C, 57.59; H, 7.10; N, 3.69%.

5.14. (−)-(η^4-Cycloocta-1,5-diene)(S)-2-(cyclopentadienyl)propan-1-ol rhodium(I) **15**

In a schlenk, at −10 °C, 0.162 g (1.3 mmol) of **10** was dissolved in 50 ml of hexane and 1 ml of BuLi (2.5 M in

hexane) was added under stirring. A white solid was isolated by filtration, dried under vacuum and dissolved in 50 ml of THF. To this solution was added 0.295 g (0.6 mmol) of $[RhCl(COD)]_2$. The solution was stirred at room temperature during one week. After evaporation of THF and addition of 50 ml Et_2O, the solution was filtered to give an orange oil after evaporation of the solvent Chromatography on a silica gel column afforded 0.30 g (68.7% yield) of a yellow powder which can be crystallized in hexane–Et_2O to give pale yellow crystals.

Chiral HPLC: Chiralcel OD-H (250 × 4.6 mm), hexane/isopropanol (95/5) as mobile phase, flow-rate = 1 ml/mn, 25 °C, detection by UV at 254 nm and polarimeter, $R_t(R, +) = 9.86$, $R_t(S, -) = 11.00$, $k(R) = 2.23$, $k(S) = 2.61$, $\alpha = 1.17$ and Rs = 1.55.

Preparative chiral HPLC: Seventy successive injections of 200 µl of a 2 mg/ml solution of enantiomerically enriched **15** were done on Chiralcel OD (250 × 10 mm), with hexane/isopropanol (95/5) as mobile phase, flow-rate = 5 ml/mn, detection by UV at 254 nm. The (*S*)-enantiomer was collected between 11 and 15 minutes. About 15 mg of the (*S*)-enantiomer with an enantiomeric excess higher than 99% were recovered.

Table 1
Crystal data and structure refinement for compounds **14** and **15**

Identification code	**14**	**15**
Empirical formula	$C_{18}H_{26}NORh$	$(C_{16}H_{23}ORh)_8$
Formula weight	375.31	2674.03
Temperature (K)	180(2)	180(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2$
a (Å)	7.9280(10)	57.638(12)
b (Å)	9.1956(11)	8.3575(17)
c (Å)	11.6783(14)	26.026(5)
α (°)	74.851(14)	90.0
β (°)	76.178(15)	116.81(3)
γ (°)	82.934(15)	90.0
Volume (Å^3)	796.33(17)	11189(4)
Z	2	4
D_{calc} (Mg/m^3)	1.565	1.587
Absorption coefficient (mm^{-1})	1.071	1.207
$F(000)$	388	5504
Crystal size (mm^3)	0.63 × 0.6 × 0.19	0.61 × 0.14 × 0.13
Theta range (°)	2.58–26.08	2.84–30.51
Reflections collected	7717	58893
Independent reflections (R_{int})	2843 (0.0328)	29696 (0.0630)
Completeness (%)	90.0	99.5
Absorption correction	Multi-scan	Multi-scan
Maximum, minimum transmission	0.8512 and 0.5256	1.00000 and 0.47896
Refinement method	F^2	F^2
Data/restraints/parameters	2843/0/193	29696/1/1305
Goodness-of-fit on F^2	1.063	0.840
R, wR_2 [$I > 2\sigma(I)$]	0.0258, 0.0689	$R_1 = 0.0478$, $wR_2 = 0.0862$
R, wR_2 (all data)	0.0264, 0.0693	$R_1 = 0.0915$, $wR_2 = 0.1034$
Absolute structure parameter		−0.04(2)
Largest difference peak/hole (e Å^{-3})	0.855/−0.843	1.141/−1.004

^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.24, 5.18, 4.84, 4.76 (m, 4H, CH Cp), 3.91 (s br, 4H, COD, CH=CH), 3.81–3.46 (m, 3H, CH_2OH and CH_2OH), 2.66 (m, 1H, CHCH_3), 2.45, 1.90 (m, ×2, 4H ×2, COD CH_2), 1.16 (d, 7.0, 3H, CHCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 109.01 (d, 3.8, Cquat Cp), 86.09 (d, 3.76, 2 CH Cp), 85.50 (d, 3.69, *C*H Cp), 83.76 (d, 3.66, *C*H Cp), 67.08 (*C*H_2OH), 63.87 (d, 6.5, CH=CH COD), 63.60 (d, 7.0, CH=CH COD), 34.98 (*C*HCH_3), 32.31 and 32.26 (CH_2 COD), 18.97 (*C*H_3CH). Anal. Calc. for $C_{16}H_{29}O_2Rh$ ($C_{16}H_{23}ORh$, $3H_2O$): C, 49.49; 7.47. Found: C, 49.97; H, 7.36%. For the (*S*)-enantiomer, $[\alpha]_D^{25} = -5.4$ ($CHCl_3$, $c = 1.25$).

X-ray structure determination: Single crystals were mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of either the Stoe IPDS diffractometer for **14** or the Oxford-Diffraction XCALIBUR CCD diffractometer for **15**. Data were collected using the monochromatic Mo Kα radiation ($\lambda = 0.71073$).

The structures were solved by direct methods (SIR97 [26]) and refined by least-squares procedures on F^2 using SHELXL-97 [27]. All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. The H atoms attached to oxygen were located in difference Fourier synthesis but they were treated as riding on their parent O atoms. For compound **15**, the absolute configuration was deduced from the refinement of the Flack's enantiopole parameter [28,29] based on a large number of Friedel pairs. The drawing of the molecules was realised with the help of ORTEP32 [30]. Crystal data and refinement parameters are shown in Table 1 (see Tables 2–4).

Table 2
Bond lengths (Å) and angles (°) for CpRh(COD)CHMe(CONMe$_2$) (**14**)

Rh(1)–CT1	1.9041(4)		
Rh(1)–CT2	1.9883(4)	Rh(1)–CT3	2.0017(3)
C(1)–C(2)	1.410(3)	C(2)–C(3)	1.431(3)
C(1)–C(5)	1.437(3)	C(3)–C(4)	1.407(4)
C(1)–C(11)	1.513(3)	C(4)–C(5)	1.428(3)
C(11)–C(12)	1.539(3)	C(11)–C(111)	1.526(3)
C(12)–O(24)	1.221(3)	C(12)–N(12)	1.347(3)
N(12)–C(122)	1.453(4)	N(12)–C(121)	1.459(3)
C(21)–C(28)	1.419(4)	C(26)–C(25)	1.517(3)
C(21)–C(22)	1.505(4)	C(25)–C(24)	1.403(3)
C(28)–C(27)	1.532(3)	C(24)–C(23)	1.530(3)
C(27)–C(26)	1.524(4)	C(23)–C(22)	1.534(4)
CT1–Rh(1)–CT2	137.187(14)		
CT1–Rh(1)–CT3	135.204(12)	CT2–Rh(1)–CT3	87.587(16)
C(2)–C(1)–C(5)	106.9(2)	C(3)–C(4)–C(5)	107.1(2)
C(1)–C(2)–C(3)	108.5(2)	C(4)–C(5)–C(1)	108.7(2)
C(4)–C(3)–C(2)	108.6(2)	C(1)–C(11)–C(12)	108.69(18)
C(2)–C(1)–C(11)	126.6(2)	C(5)–C(1)–C(11)	126.5(2)
C(1)–C(11)–C(111)	112.76(19)	C(111)–C(11)–C(12)	109.0(2)
O(24)–C(12)–N(12)	121.4(2)	O(24)–C(12)–C(11)	120.1(2)
N(12)–C(12)–C(11)	118.4(2)	C(28)–C(21)–C(22)	124.8(2)
C(12)–N(12)–C(122)	125.7(2)	C(21)–C(28)–C(27)	122.5(2)
C(12)–N(12)–C(121)	119.3(2)	C(26)–C(27)–C(28)	111.9(2)
C(122)–N(12)–C(121)	115.0(2)	C(25)–C(26)–C(27)	112.5(2)
C(24)–C(25)–C(26)	124.8(2)	C(24)–C(23)–C(22)	112.0(2)
C(25)–C(24)–C(23)	122.7(2)	C(21)–C(22)–C(23)	112.4(2)

Table 3
Bond lengths (Å) and angles (°) for $C_5H_4CH(Me)(CH_2OH)Rh(COD)$ (**15**)

Rh(1)–CT1	1.896(7)	Rh(2)–CT2	1.894(7)
Rh(1)–C(15A)	2.089(7)	Rh(2)–C(22B)	2.095(7)
Rh(1)–C(11A)	2.093(7)	Rh(2)–C(25B)	2.099(7)
Rh(1)–C(12A)	2.099(7)	Rh(2)–C(21B)	2.103(7)
Rh(1)–C(16A)	2.138(7)	Rh(2)–C(26B)	2.133(7)
O(1)–C(112)	1.444(8)	O(2)–C(212)	1.400(8)
Rh(3)–CT3	1.896(7)	Rh(4)–CT4	1.893(8)
Rh(3)–C(35C)	2.104(7)	Rh(4)–C(41D)	2.087(7)
Rh(3)–C(32C)	2.108(7)	Rh(4)–C(46D)	2.090(7)
Rh(3)–C(31C)	2.119(7)	Rh(4)–C(45D)	2.094(7)
Rh(3)–C(36C)	2.147(7)	Rh(4)–C(42D)	2.115(7)
O(3)–C(312)	1.425(8)	O(4)–C(412)	1.412(7)
Rh(5)–CT5	1.887(8)	Rh(6)–CT6	1.901(8)
Rh(5)–C(56E)	2.095(8)	Rh(6)–C(66F)	2.084(7)
Rh(5)–C(52E)	2.096(7)	Rh(6)–C(65F)	2.095(7)
Rh(5)–C(51E)	2.111(7)	Rh(6)–C(61F)	2.112(7)
Rh(5)–C(55E)	2.111(8)	Rh(6)–C(62F)	2.131(7)
O(5)–C(512)	1.442(8)	O(6)–C(612)	1.411(7)
Rh(7)–CT7	1.897(8)	Rh(8)–CT8	1.898(8)
Rh(7)–C(75G)	2.075(7)	Rh(8)–C(85H)	2.107(8)
Rh(7)–C(71G)	2.088(7)	Rh(8)–C(86H)	2.113(7)
Rh(7)–C(72G)	2.094(7)	Rh(8)–C(81H)	2.115(7)
Rh(7)–C(76G)	2.111(7)	Rh(8)–C(82H)	2.123(7)
O(7)–C(712)	1.414(7)	O(8)–C(812)	1.441(8)
CT1–Rh(1)–CT11	135.76(9)	CT2–Rh(2)–CT21	135.09(6)
CT1–Rh(1)–CT12	135.5(2)	CT2–Rh(2)–CT22	137.7(2)
CT11–Rh(1)–CT12	88.5(3)	CT21–Rh(2)–CT22	87.2(3)
O(1)–C(112)–C(111)	110.7(6)	O(2)–C(212)–C(211)	115.5(6)
CT3–Rh(3)–CT31	136.0(2)	CT4–Rh(4)–CT42	137.85(10)
CT3–Rh(3)–CT32	134.84(9)	CT4–Rh(4)–CT41	135.6(2)
CT31–Rh(3)–CT32	88.7(3)	CT42–Rh(4)–CT41	86.6(3)
O(3)–C(312)–C(311)	114.7(6)	O(4)–C(412)–C(411)	112.3(6)
CT5–Rh(5)–CT52	136.92(10)	CT6–Rh(6)–CT62	137.2(2)
CT5–Rh(5)–CT51	134.7(2)	CT6–Rh(6)–CT61	135.20(10)
CT52–Rh(5)–CT51	88.4(3)	CT62–Rh(6)–CT61	87.5(3)
O(5)–C(512)–C(511)	109.6(6)	O(6)–C(612)–C(611)	112.2(6)
CT7–Rh(7)–CT71	137.02(9)	CT8–Rh(8)–CT82	136.40(12)
CT7–Rh(7)–CT72	135.5(2)	CT8–Rh(8)–CT81	135.13(19)
CT71–Rh(7)–CT72	87.3(3)	CT82–Rh(8)–CT81	88.4(3)
O(7)–C(712)–C(711)	111.1(6)	O(8)–C(812)–C(811)	111.0(6)

Table 4
Hydrogen bonding interactions for compound **15**

	D–H	H···A	D···A	∠(DHA)
O1–H1···O4	0.84	1.86	2.695(7)	177.4
O4–H4···O7	0.84	1.91	2.679(8)	151.3
O7–H7···O5	0.84	2.05	2.731(7)	137.5
O5–H5···O1^{i}	0.85	1.82	2.673(8)	179.2
O3–H3···O2	0.84	1.81	2.631(8)	165.6
O2–H2···O6	0.84	1.89	2.645(8)	149.3
O6–H6···O8	0.84	1.78	2.621(7)	178.1
O8–H8···O^{ii}	0.85	1.76	2.607(8)	159.0

Symmetry codes: (i) 1 x, $y+1$, z; (ii) x, $y-1$, z.

6. Supplementary material

CCDC 654660 and 654661 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] R. Laï, A. Archavlis, R. Faure, M. Sanz, J. Chem. Soc., Dalton Trans. (1997) 3259.
[2] R. Laï, S. Martin, Tetrahedron: Asymm. 7 (1996) 2783.
[3] R. Laï, S. Martin, R. Touret, Dalton Trans. (2006) 3478.
[4] R. Laï, J.-F. Berthome, I. Lyothier, C. Scheidecker, S. Martin, Inorg. Chim. Acta (2003) 568.
[5] R. Laï, L. Bousquet, A. Heumann, J. Organomet. Chem. 444 (1993) 115.
[6] R.S. Threlkel, J.E. Bercaw, P.F. Seidler, J.M. Stryker, R.G. Bergman, in: E. Vedjs (Ed.), Organic Synthesis, vol. 65, Organic Synthesis Inc., 1987, p. 42.
[7] M. Sanz, Ph.D. Thesis, Université Aix-Marseille III, 1998.
[8] F. Wochner, L. Zsolnai, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 288 (1985) 69.
[9] R.L. Halterman, Chem. Rev. 92 (1992) 965.
[10] P. Vedso, R. Chauvin, Z. Li, B. Bernet, A. Vasella, Helv. Chim. Acta 77 (1994) 1631.
[11] E. Cesarotti, H.B. Kagan, J. Organomet. Chem. 162 (1978) 297.
[12] Z. Chen, K. Eriks, R.L. Halterman, Organometallics 10 (1991) 3449.
[13] R.L. Halterman, P.C. Vollhardt, Tetrahedron Lett. 27 (1986) 1461.
[14] R.L. Halterman, P.T.C. Vollhardt, M.E. Welker, D. Bläser, R. Boese, J. Am. Chem. Soc. 109 (1987) 8105.
[15] Z. Chen, R.L. Halterman, J. Am. Chem. Soc. 114 (1992) 2276.
[16] C.G. Venier, E.W. Casserly, J. Am. Chem. Soc. 112 (1990) 2808.
[17] R.A. Williams, K.F. Tesh, T.P. Hanusa, J. Am. Chem. Soc. 113 (1991) 4843.
[18] P. Beak, S.T. Kerrick, S. Wu, J. Chu, J. Am. Chem. Soc. 116 (1994) 3231.
[19] S.T. Kerrick, P. Beak, J. Am. Chem. Soc. 113 (1991) 9708.
[20] A. Trifonov, F. Ferri, J. Collin, J. Organomet. Chem. 582 (1999) 211.
[21] G.M. Diamond, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 118 (1996) 8024.
[22] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1988.
[23] J. Gabard, A. Collet, New J. Chem. 10 (1986) 685.
[24] F. Effenberger, U. Burkard, J. Willfahrt, Liebigs Ann. Chem. (1986) 314.
[25] C. Roussel, N. Vanthuyne, M. Serradeil-Albalat, J.C. Vallejos, J. Chromatogr., Sect. A 995 (2003) 79.
[26] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagn, J. Appl. Cryst. 32 (1999) 115.
[27] G.M. Sheldrick, SHELXL 97. Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[28] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.
[29] G. Bernardinelli, H.D. Flack, Acta Crystallogr., Sect. A 41 (1985) 500.
[30] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.