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# Stabilization of the labile metal configuration in halfsandwich complexes [CpRh(PN)Hal]X ☆

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**Abstract**

PN ligands **3** and **4**, derived from 2-diphenylphosphanylmethylpyridine **2a**, were synthesized, to which in the backbone a tether to a cyclopentadiene system and for comparison an $^{i}$Pr substituent were attached. The chiral compounds were resolved by introduction of a menthoxy substituent into the 2-position of the pyridine system and/or palladium complexes with enantiomerically pure co-ligands. The tripod ligand **3b** contains three different binding sites (Cp, P, N) connected by a resolved chiral carbon atom. ($S_C$)-configuration of this tripod ligand enforces ($R_{Rh}$)-configuration at the metal atom in the halfsandwich rhodium complex ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b**. The opposite metal configuration is inaccessible. Substitution of the chloro ligand in ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** by halide (Br, I) or pseudohalide ($N_3$, CN, SCN) ligands occurs with retention of configuration to give complexes **8b**–**11b**. However, in the reaction of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** with $PPh_3$ the pyridine arm of the tripod ligand in compound **13b** becomes detached from the metal atom. In the Cp*Rh and CpRh compounds of the bidentate PN ligands **4a** and **4b** both metal configurations are accessible and in complexes **14a**–**17a** and **14b**–**17b** they equilibrate fast. The stereochemical assignments are corroborated by 9 X-ray analyses.


*Keywords:* Rhodium; Chirality; Metal configuration; Retention

## 1. Introduction

In three-legged pianostool complexes of the type [($\eta^n$-Ar)M(LL′)X], L–L′ = unsymmetrical chelate ligand and X = monodentate ligand, the metal atom is a chiral center. With an enantiomerically pure chelate ligand, e.g. an $^{i}$Pr-substituted ($S_C$)-configurated PN ligand, two diastereomers ($S_C$,$R_{Rh}$) and ($S_C$,$S_{Rh}$) arise in compounds of the type [($\eta^5$-$C_5H_5$)Rh(PN)Cl]$PF_6$ (Scheme 1, top), which only differ in the metal configuration [1–3]. In solution these compounds epimerize by a change of the labile metal configuration initiated by dissociation of the monodentate ligand or by chelate ring opening [4,5]. Compounds of this type are catalysts in organic transformations, such as transfer hydrogenation, isomerization, Diels–Alder reactions, etc. [6–8].

As usually the epimerization at the metal atom is much faster than the catalytic reaction, two diastereomeric catalysts are present [6,7]. It is known that the stereochemistry of reactions occurring at a metal center strongly depend on the metal configuration [9]. Thus, reaction channels with diastereomeric catalysts differing in the metal configuration tend to produce products

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[1] X-ray structure analyses.

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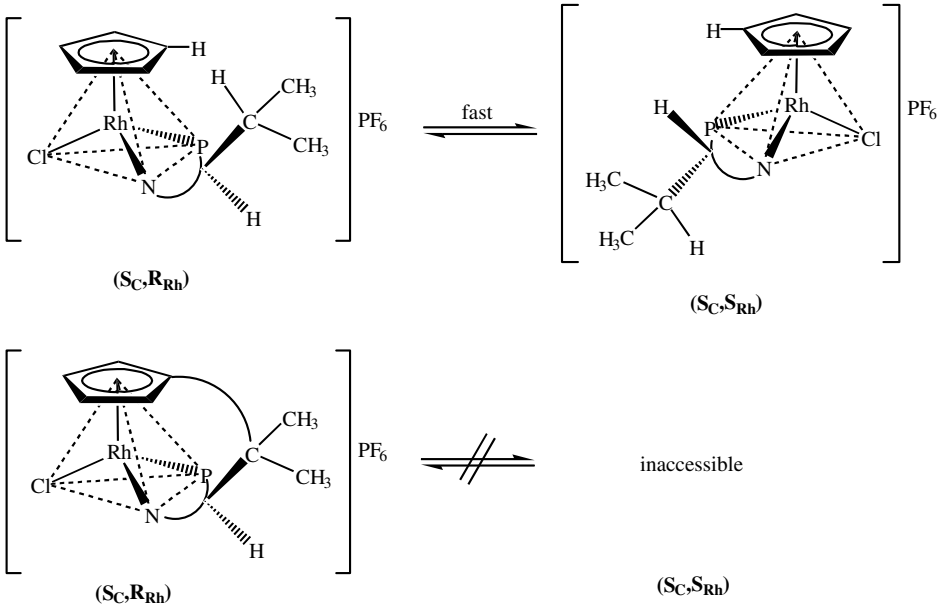



Scheme 1. Stabilization of the metal configuration with a tripod ligand.

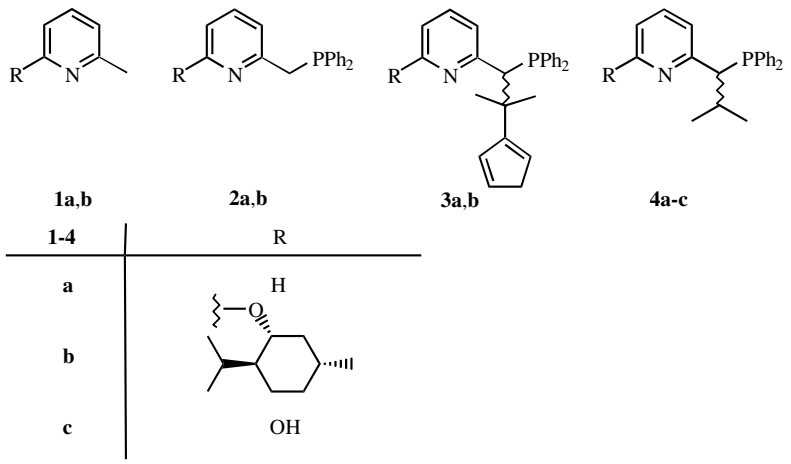
with opposite configuration. Diastereomer equilibria in chiral-at-metal halfsandwich complexes may lie between 50:50 and 99:1 [10–13]. However, although in a 99:1 equilibrium one of the two diastereomers is dominating by two powers of ten, this is no general solution of the problem, because the more stable isomer may be the less reactive catalyst and vice versa as shown for diastereomeric complexes of prochiral olefins bonded to Rh(LL*) fragments in asymmetric hydrogenations [14]. Therefore, it would be desirable to control the metal configuration such that only a catalyst with a single metal configuration is present during catalysis. In this paper, we describe a new tripod ligand CpH($PN_{Ment}$) which fix the metal chirality inhibiting any configurational change. This ligand has three different binding sites, a cyclopentadiene system (CpH), a diphenylphosphanyl group (P) and a pyridine ring ($N_{Ment}$) connected by an asymmetric carbon atom. We also report on the bidentate ligand $PN_{Ment}$. The tripod ligand CpH($PN_{Ment}$) afforded cationic half-sandwich complexes with $RhCl_3 \cdot 3H_2O$ in which only one additional chloro ligand is bonded to the Rh atom. For comparison the corresponding complexes with a combination of the bidentate ligand $PN_{Ment}$ with a separated Cp or Cp* ligand were synthesized. Due to the L-menthyl substituent diastereomers arise with respect to the configuration of the branching position ($R_C$)/($S_C$) and the metal configuration ($R_{Rh}$)/($S_{Rh}$). Fortunately, these diastereomers differ in their $^1H$ and $^{31}P$ NMR spectra allowing to monitor separation procedures and to determine diastereomer ratios. Part of this work has been published in a communication [15]. In addition, the synthesis of the ligands CpH(PN) and PN, devoid of the L-menthyl substituent and, thus, the source of diastereomerism, and their complexes is included in the present study.

## 2. The Ligands 2–4

Starting materials for the ligands **2**–**4** were the *ortho*-methylpyridines **1a**,**b** (Scheme 2). 2-Methylpyridine (**1a**) is commercially available. 2-Menthoxy-6-methylpyridine (**1b**) was prepared by substitution of the bromo substituent in 2-bromo-6-methylpyridine [16] for the anion of L-(−)-menthol. 2-Diphenylphosphanylmethylpyridine (**2a**) is a known compound [17–19]. For the synthesis of 6-diphenylphosphanylmethyl-2-menthoxypyridine (**2b**) the methyl group in α-position of the pyridine ring was deprotonated with BuLi and reacted with $PPh_2Cl$ to introduce the diphenylphosphanyl group. The yields of **2a** and **2b** could be improved provided the syntheses were carried out at low temperatures in dilute solutions. In addition, the lithiated 2-methylpyridine (**1a**) and 2-menthoxy-6-methylpyridine (**1b**) should be slowly added to the $PPh_2Cl$ solution to avoid transmetallation and addition of a second $PPh_2$ group [20].

In the synthesis of the cyclopentadiene derivatives **3a** and **3b** the intermediates **2a** and **2b** were not isolated. After deprotonation of **2a** and **2b** with BuLi 6,6′-dimethylfulvene was added. Hydrolysis afforded the tripod ligands **3a** and **3b**, containing a new asymmetric carbon atom at the branching point of the three different binding sites CpH, P and N. We have reported on the synthesis of **3a** in a previous study [21].

In the case of **3a** two of the three possible double bond isomers with respect to the cyclopentadiene system




Scheme 2. Ligands **2**–**4** (only 2-cyclopentadiene isomers shown for **3a** and **3b**).

were observed in the $^1$H NMR spectrum in a ratio of 75:25. Only the main isomer is shown in Scheme 2. Slow diffusion of petroleum ether into an acetone solution of **3a** afforded single crystals which X-ray analysis proved to be the racemate with an inversion center between the (*R*)- and (*S*)-enantiomer (Fig. 1). The bond lengths indicated that the double bonds were between C1/C5 and C2/C3. The saturated carbon atom was C4. After dissolution of the crystals in $CDCl_3$ both double bond isomers were observed in the $^1$H NMR spectrum.

Resolution of **3a** was attempted with the palladium(II) complex of the *ortho*-metallated ligand (*S*)-

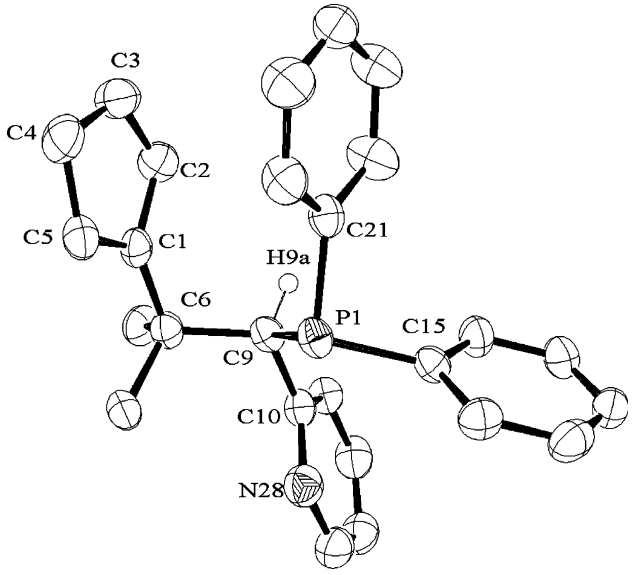
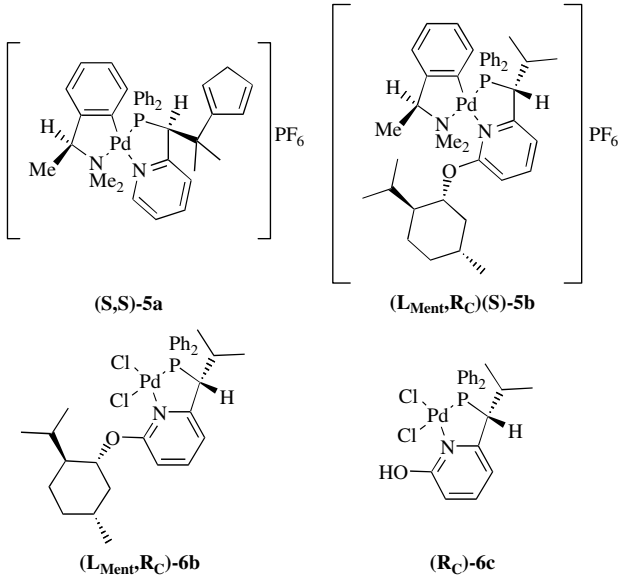



Fig. 1. Molecular structure of racemate **3a** (only (*R*)-enantiomer shown). Hydrogen atoms omitted except of α-carbon atom. Selected bond lengths [Å] and angles [°]: C1–C2 1.468(3), C2–C3 1.351(3), C3–C4 1.483(4), C4–C5 1.494(3), C5–C1 1.350(3), C1–C6 1.518(3), P1–C9 1.8894(19), P1–C15 1.8503(19), P1–C21 1.853(2); C10–C9–C6 112.40(15), C6–C9–P1 112.16(12), C10–C9–H9a 107.71, H9a–C9–P1 107.71, C9–P1–C15 101.35(8), C15–P1–C21 100.08(9), C21–P1–C9 102.65(9).




Scheme 3. Complexes (*S,S*)-**5a**, ($L_{Ment}$,$R_C$)(*S*)-**5b**, ($L_{Ment}$,$R_C$)-**6b** and ($R_C$)-**6c**.

(−)-*N,N*-dimethyl-1-phenylethylamine ($NMe_2$pea). A suspension of $[(NMe_2pea–H^+)PdCl]_2$ [22] dissolved in methanol on addition of the racemic mixture of **3a**. After adding $NH_4PF_6$ two diastereomeric Pd complexes (*S,S*)- and (*R,S*)-**5a** formed in a 1:1 ratio (Scheme 3).

Similar to the free ligand for each diastereomer there were two double bond isomers with respect to the uncoordinated cyclopentadiene system in a ratio of 75:25. Advantageously, the air-sensitive phosphorus atom of the ligand was protected in the palladium complex such that all manipulations could be carried out on air including chromatography. However, all the experiments to separate the diastereomers by fractional crystallization failed. The reason was obvious from an X-ray analysis of crystals obtained by crystallization from THF solution at −27 °C. The single crystals con-

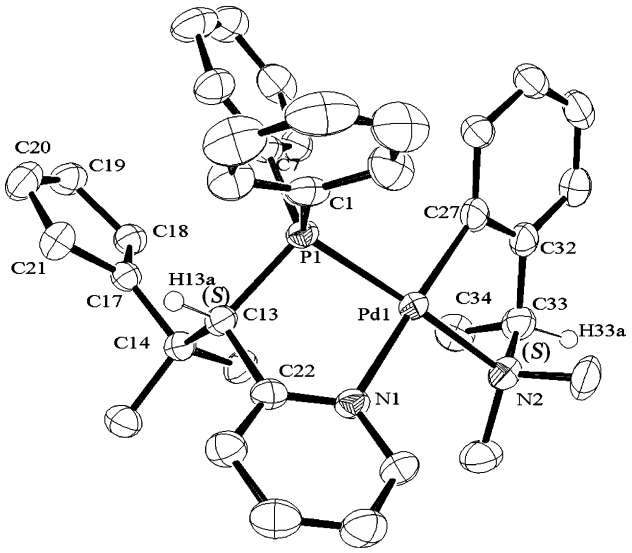



Fig. 2. Molecular structure of the 1:1 diastereomer mixture of **5a** (only (*S,S*)-diastereomer shown). Hydrogen atoms omitted except of α-carbon atom. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.159(3), Pd1–N2 2.159(3), Pd1–C27 1.994(4), Pd1–P1 2.2342(9), P1–C13 1.880(3), P1–C1 1.827(3), P1–C7 1.833(3), C17–C18 1.356(5), C18–C19 1.484(5), C19–C20 1.437(6), C20–C21 1.388(5), C21–C17 1.456(5); N1–Pd1–N2 102.46(12), N2–Pd1–C27 80.57(14), C27–Pd1–P1 98.92(11), P1–Pd1–N1 79.61(9), Pd1–P1–C7 119.36(11), C7–P1–C1 106.01(15), C1–P1–C13 101.27(10), C13–P1–Pd1 101.27(10).

tained the two diastereomers in a 1:1 ratio (Fig. 2) [20]. In the crystal only the 2-cyclopentadiene isomers were found. On dissolution the 75:25 isomer ratio for both diastereomers was re-established. Attempts to separate the diastereomers by chromatography proved difficult. Successive chromatographies with Merck–Lobar columns using $CH_2Cl_2$/MeOH 50:1 only gave an enrichment of 65:35 of the two diastereomers. Substitution of the resolving agent $NMe_2$pea in the Pd complex by the unsubstituted ligand $NH_2$pea (oily products) and the corresponding naphthyl compound $NH_2$nea (expensive resolving agent) was also unsuccessful [20].

Whereas **3a** was a racemate, due to the L-menthyl substituent **3b** was a pair of diastereomers. The two diastereomers formed in the ratio ($L_{Ment}$,$R_C$)-**3b**:($L_{Ment}$,$S_C$)-**3b** = 60:40. From a concentrated pentane solution of the 60:40-mixture only the ($L_{Ment}$,$S_C$)-**3b** diastereomer (the ''40%-isomer'') crystallized at −27 °C. The ($L_{Ment}$,$R_C$)-**3b** diastereomer (the ''60%-isomer'') remained in solution. Thus, it was possible to prepare the tripod ligand ($L_{Ment}$,$S_C$)-**3b** with a resolved branching position in an operationally simple way in multigram quantities.

An X-ray analysis of single crystals of ($L_{Ment}$,$S_C$)-**3b** proved the absolute configuration of the newly generated asymmetric carbon atom at the branching position to be ($S_C$) (Fig. 3). Only the 2-cyclopentadiene isomer was found in the crystal. The double bonds are between C17/C21 and C18/C19. The $CH_2$ group is located in 3-position of the cyclopentadiene ring at C20.

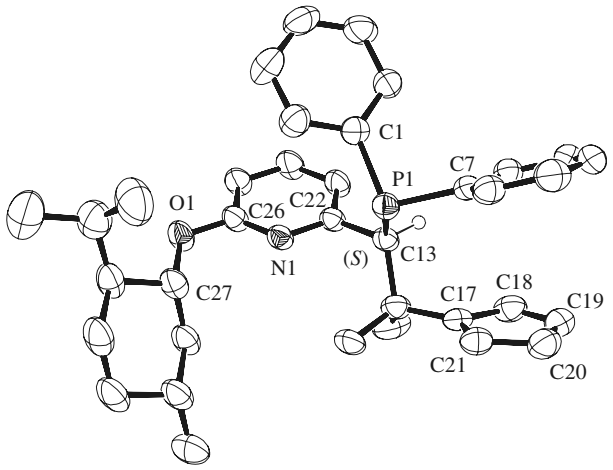



Fig. 3. Molecular structure of ($L_{Ment}$,$S_C$)-**3b**. Hydrogen atoms omitted except of α-carbon atom. Selected bond lengths [Å] and angles [°]: P1–C1 1.8504(8), P1–C7 1.8470(15), P1–C13 1.8953(17), O1–C26 1.366(2), O1–C27 1.455(2), C17–C18 1.464(3), C18–C19 1.340(3), C19–C20 1.474(3), C20–C21 1.480(3), C21–C17 1.348(3); C1–P1–C7 101.06(8), C7–P1–C13 104.35(9), C13–P1–C1 100.84(8), C27–O1–C26 118.12(13).

The cyclopentadiene isomers of **3b** interchange in solution. Therefore, the $^{31}P\{^1H\}$ NMR spectra of both diastereomers are broad at room temperature. Whereas the $^{31}P\{^1H\}$ NMR spectrum of ($L_{Ment}$,$R_C$)-**3b** showed only an extremely broad peak, for ($L_{Ment}$,$S_C$)-**3b** the signals of two cyclopentadiene isomers at −9.10 and −8.45 ppm appeared relatively sharp integrating 76:24. On lowering the temperature the two $^{31}P\{^1H\}$ NMR signals of the 76:24 cyclopentadiene isomers of ($L_{Ment}$,$S_C$)-**3b** splitted into 6 signals due to slowly interconverting conformers. The mixture of diastereomers ($L_{Ment}$,$S_C$)-**3b**/($L_{Ment}$,$R_C$)-**3b** gave a total of 12 separate signals on cooling [20].

The synthesis of the $^i$Pr-substituted ligands **4a** and **4b** was similar to that of **3a** and **3b**. Without isolation the intermediates **2a** and **2b** were metallated with BuLi and subsequently reacted with 2-iodopropane. The racemic mixture **4a** was not resolved. After chromatographic purification the two diastereomers of **4b** were present in a ratio of 55:45. It was not possible to separate the two diastereomers by column chromatography. Attempts to isolate one or both of the diastereomers by crystallization failed due to the good solubility in all organic solvents. To convert the oily diastereomer mixture of **4b** into a crystallizing solid, simultaneously protecting the air-sensitive phosphorus atom, we introduced **4b** as a ligand into palladium complexes. As a separation of the diastereomers of **4b** with the help of the Pd(II) complex containing the *ortho*-metallated ligand $NH_2$pea was unsuccessful, we concentrated on the corresponding complex with the *N,N*-dimethylated ligand $NMe_2$pea. The diastereomer mixture ($L_{Ment}$,$R_C$)(*S*)- and ($L_{Ment}$,$S_C$)(*S*)-**5b** was prepared by treatment of [($NMe_2$pea–$H^+$)$PdCl]_2$ [22] with the diastereomers of **4b** in methanol in the presence of $NH_4PF_6$. Recrystallization of the

white crystalline solid from acetone afforded the pure diastereomer ($L_{Ment}$,$R_C$)($S$)-**5b** (see below) as colorless prisms (Scheme 3). No evidence for the presence of the other diastereomer ($L_{Ment}$,$S_C$)($S$)-**5b** was observed in the $^1$H NMR spectrum of recrystallized samples.

Transformation of the pure diastereomer ($L_{Ment}$,$R_C$)($S$)-**5b** into the dichloro complex ($L_{Ment}$,$R_C$)-**6b** was achieved in sulfuric acid (70%), which removed the optically active amine. Addition of lithium chloride afforded the dichloro complex ($L_{Ment}$,$R_C$)-**6b**, which was extracted into dichloromethane. Recrystallization from $CH_2Cl_2$/petroleum ether resulted in fine yellow needles suitable for X-ray analysis. The coordination around palladium was square planar with a tetrahedral distortion indicated by the dihedral angles given in Fig. 4. The Pd–Cl2 bond (2.41 Å) was slightly longer than the Pd–Cl1 bond (2.30 Å) consistent with the trans influence of the phosphorus atom. The five-membered chelate ring was not planar but had an envelope structure. The bite angle of the chelate ring P–Pd–N was 80°. The isopropyl group adopted an axial position with respect to the five-membered chelate ring. ($R_C$)-configuration was assigned to the chiral carbon atom in the ligand backbone indicating ($L_{Ment}$,$R_C$)-configuration for the diastereomer ($L_{Ment}$,$R_C$)($S$)-**5b** obtained on crystallization and for the ligand liberated from ($L_{Ment}$,$R_C$)-**6b**. Ligand ($L_{Ment}$,$R_C$)-**4b** was liberated by treating ($L_{Ment}$,$R_C$)-**6b** with KCN in water/$CH_2Cl_2$ under nitrogen protection.

Following the protocol to remove the *ortho*-metallated ligand $NMe_2$pea from the crystallized complex ($L_{Ment}$,$R_C$)($S$)-**5b** with $H_2SO_4$/LiCl a crystalline product was obtained the X-ray analysis of which showed that it

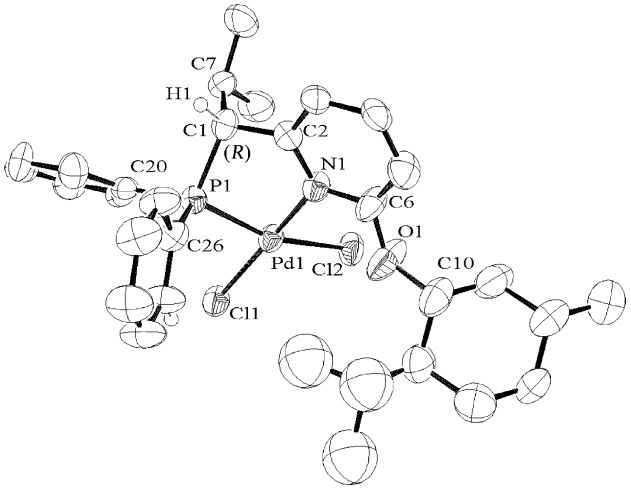



Fig. 4. Molecular structure of ($L_{Ment}$,$R_C$)-**6b**. Hydrogen atoms omitted except of α-carbon atom. Selected bond lengths [Å], angles and torsion angles [°]: Pd1–Cl1 2.300(5), Pd1–Cl2 2.410(2), Pd1–N1 2.087(6), Pd1–P1 2.210(2), P1–C1 1.846(10); Cl1–Pd1–Cl2 93.35(9), Cl2–Pd1–N1 95.39(14); Cl1–Pd1–P1 93.82(9), N1–Pd1–P1 80.01(14), Pd1–P1–C1 98.96(17); C2–N1–Pd1–P1 −26.04(45), Cl1–Pd1–N1–C2 −58.7(8), Pd1–P1–C1–C7 80.54(45), Pd1–N1–C2–C1 0.79(75), N1–C2–C1–C7 −92.99(70).

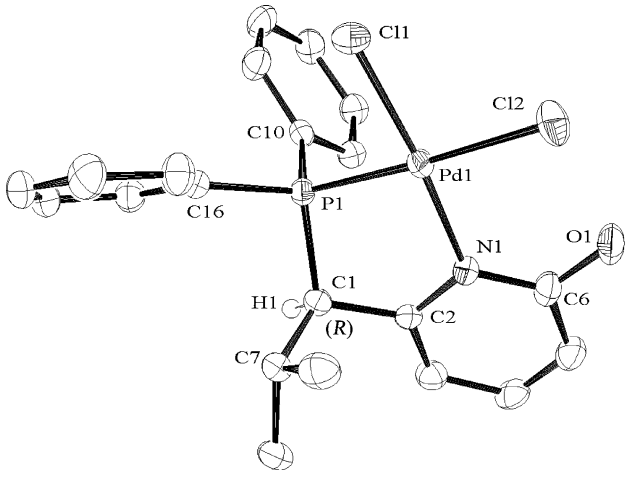


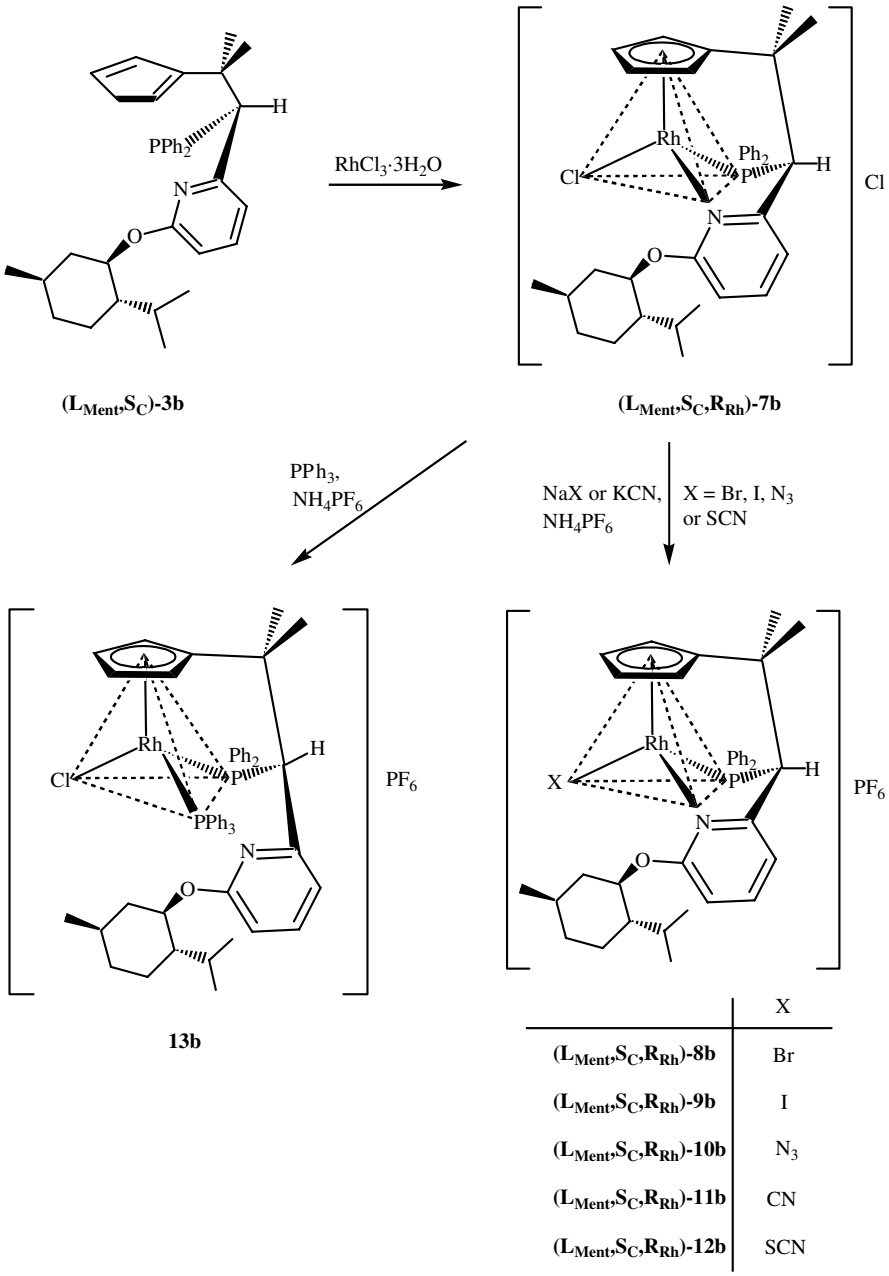

Fig. 5. Molecular structure of ($R_C$)-**6c**. Hydrogen atoms omitted except of α-carbon atom. Selected bond lengths [Å], angles and torsion angles [°]: Pd1–Cl1 2.2861(8), Pd1–Cl2 2.4082(8), Pd1–P1 2.1939(7), Pd1–N1 2.1237(19), P1–C1 1.845(3), P1–C10 1.800(3), P1–C16 1.811(2), C1–C2 1.512(3), C1–C7 1.561(4); Cl1–Pd1–Cl2 88.70(3), Cl1–Pd1–P1 87.01(3), Cl1–Pd1–N1 169.91(7), Cl2–Pd1–P1 174.98(3), Cl2–Pd1–N1 100.48(6), P1–Pd1–N1 84.00(6), Pd1–P1–C1 101.98(8), Pd1–P1–C10 110.06(9), Pd1–P1–C16 122.29(10); Cl2–Pd1–N1–C2 167.4(2), P1–Pd1–N1–C2 −10.3(2), Pd1–P1–C1–C7 92.14(16), Pd1–N1–C2–C1 −9.7(3).

was not complex ($L_{Ment}$,$R_C$)-**6b** containing the menthylated PN ligand but the product of an ether cleavage. It was complex ($L_{Ment}$,$R_C$)-**6c** with the PN ligand having a free phenolic OH group which formed a hydrogen bond to one of the chlorine ligands. Fig. 5 shows the results of the X-ray analysis.

## 3. The configurationally stable tripod complex ($L_{Ment}$,$S_C$,$R_{Rh}$)-7b and the substitution of its chloro ligand with retention of configuration

Complexation of ($L_{Ment}$,$S_C$)-**3b** with $RhCl_3 \cdot 3H_2O$ in ethanol at room temperature afforded the complex ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** (Scheme 4, top). After a few minutes an orange precipitate was formed, which dissolved within some hours indicating that ligand ($L_{Ment}$,$S_C$)-**3b** coordinated slowly and stepwise to the metal center. After 24 h the red–orange compound ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** was precipitated with pentane. It is soluble in polar solvents, such as alcohols or chlorinated solvents, and it is air-stable not only in the solid state but also in solution.

Interestingly, the cyclopentadiene isomerism present in ligand ($L_{Ment}$,$S_C$)-**3b** disappeared on complexation to ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b**, because a cyclopentadienyl system without stereogenicity was formed. Consequently, the $^{31}P\{^1H\}$ NMR spectrum of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** showed only one doublet at 72.6 ppm with a P–Rh coupling of 145 Hz. The configuration at the rhodium atom was assigned on the basis of the ligand priority sequence Cp > Cl > P > N [23,24].




Scheme 4. Synthesis of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b**, **8b**, **9b**, **10b**, **11b**, **12b** and **13b**.

Remarkably, the ($L_{Ment}$,$S_C$)-diastereomer of ligand **3b** can only form the complex ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b**. The ($S_{Rh}$)-configuration is inaccessible for the metal atom (Scheme 1, bottom). Thus, the ($S_C$)-configuration of the α-carbon of the ligand predetermines the ($R_{Rh}$)-configuration of the metal center [25]. Even if ligand arms dissociate from the metal center, the chirality at the metal center does not get lost, because on coming back the original ($R_{Rh}$)-configuration inevitably is restored. Heating a sample of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** at 60 °C for 3 d did not show any epimerization, whereas similar compounds lacking the ligand tether typical for ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** (see below) epimerized already under mild conditions by change of the metal configuration. Clearly, the opposite metal configuration ($S_{Rh}$) is only accessible with the other diastereomer ($L_{Ment}$,$R_C$)-**3b**. Recently there has been a different approach to fix the metal configuration in ($\eta^6$-arene)ruthenium complexes using planar chirality [26,27]. The synthesis of chiral CpH(PP′) and IndH(PP′) ligands has been described [28]. However, they have been used in complexation studies unresolved with respect to the branching position.

In the reaction with $RhCl_3 \cdot 3H_2O$ the 40:60 mixture of ($L_{Ment}$,$S_C$)-**3b**/($L_{Ment}$,$R_C$)-**3b** gave a ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b**/($L_{Ment}$,$R_C$,$S_{Rh}$)-**7b** = 40:60 product mixture. The

$^{31}P\{^{1}H\}$ NMR spectrum showed two doublets at 72.6 ppm for ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** and at 71.3 ppm for ($L_{Ment}$,$R_C$,$S_{Rh}$)-**7b**, both with a P–Rh coupling of 145 Hz [20]. We also synthesized the parent complex [(CpPN)RhCl]Cl of tripod ligand (CpH)PN **3a** without the L-menthoxy substituent in 2-position. However, the racemic mixture was not resolved and the Rh complex turned out to be nearly insoluble in common organic solvents [20].

Complex ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** is an air-stable, unreactive compound. Activation for catalysis should be possible by chloride abstraction to give a Lewis acidic fragment. Furthermore, the easily accessible ligand ($L_{Ment}$,$R_C$)-**3b** should form compounds similar to ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** with a variety of transition metal precursors. Here, a comparison of complexes of $CpPN_{Ment}$ systems with complexes containing a combination of a Cp and a $PN_{Ment}$ ligand will demonstrate the value of a fixed metal configuration.

The predetermination of the metal configuration by the tripod ligand ($L_{Ment}$,$S_C$)-**3b** implies that substitution reactions of the chloro ligand in ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** must occur with retention of the metal configuration. Stirring ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** with an excess of NaBr or NaI in methanol at room temperature and subsequent addition of $NH_4PF_6$ afforded the bromo and iodo derivatives ($L_{Ment}$,$S_C$,$R_{Rh}$)-**8b** and ($L_{Ment}$,$S_C$,$R_{Rh}$)-**9b** (Scheme 4, bottom right). The UV–Vis spectra of the starting material and products showed a strong absorption maximum at 275–280 nm. Characteristic for the CD spectra is a strong negative Cotton effect around 280–290 nm. The similarity of the CD spectra of the chloro, bromo and iodo complexes in Fig. 6 is in accordance with the same configuration at the metal center.

Reaction of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** with $NaN_3$, KCN and NaSCN, respectively, afforded the corresponding azido, cyano and thiocyanato substitution products ($L_{Ment}$,$S_C$,$R_{Rh}$)-**10b**, ($L_{Ment}$,$S_C$,$R_{Rh}$)-**11b** and ($L_{Ment}$,$S_C$,$R_{Rh}$)-**12b** (Scheme 4, bottom right). The UV–Vis and CD spectra were similar to the chloro complex except the thiocyanato compound, the 290 nm CD band of which had the same position but double intensity. This is interpreted as an indication that the ambidentate $SCN^-$ ligand binds via the soft sulfur atom and not the hard nitrogen atom as, e.g. in the azido complex. Increase of the band intensity is also observed in Fig. 6 in going from the hard chloro ligand to the soft iodo ligand.

The chloro complex ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** underwent clean substitution with $PPh_3$ in the presence of $NH_4PF_6$ to produce complex **13b** in quantitative yield. The UV–Vis and CD spectra of the orange substitution product were similar to the chloro complex (Fig. 7). However, the mass spectrum (ESI in $CH_2Cl_2$) of substitution product **13b** showed the peak for the cation at *m*/*z* 936 and not as expected for a $Cl^-$ substitution at *m*/*z* 901 which indicated the presence of a chlorine atom along with a

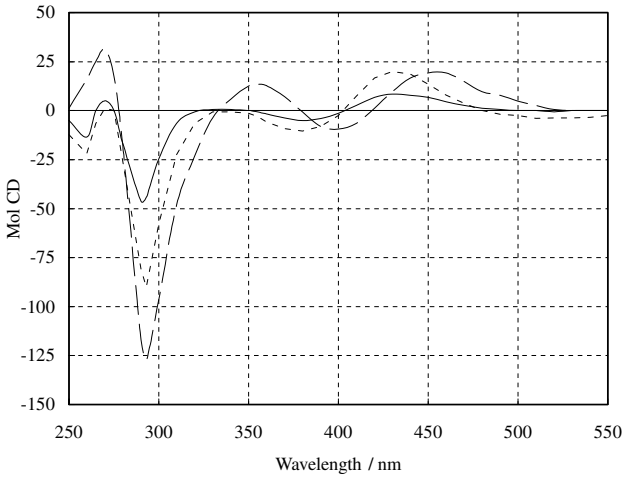



Fig. 6. CD spectra of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** ($c = 2.4 \times 10^{-4}$ mol $l^{-1}$: —), of its Br analog ($L_{Ment}$,$S_C$,$R_{Rh}$)-**8b** ($c = 2.3 \times 10^{-4}$ mol $l^{-1}$: - - - - -) and of its I analog ($L_{Ment}$,$S_C$,$R_{Rh}$)-**9b** ($c = 2.2 \times 10^{-4}$ mol $l^{-1}$: – – –) in $CH_2Cl_2$.

$PPh_3$ ligand in the cation. Therefore, on the basis of the mass spectral data as well as the elemental analysis which also showed the presence of Cl, it had to be assumed that during the substitution the pyridine–rhodium bond broke resulting in the formation of **13b** having the central rhodium atom coordinated to Cp and P only of the tripod together with the two monodentate ligands Cl and $PPh_3$ (Scheme 4, bottom left). The chloro ligand remained a constituent of the cation. Thus, in this case it was not the chloro ligand which was replaced but the pyridine system of the tripod ligand.

Interestingly, a ruthenium complex of the non-menthylated ligand **3a** had been synthesized and formulated as a chloride salt [(CpPN)Ru($PPh_3$)]Cl [21]. The cation was thought to be fully coordinated by Cp, P and N of the tripod with $PPh_3$ occupying the last

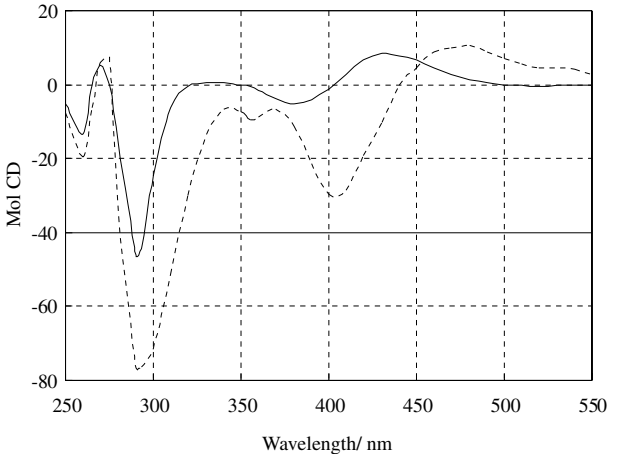


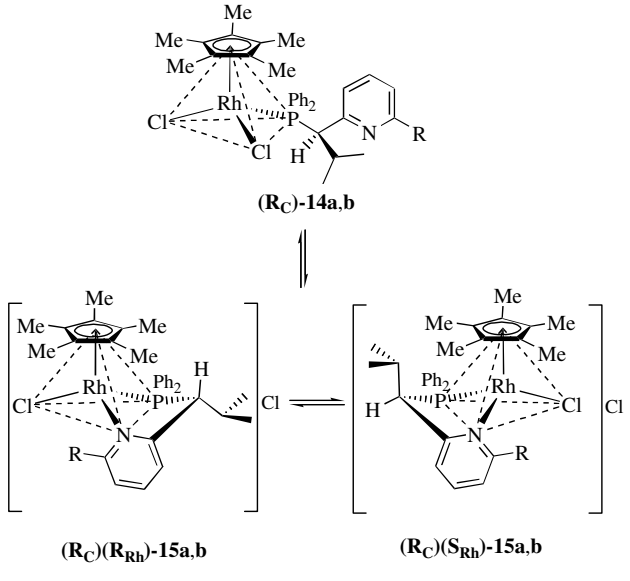

Fig. 7. CD spectra of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** ($c = 2.4 \times 10^{-4}$ mol $l^{-1}$: —) and its $PPh_3$ substitution product **13b** ($c = 1.9 \times 10^{-4}$ mol $l^{-1}$: - - - -) in $CH_2Cl_2$.

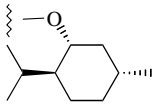
coordination site. However, in its mass spectrum the molecular ion included chlorine and the loss-of-chlorine fragmentation step was observed. Thus, the compound has to be re-interpreted as [(CpPN)Ru($PPh_3$)Cl] with the tripod coordinated only by Cp and P containing a dangling pyridine.

## 4. Half-sandwich Rh complexes with bidentate PN ligands

Formal cleavage of the C–C bond between the cyclopentadienyl ring and the $CMe_2$ group of the tether to the branching position in ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** results in a combination of a Cp ligand and the bidentate $PN_{Ment}$ ($L_{Ment}$,$S_C$)-**4b**. As shown in Scheme 1 (top), for such a ligand combination two different metal configurations ($R_{Rh}$) and ($S_{Rh}$) are accessible. Therefore, compounds of type ($L_{Ment}$,$S_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)-[Cp($PN_{Ment}$)RhCl]X (both metal configurations possible) should be prepared and contrasted with tripod complexes ($L_{Ment}$,$S_C$,$R_{Rh}$)-[(Cp$PN_{Ment}$)RhCl]X (fixed metal configuration) such as ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b**. As the pentamethylcyclopentadienyl ($\eta^5$-$C_5Me_5$ = Cp*) compounds of rhodium are more stable than the cyclopentadienyl ($\eta^5$-$C_5H_5$ = Cp) compounds, the Cp*-derivatives are included in the present study. In a previous study unsymmetrical tridentate ligands had not been superior compared to a similar combination of bidentate and monodentate ligands [29].

Reaction of [(Cp*RhCl)$_2$(μ-Cl)$_2$] with a 1:1 mixture of the diastereomers ($L_{Ment}$,$R_C$)- and ($L_{Ment}$,$S_C$)-**4b** afforded the diastereomers ($L_{Ment}$,$R_C$)- and ($L_{Ment}$,$S_C$)-**14b** in which ligand **4b** is only mono-coordinated via the phosphorus atom (Scheme 5, top). Thus, the products of the first complexation step could be isolated here, whereas in the synthesis of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** in the isolated product the P, N and Cp ligand parts coordinated simultaneously. Diastereomer ($L_{Ment}$,$R_C$)-**14b** was




| 14, 15 | R |
|---|---|
| a | H |
| b |  |

| Temp./K | ($R_C$)($R_{Rh}$)/($S_C$)($S_{Rh}$)-**15a** | | ($R_C$)/($S_C$)-**14a** | | ($R_C$)($S_{Rh}$)/($S_C$)($R_{Rh}$)-**15a** |
|---|---|---|---|---|---|
| 193 | 75 | : | 13 | : | 12 |
| 213 | 66 | : | 11 | : | 23 |
| 233 | 71 | : | 3 | : | 26 |
| 253 | 69 | : | 0 | : | 31 |
| 273 | 72 | : | 0 | : | 28 |

Scheme 5. Only ($R_C$)-enantiomers of **14a** and ($R_C$)-diastereomers of **14b**, **15a** and **15b** shown, respectively (top). Temperature dependence of isomer composition in system **14a/15a** (bottom).

isolated in pure form as a sparingly soluble material by washing the mixture of diastereomers with ether. The other diastereomer ($L_{Ment}$,$S_C$)-**14b** was obtained purely by silica gel chromatography of the concentrated mother liquor. Although the complexes ($L_{Ment}$,$R_C$)-**14b** and ($L_{Ment}$,$S_C$)-**14b** are diastereomers, their CD spectra are similar but opposite to each other. Thus, they are dominated by the asymmetric center in the ligand backbone. The stereochemistries of both diastereomers were determined by X-ray analyses (Figs. 8 and 9).

Surprisingly, the reaction of [(Cp*RhCl)$_2$(μ-Cl)$_2$] with the racemic ligand **4a** was different from that with the menthylated ligand **4b**, in which no ionic species of the type **15b** were detected. The molecular dichloro complex

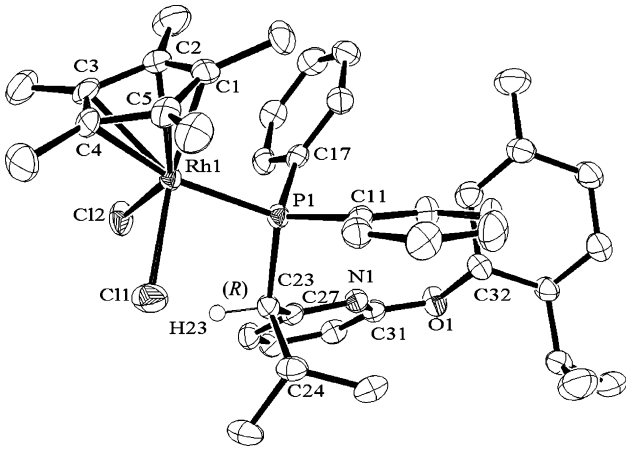



Fig. 8. Molecular structure of ($L_{Ment}$,$R_C$)-**14b**. Hydrogen atoms omitted except of α-carbon atom. Selected bond lengths [Å] and angles [°]: Rh1–Cl1 2.4124(10), Rh1–Cl2 2.4057(9), Rh1–P1 2.3476(7), Rh1–C1 2.1922(2), Rh1–C2 2.178(3), Rh1–C3 2.207(3), Rh1–C4 2.213(3), Rh1–C5 2.173(3); Cl1–Rh1–Cl2 91.77(3), Cl1–Rh1–P1 91.84(3), Cl2–Rh1–P1 84.90(3), Rh1–P1–C11 117.17(10).

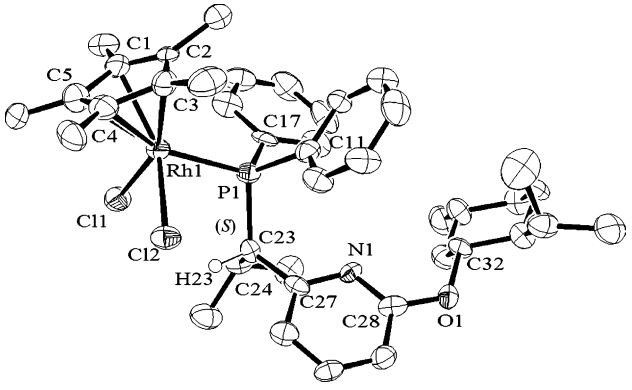
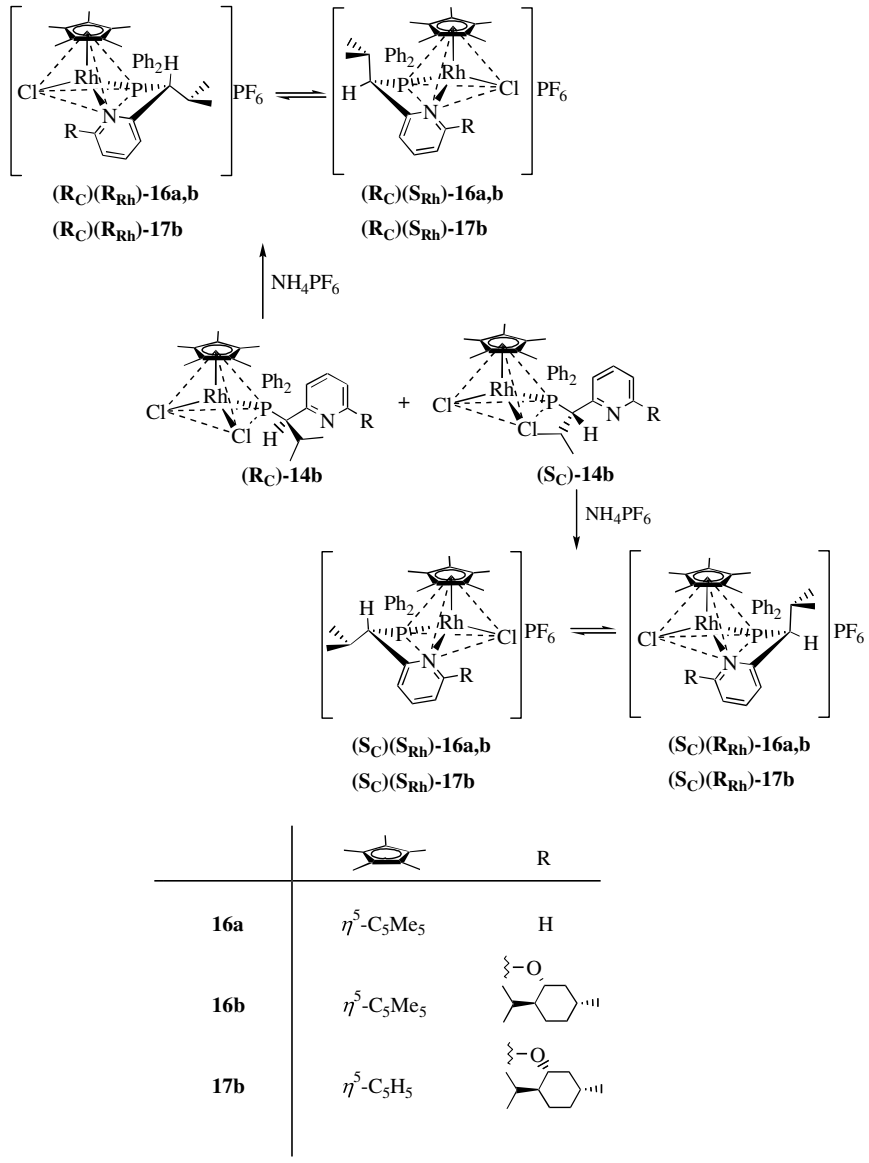



Fig. 9. Molecular structure of ($L_{Ment}$,$S_C$)-**14b**. Hydrogen atoms omitted except of α-carbon atom. Selected bond lengths [Å] and angles [°]: Rh1–Cl1 2.404(2), Rh1–Cl2 2.404(2), Rh1–P1 2.354(2), Rh1–C1 2.189(9), Rh1–C2 2.193(5), Rh1–C3 2.151(8), Rh1–C4 2.232(9), Rh1–C5 2.227(8); Cl1–Rh1–Cl2 92.97(7), Cl1–Rh1–P1 87.77(7), Cl2–Rh1–P1 87.03(8), Rh1–P1–C11 110.4(3).

**14a** could be observed in the NMR spectra at low temperatures. In addition, however, there were the salt-like chelate complexes ($R_C$)($R_{Rh}$)/($S_C$)($S_{Rh}$)- and ($R_C$)($S_{Rh}$)/($S_C$)($R_{Rh}$)-**15a** in which the metal atom is a chiral center (Scheme 5). In these ionic species chloride is the counterion. The $^{31}P\{^1H\}$ NMR spectrum of **14a**/**15a** in $CD_2Cl_2$ at 193 K showed three phosphorus signals at 75.0 (br d, $J_{Rh-P}$ = 125.1 Hz), 59.9 (d, $^1J_{Rh-P}$ = 141.9 Hz) and 31.0 (d, $^1J_{Rh-P}$ = 141.9 Hz) ppm, respectively. It is assumed that the 31.0 ppm signal is the dichloride complex **14a**, the other two signals are due to the two diastereomers ($R_C$)($R_{Rh}$)/($S_C$)($S_{Rh}$)- and ($R_C$)($S_{Rh}$)/($S_C$)($R_{Rh}$)-**15a**. The ratios ($R_C$)($R_{Rh}$)/($S_C$)($S_{Rh}$)-**15a**:($R_C$)/($S_C$)-**14a**:($R_C$)($S_{Rh}$)/($S_C$)($R_{Rh}$)-**15a** were temperature dependent (see bottom of Scheme 5). With increasing temperature, the signal at 31.0 ppm disappeared and the ratios ($R_C$)($R_{Rh}$)/($S_C$)($S_{Rh}$)-**15a**:($R_C$)($S_{Rh}$)/($S_C$)($R_{Rh}$)-**15a** increased. This suggested that equilibration between **14a** and the diastereomers of **15a** was fast. Assignment of configurations to the signals in the $^{31}P\{^1H\}$ NMR spectra of the chloride diastereomers of **15a** was made by comparison with the hexafluorophosphate diastereomers of **16b** for which the stereochemistry was established by X-ray analyses (see below).

Reaction of **15a** with $NH_4PF_6$ in THF afforded the chiral-at-metal $PF_6$ salts **16a** (Scheme 6, top and bottom). The ratio was ($R_C$)($R_{Rh}$)/($S_C$)($S_{Rh}$)-**16a**:($R_C$)($S_{Rh}$)/($S_C$)($R_{Rh}$)-**16a** = 74:26. Similarly, treatment of the pure isomer ($L_{Ment}$,$S_C$)-**14b** with $NH_4PF_6$ in THF gave the diastereomers ($L_{Ment}$,$S_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** (Scheme 6, bottom). Thus, in the presence of $NH_4PF_6$ both in the a- and in the b-series the PN ligands **4a** and **4b** coordinated in a bidentate way. The $^{31}P\{^1H\}$ NMR spectrum of ($L_{Ment}$,$S_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** at 193 K showed the signals of two diastereomers at 52.7 (main; $^1J_{Rh-P}$ = 143.6 Hz) and 61.3 (minor; $^1J_{Rh-P}$ = 130.3 Hz) ppm in the ratio 96:4. The $^{31}P\{^1H\}$ NMR spectrum was temperature dependent. In the range between 213 and 273 K the minor phosphorus signal disappeared, whilst the major broadened appreciably. At 300 K there was one phosphorus signal at 53.2 ppm as a sharp doublet having $^1J_{Rh-P}$ = 142.3 Hz. Similar tendencies were also observed in the $^1H$ NMR spectra. Processes underlying this temperature dependency were the sterically hindered rotation of the menthyl substituent and the inversion within the puckered chelate ring. Single crystals of the major isomer were obtained by recrystallization using acetone/petroleum ether. X-ray analysis established ($L_{Ment}$,$S_C$)($S_{Rh}$)-configuration (Fig. 10). On dissolution of the crystals in $CD_2Cl_2$ at 193 K the $^{31}P\{^1H\}$ NMR spectrum showed the equilibrium ($L_{Ment}$,$S_C$)($R_{Rh}$)-**16b**:($L_{Ment}$,$S_C$)($R_{Rh}$)-**16b** = 4:96. Thus equilibration between ($L_{Ment}$,$S_C$)($R_{Rh}$)-**16b** and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** took place rapidly.

Similar to ($L_{Ment}$,$S_C$)-**14b** (Scheme 6, bottom), reaction of ($L_{Ment}$,$R_C$)-**14b** with $NH_4PF_6$ afforded the dia-




Scheme 6. Synthesis of half-sandwich Rh complexes with the bidentate PN ligands **4a** and **4b**.

stereomers ($L_{Ment}$,$R_C$)($R_{Rh}$)- and ($L_{Ment}$,$R_C$)($S_{Rh}$)-**16b** (Scheme 6, top). The $^{31}P\{^1H\}$ NMR spectrum showed the presence of two diastereomers [major: 55.8 ppm ($^1J_{Rh-P}$ = 139.0 Hz), minor: 61.6 ppm ($^1J_{Rh-P}$ = 142.1 Hz) at 300 K in $CD_2Cl_2$] in temperature dependent ratios. At 193 K the major:minor ratio of the diastereomers was 76:24, whereas at 300 K it was 92:8. Reaction of the diastereomer mixture ($L_{Ment}$,$R_C$)- and ($L_{Ment}$,$S_C$)-**14b** with $NH_4PF_6$ led to a single crystal containing a 1:1 mixture of the diastereomers ($L_{Ment}$,$R_C$)($R_{Rh}$)-**16b** and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** (Fig. 11).

Analogous to the menthylated molecular chlorides **14b**, in the reaction with $NH_4PF_6$ in THF the chloride mixture **14a/15a** was converted into the $PF_6$ salts **16a** (Scheme 6, top and bottom). The $^{31}P\{^1H\}$ NMR spectrum of **16a** in $CD_2Cl_2$ at 193 K and at 300 K showed two phosphorus signals for the two diastereomeric pairs of enantiomers.

To switch to the unsubstituted Cp compounds [(CpRhCl)$_2$(μ-Cl$_2$)] was reacted with the 1:1 diastereomer mixture of **4b** in THF in the presence of $NH_4PF_6$. As expected there were four diastereomers of **17b** at 300 K the $^{31}P\{^1H\}$ NMR spectra, in addition to the $PF_6$ signal (Scheme 6, top and bottom). By comparison with the diastereomers of **16b** the two low field signals were assigned to ($L_{Ment}$,$S_C$)($R_{Rh}$)- and ($L_{Ment}$,$R_C$)($S_{Rh}$)-**17b** (isopropyl group towards Cp), while the two high field signals were due to ($L_{Ment}$,$R_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**17b**. The main product was the ($L_{Ment}$,$S_C$)($S_{Rh}$)-isomer. Thus, surprisingly, compared

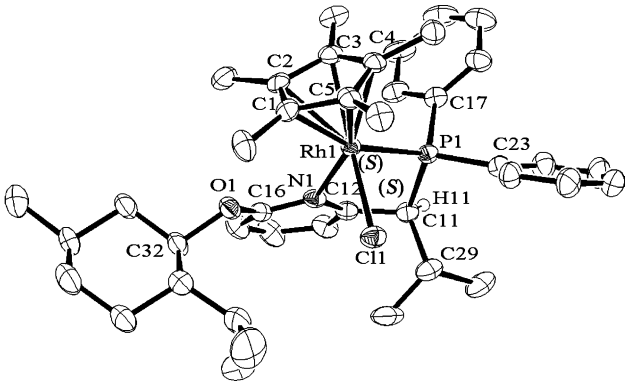



Fig. 10. Molecular structure of ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b**. Hydrogen atoms, $PF_6$ anion and two acetone molecules omitted except of α-carbon atom. Selected bond lengths [Å], angles and torsion angles [°]: Rh1–Cl1 2.3993(12), Rh1–P1 2.3028(10), Rh1–N1 2.1781(3), Rh1–C1 2.240(4), Rh1–C2 2.252(5), Rh1–C3 2.202(4), Rh1–C4 2.168(4), Rh1–C5 2.170(4); Cl1–Rh1–P1 93.02(4), Cl1–Rh1–N1 86.88(9), P1–Rh1–N1 81.58(8), Rh1–P1–C11 102.10(13), Rh1–N1–C12 118.62(2), Rh1–N1–C16 124.0(3), P1–C11–C12 107.4(3), N1–C12–C11 117.7(3), P1–C11–H11 108.04, C12–C11–H11 107.95; Rh–N1–C12–C11 26.4(4), N1–C12–C11–P1 −39.5(4), C12–C11–P1–Rh1 32.5(3), C11–P1–Rh1–N1 −16.13(15), P1–Rh1–N1–C12 −2.1(2).

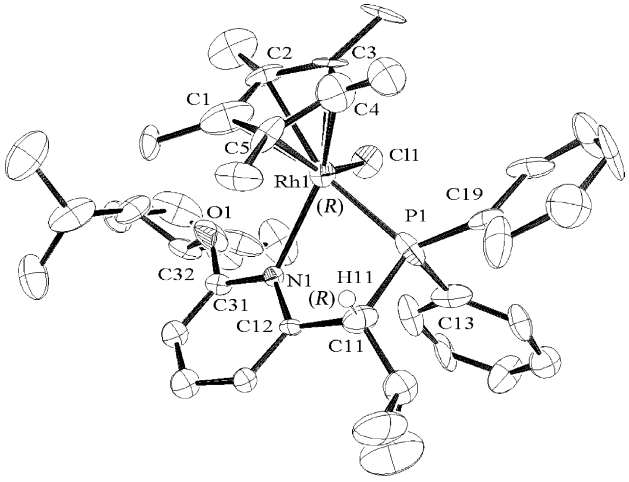



Fig. 11. Molecular structure of the 1:1 diastereomer mixture of ($L_{Ment}$,$R_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** (only ($L_{Ment}$,$R_C$)($R_{Rh}$)-diastereomer shown). Hydrogen atoms (except of α-carbon atom) and $PF_6$ anion omitted. Selected bond lengths [Å], angles and torsion angles [°]: Rh1–Cl1 2.3810(10), Rh1–P1 2.2697(10), Rh1–N1 2.214(2), Rh1–C1 2.165(4), Rh1–C2 2.225(3), Rh1–C3 2.162(3), Rh1–C4 2.223(4), Rh1–C5 2.196(3); Cl1–Rh1–P1 91.51(4), Cl1–Rh1–N1 100.09(7), P1–Rh1–N1 76.90(6), Rh1–P1–C11 100.22(11), Rh1–N1–C12 115.02(18), Rh1–N1–C31 122.23(18), P1–C11–C12 107.9(2), N1–C12–C11 118.3(3), P1–C11–H11 104.84, C12–C11–H11 104.88; Rh1–N1–C12–C11 −22.3(3), N1–C12–C11–P1 −13.3(3), C12–C11–P1–Rh1 39.2(2), C11–P1–Rh1–N1 −37.26(2), P1–Rh1–N1–C12 38.2(2).

to the tripod complex ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** the "less stable" Rh configuration was stabilized in the Cp and Cp* series with the bidentate $PN_{Ment}$ ligand **4b**.

## 5. Experimental

### 5.1. General

All manipulations and reactions were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Melting points: Büchi SMP 20 (uncorrected). Mass spectra: Finnigan MAT 95, Finnigan MAT 311 A and Thermoquest TSQ 7000 spectrometers (only the most intense peak of a cluster is given). Optical rotations: Perkin–Elmer 241 polarimeter. CD spectra: JASCO J-710 spectrophotometer. $^1$H NMR spectra: Bruker AC 250 and ARX 400 and Bruker Avance 300 and 400 spectrometers. $^{31}$P NMR spectra: Bruker ARX 400 and Avance 400 spectrometers ($H_3PO_4$ ext.). IR spectra: Beckman IR 4240 spectrophotometer. Elemental analyses: Elementar Vario EL III. X-ray structure analyses: STOE-IPDS diffractometer (Mo Kα radiation, 173 K, Oxford cryosystems cooler [30], graphite monochromator), SIR-97 [31] and SHELXS-97 [32]. For crystallographic data see Tables 1 and 2. 2-Methylpyridine (α-picoline) **1a** and $RhCl_3 \cdot 3H_2O$ are commercially available. 2-Diphenylphosphanylmethylpyridine [17–19] **2a** and 2-(2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)pyridine [21] **3a** are known compounds. $[(CpRhCl)_2(\mu\text{-}Cl)_2$ [33] and $[(Cp^*RhCl)_2(\mu\text{-}Cl)_2]$ [34] were prepared as published.

### 5.2. 2-(1R,2S,5R)-Menthoxy-6-methylpyridine *1b*

L-(−)-Menthol (120 g, 768 mmol) was added to NaH (8.23 g, 343 mmol) under $N_2$ protection without a solvent and heated to 60 °C. After the formation of $H_2$ had ceased, the temperature was raised to 90 °C for 2 h. 2-Bromo-6-methylpyridine [16] (40 g, 232 mmol) was added and the mixture was kept at 90 °C for 20 h. The excess of L-(−)-menthol was removed at 100 °C/2 Torr. In a bulb-to-bulb distillation at 100 °C/$10^{-3}$ Torr **1b** was isolated and purified by chromatography ($SiO_2$, petroleum ether (40/60):ethyl acetate (10:1), $R_f$ of **1b** = 0.77, $R_f$ of 2-bromo-6-methylpyridine = 0.29). Yield 46.3 g (81%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7.40 (dd, $^3J$ = 8.2 Hz, $^3J$ = 7.2 Hz, 1H, Py–H$^4$), 6.56 (dd, $^3J$ = 7.2 Hz, $^4J$ = 0.7 Hz, 1H, Py–H$^{3/5}$), 6.45 (dd, $^3J$ = 8.2 Hz, $^4J$ = 0.7 Hz, 1H, Py–H$^{3/5}$), 4.99 (dt, $^3J$ = 10.7 Hz, $^3J$ = 4.4 Hz, 1H, OCH), 2.41 (s, 1H, Py–$CH_3$), 2.23–2.13 (m, 1H, Ment), 2.05 (dsept, $^3J$ = 2.7 Hz, $^3J$ = 6.8 Hz, 1H, C*H*($CH_3$)$_2$), 1.78–1.43 (m, 4H, Ment), 1.27–0.94 (m, 3H, Ment), 0.92 (d, $^3J$ = 6.8 Hz, 3H, Ment–$CH_3$), 0.89 (d, $^3J$ = 6.8 Hz, 3H, Ment–$CH_3$), 0.77 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$) ppm. MS (PI–EI, 70 eV): *m/z* (%) = 247 (M, 9), 110 (100). Optical rotation (*c* = 2.0, $CHCl_3$): $[\alpha]_D^{RT} = -94$, $[\alpha]_{578}^{RT} = -99$, $[\alpha]_{546}^{RT} = -122$, $[\alpha]_{436}^{RT} = -170$, $[\alpha]_{365}^{RT} = -316$. $C_{16}H_{25}NO$ (247.4): Calc. C 77.68, H 10.19, N 5.66. Found C 77.52, H 11.09, N 6.06%.

Table 1
Crystallographic data for **3a**, **3b**, (*S S*)-**5a**, ($L_{Ment}$,$R_C$)-**6b** and ($R_C$)-**6c**

| Compound | **3a** | **3b** | (*S*,*S*)-**5a** | ($L_{Ment}$,$R_C$)-**6b** | ($R_C$)-**6c** |
|---|---|---|---|---|---|
| Empirical formula | $C_{26}H_{26}NP$ | $C_{36}H_{44}NOP$ | 2($C_{36}H_{40}N_2PPd$), 2($C_4H_8O$), 2($F_6P$) | $C_{31}H_{40}Cl_2$ NOPPd | C $_{21}H_{22}Cl_2NOPPd$ |
| Formula weight | 238.44 | 537.69 | 1708.27 | 650.93 | 512.69 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic | Orthorhombic |
| Space group | $P2_1/c$ | $I2$ | $P1$ | $P2_1$ | $P2_12_12_1$ |
| $a$ (Å) | 15.9797(15) | 11.1441(6) | 10.7999(9) | 10.4972(7) | 9.5881(11) |
| $b$ (Å) | 15.9797(15) | 8.1570(4) | 11.1133(9) | 15.5449(8) | 12.2895(10) |
| $c$ (Å) | 20.9306(17) | 35.251(2) | 16.4442(13) | 10.4891(9) | 17.7887(13) |
| $\alpha$ (°) | 90 | 90 | 88.448(10) | 90 | 90 |
| $\beta$ (°) | 98.511(10) | 94.988(7) | 89.082(10) | 117.861(9) | 90 |
| $\gamma$ (°) | 90 | 90 | 85.726(10) | 90 | 90 |
| $V$ (Å$^3$) | 2093.9(3) | 3192.3(3) | 1967.3(3) | 1513.2(2) | 2096.1(3) |
| $Z$ | 4 | 4 | 1 | 2 | 4 |
| $\rho_{calcd}$ (Mg/m$^3$) | 1.213 | 1.119 | 1.442 | 1.429 | 1.625 |
| Abs coeff (mm$^{-1}$) | 0.142 | 0.113 | 0.615 | 0.867 | 1.228 |
| Abs correct | None | None | None | Empirical | Numerical |
| Transmiss min/max | | | | 0.795/0.399 | 0.9381/0.6192 |
| $F$ (0 0 0) | 812 | 1160 | 878 | 672 | 1032 |
| Crystal size (mm) | 0.60 × 0.24 × 0.14 | 0.36 × 0.34 × 0.08 | 0.30 × 0.20 × 0.08 | 0.12 × 0.06 × 0.04 | 0.540 × 0.260 × 0.040 |
| $\theta$ range (°) | 1.97–25.70 | 1.97–25.80 | 2.19–26.76 | 2.27–25.90 | 2.41–25.78 |
| No. of rflns/unique | 16127/3973 | 18814/6079 | 30524/15478 | 12473/5588 | 14991/3975 |
| $R_{int}$ | 0.0805 | 0.0492 | 0.0452 | 0.0630 | 0.0485 |
| No. of data/params | 3973/253 | 6079/352 | 15478/892 | 5588/319 | 3975/248 |
| Goodness of fit on $F^2$ | 0.924 | 0.949 | 0.978 | 0.799 | 1.035 |
| $R_1/wR_2$ ($I > 2\sigma(I)$) | 0.0449/0.1131 | 0.0363/ 0.0826 | 0.0326/0.0755 | 0.0416/0.0774 | 0.0230/0.0551 |
| $R_1/wR_2$ (all data) | 0.0666/0.1218 | 0.0448/0.0855 | 0.0371 /0.0768 | 0.0691/0.0833 | 0.0242/0.0554 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.473/−0.314 | 0.338/ −0.155 | 0.942/−0.343 | 0.554/−0.730 | 0.604/−0.344 |
| CCDC No. | 233216 | 203094 | 233215 | 233217 | 233219 |

Table 2
Crystallographic data for Complexes ($L_{Ment}$,$R_C$)-**14b**, ($L_{Ment}$,$S_C$)-**14b**, ($L_{Ment}$,$R_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)**16b** and ($L_{Ment}$,$S_C$)($S_{Rh}$)**16b**

| Compound | ($L_{Ment}$,$R_C$)-**14b** | ($L_{Ment}$,$S_C$)-**14b** | ($L_{Ment}$,$R_C$)($R_{Rh}$)-and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** | ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** |
|---|---|---|---|---|
| Empirical formula | $C_{41}H_{55}Cl_2NOPRh$ | C $_{41}H_{55}Cl_2NOPRh$ | 2($C_{41}H_{55}ClNOPRh$), 2($F_6P$) | $C_{41}H_{55}ClNOPRh$, 2($C_3H_6O$), $F_6P$ |
| Formula weight | 782.64 | 782.64 | 1784.32 | 1008.32 |
| Crystal system | Orthorhombic | Orthorhombic | Triclinic | Monoclinic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P1$ | $P2_1$ |
| $a$ (Å) | 14.5510(10) | 10.4475(8) | 8.8682(8) | 9.9515(7) |
| $b$ (Å) | 15.6678(9) | 17.7055(16) | 15.1841(13) | 17.9193(12) |
| $c$ (Å) | 16.8954(12) | 21.0407(15) | 16.5209(13) | 14.2159(11) |
| $\alpha$ (°) | 90 | 90 | 91.367(10) | 90 |
| $\beta$ (°) | 90 | 90 | 105.515(10) | 106.791(9) |
| $\gamma$ (°) | 90 | 90 | 100.659(10) | 90 |
| $V$ (Å$^3$) | 3851.8(4) | 3892.1(5) | 2100.3(3) | 2427.0(3) |
| $Z$ | 4 | 4 | 1 | 2 |
| $\rho_{calcd}$ (Mg/m$^3$) | 1.350 | 1.336 | 1.411 | 1.380 |
| Abs coeff (mm$^{-1}$) | 0.656 | 0.649 | 0.605 | 0.535 |
| Abs correct | Numerical | Numerical | Numerical | Empirical |
| Transmiss min/max | 0.9495/0.8926 | 0.9620/0.9385 | 0.9765/0.9335 | 0.879/0.596 |
| $F$ (0 0 0) | 1640 | 1640 | 924 | 1052 |
| Crystal size (mm) | 0.260 × 0.180 × 0.140 | 0.13 × 0.08 × 0.08 | 0.16 × 0.08 × 0.04 | 0.580 × 0.100 × 0.040 |
| $\theta$ range (°) | 1.85–25.78 | 1.94–25.21 | 1.95–25.82 | 1.88–25.79 |
| No. of rflns/unique | 33156/7349 | 31162/6982 | 10131/9496 | 17232/9250 |
| $R_{int}$ | 0.0576 | 0.1720 | 0.0739 | 0.0346 |
| No. of data/params | 7349/424 | 6982/424 | 9496/875 | 9250/508 |
| Goodness of fit on $F^2$ | 0.938 | 0.699 | 0.735 | 0.968 |
| $R_1/wR_2$ ($I > 2\sigma(I)$) | 0.0277/0.0617 | 0.0489/0.0766 | 0.0454/0.0735 | 0.0391/0.0875 |
| $R_1/wR_2$ (all data) | 0.0362/0.0635 | 0.1126/0.0910 | 0.1078/0.0878 | 0.0487/0.0904 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.567/−0.275 | 0.524/−0.359 | 0.645/−0.354 | 0.788/−0.586 |
| CCDC No. | 233220 | 233222 | 233221 | 233214 |

### 5.3. 2-(2-Cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)-6-[(1R,2S,5R)-menthoxy]pyridine **3b**

**1b** (3.01 g, 12.2 mmol) in 30 ml of $Et_2O$ was added at −10 °C to a solution of BuLi (12.3 mmol, 7.7 ml of a 1.6 M solution in hexane) in 30 ml of abs. $Et_2O$. The red–orange solution was warmed up to 20 °C, stirred for 1 h and slowly added to a solution of $PPh_2Cl$ (2.23 ml, 12.2 mmol) in 40 ml of $Et_2O$ at −80 °C. The solution was allowed to warm up and stirred for 10 h at 20 °C. BuLi (12.3 mmol, 7.7 ml of a 1.6 M solution in hexane) was added at 0 °C and the solution was stirred for 1 h at 20 °C. Then, 6,6′-dimethylfulvene (1.63 ml, 12.2 mmol) was added and the reaction mixture was stirred for 20 h at 20 °C. $NH_4Cl$ (651 mg, 12.2 mmol) was added in 20 ml of $H_2O$ and the layers were separated under nitrogen. The organic layer was dried over $Na_2SO_4$ and the solvent was removed to give the two diastereomers ($L_{Ment}$,$S_C$)-**3b** and ($L_{Ment}$,$R_C$)-**3b**, ratio 40:60 as a honey-like oil in 81% yield (5.31 g).

### 5.4. ($L_{Ment}$,$S_C$)-**3b**

The mixture of diastereomers was dissolved in 90 ml of pentane. At −27 °C only the ($L_{Ment}$,$S_C$)-diastereomer of **3b** crystallized. Its crystals were washed 3× with 10 ml of cold pentane (−27 °C). Yield 1.91 g (29%), m.p. 100–104 °C. $^1H\{^{31}P\}$ NMR (400 MHz, 233 K, $CDCl_3$, major diastereomer (76%) with respect to the double bonds in the Cp ring, minor diastereomer (24%) in brackets): $\delta$ = 7.66–7.57 (m, 2H, Ph), 7.28–7.13 (m, 5H, Ph), 7.08 [7.07] (dd, $^3J$ = 8.1 Hz, $^3J$ = 7.4 Hz, 1H, Py–$H^4$), 7.01–6.89 (m, 3H, Ph), 6.52 [6.17] (ddt, $^3J$ = 5.3 Hz, $^{3/4}J$ = 1.5 Hz, $^{3/4}J$ = 1.4 Hz, 1H, Cp–H), 6.40 [6.34] (d, $^3J$ = 7.4 Hz, 1H, Py–$H^{3/5}$), 6.21 [6.20] (d, $^3J$ = 8.1 Hz, 1H, Py–$H^{3/5}$), 6.14 [6.03] (ddt, $^3J$ = 5.3 Hz, $^{3/4}J$ = 2.0 Hz, $^{3/4}J$ = 1.5 Hz, 1H, Cp–H), [6.08] 5.82 (ddt, $^{3/4}J$ = 1.6 Hz, $^{3/4}J$ = 2.0 Hz, $^{3/4}J$ = 1.5 Hz, 1H, Cp–H), 4.90 [4.84] (dt, $^3J$ = 4.1 Hz, $^3J$ = 10.8 Hz, 1H, OCH), 4.05 [4.04] (d, $^3J$ = 6.5 Hz, 1H, PCHPy), [2.87] 2.63 (md, $^2J$ = 23.8 Hz, 1H, Cp–$CH_2$), [2.67] 2.49 (md, $^2J$ = 23.8 Hz, 1H, Cp–$CH_2$), 2.24–2.14 (m, 1H, Ment), 2.02 (dsept, $^3J$ = 2.6 Hz, $^3J$ = 6.9 Hz, 1H, C$H$($CH_3$)$_2$), 1.79–1.55 (m, 3H, Ment), 1.52–1.42 (m, 1H, Ment), 1.48 [1.40] (s, 3H, $CH_3CCH_3$), [1.38] 1.28 (s, 3H, $CH_3CCH_3$), 1.31–1.10 (m, 2H, Ment), 1.0–0.86 (m, 1H, Ment), 0.96 (d, $^3J$ = 6.9 Hz, 3H, Ment–$CH_3$), 0.89 (d, $^3J$ = 6.9 Hz, 3H, Ment–$CH_3$), [0.88] 0.76 (d, $^3J$ = 7.0 Hz, 3H, Ment–$CH_3$) ppm.$^{31}P\{^1H\}$ NMR (162 MHz, 233 K, $CDCl_3$): $\delta$ = [−8.45] −9.10 (s, 1P) ppm. MS (PI–EI, 70 eV): *m/z* (%) = 537 (M, 100). Optical rotation (*c* = 2.0, $CH_2Cl_2$): $[\alpha]_D^{RT} = -210$, $[\alpha]_{578}^{RT} = -221$, $[\alpha]_{546}^{RT} = -258$, $[\alpha]_{436}^{RT} = -520$, $[\alpha]_{365}^{RT} = -1117$. $C_{36}H_{44}NOP$ (537.7): Calc. C 80.41, H 8.25, N 2.60. Found C 80.10, H 8.81, N 2.55%.

### 5.5. 2-(1-Diphenylphosphanyl-2-methylprop-1-yl)pyridine **4a**

BuLi (0.03 mol, 20 ml of a 1.6 M solution in hexane) was mixed with absolute ether (30 ml). At −5 °C an ether solution of 3.2 ml (3.0 g, 0.03 mol) of 2-methylpyridine **1a** was added dropwise. The color of the solution changed to yellow–orange after a few min. The reaction mixture was stirred for 1 h at 20 °C. The solution was added dropwise to a cooled solution (−78 °C) of $PPh_2Cl$ (5.5 ml, 0.03 mol) in ether. The mixture was warmed to 20 °C and stirred for 10 h. To the reaction mixture was added another 20 ml of BuLi at 0 °C and stirred for 1 h at 20 °C. To the orange–red reaction mixture was added dropwise 2-iodopropane (3.0 ml, 0.03 mol) and stirred for 20 h. Hydrolysis was performed with $NH_4Cl$ (1.6 g, 0.03 mol) in 20 ml of water. The organic layer was dried over $Na_2SO_4$. The solvent was removed to give an oily product. Yield 7.7 g (75%). $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.35–8.33 (m, 1H, Py–$H^6$), 7.95–7.90 (m, 1H, Ph), 7.67–7.61 (m, 4H, Ph, Py), 7.46–7.39 (m, 6H, Ph), 7.23–7.18 (m, 1H, Py), 6.99–6.98 (m, 1H, Py–$H^5$), 3.83–3.79 (m, 1H, PCHPy), 2.58–2.51 (m, 1H, C$H$($CH_3$)$_2$), 1.14 (d, $^3J$ = 6.8 Hz, 3H, $CH_3$), 0.96 (d, $J$ = 6.7 Hz, 3H, $CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = −6.33 (br s, 1P) ppm. $C_{21}H_{22}NP$ (319.4). MS (CI, $NH_3$): *m/z* (%) = 320 (MH, 27), 247 (100).

### 5.6. 2-(1-Diphenylphosphanyl-2-methylprop-1-yl)-6-(1R,2S,5R)-menthoxypyridine **4b**

The synthesis of **4b** was similar to that of **4a** with 2-menthoxy-6-methylpyridine **1b** instead of 2-methylpyridine **1a**. After work-up the reaction mixture was passed through a $SiO_2$ column using petroleum ether/dichloromethane (70:30) to remove the impurities. The two diastereomers were present in a ratio of 55:45 in the mixture. Colorless oil. Yield 73%. $^1H$ NMR (400 MHz, $CDCl_3$, signals of the 45%-diastereomer in parentheses if distinguishable from the 55%-diastereomer): $\delta$ = 7.78–7.68 (m, 1H, Ph), 7.66–7.56 (m, 1H, Ph), 7.54–7.22 (m, 8H, Ph, Py–$H^4$), 7.13–7.03 (m, 1H, Ph), [6.70 (m, 1H, Py–$H^{3/5}$)], 6.63 (d, $^3J$ = 7.2 Hz, 1H, Py–$H^{3/5}$), [6.37 (ddd, $^3J$ = 8.2 Hz, $J$ = 1.3 Hz, $^4J$ = 0.7 Hz, 1H, Py–$H^{3/5}$)], 6.35 (ddd, $^3J$ = 8.2 Hz, $J$ = 1.3 Hz, $^4J$ = 0.7 Hz, 1H, Py–$H^{3/5}$), 5.12–5.05 (m, 1H, OCH), 3.60–3.57 (m, 1H, PCHPy), 2.09–1.98 (m, 2H, Ment, C$H$($CH_3$)$_2$), 1.74–1.63 (m, 2H, Ment), 1.61–0.72 (m, 5H, Ment), 0.93 (d, $^3J$ = 6.3 Hz, 3H, $CH_3$), [0.90 (d, $^3J$ = 6.9 Hz, 3H, $CH_3$)], 0.86 (d, $^3J$ = 6.9 Hz, 6H, $CH_3$), [0.91 (d, $^3J$ = 6.6 Hz, 6H, 2× $CH_3$)], 0.78 (d, $^3J$ = 7.4 Hz, 3H, $CH_3$), [0.77 (d, $^3J$ = 6.6 Hz, 3H, $CH_3$)] ppm. $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ = −6.83 (s, 1P), [−7.50 (s, 1P)] ppm. $C_{31}H_{40}NOP$ (473.6). MS (PI–DCI, $NH_3$): *m/z* (%) = 474 (MH, 100).

*5.7. {2-[(S)-1-N,N-Dimethylaminoethylphenylene-C,N]-2-[(R/S)-(2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)-6-(1R,2S,5R)]-menthoxypyridinepalladium(II)}-hexafluorophosphate* ***5a***

To 200 mg (0.523 mmol) of the air-sensitive ligand **3a**, dissolved in 15 ml of abs. methanol, the suspension of 151 mg (0.260 mmol) of (+)-bis{(μ-chloro)[2-(*S*)-1-dimethylaminoethylphenylene-*C,N*]palladium(II)} in 15 ml of methanol was added. After 2 h a twofold excess of $NH_4PF_6$ (170 mg, 1.04 mmol) in 2 ml of water was added. The solution was stirred for 10 h. Then, it was concentrated to 8–10 ml. On addition of water (80 ml) the palladium complex precipitated as the $PF_6$ salt. It was filtered and washed with water. For crystallization it was dissolved in acetone and layered with petroleum ether 40/60. Yield: 340 mg (83%). $^1H\{^{31}P\}$ NMR (400 MHz, $CD_2Cl_2$, signals of the two diastereomers separated by a slash; signals of the double bond isomers given in brackets if distinguishable): $\delta$ = 8.57 (m, 1H, Py–$H^6$), 8.11–7.98 (m, 2H, Ph), 7.65–7.24 (m, 8H, Ph), 7.20–6.95 (m, 4H, Ph, Py), 6.67–6.54 (m, 2H, Ph, Py), 6.25/6.22 (m, 1H, Py), 6.00 (m, 1H, Cp–H), 5.57/5.53 [5.85/5.82] (m, 1H, Cp–H), 4.90 (m, 1H, Cp–H), 4.57/4.53 (d, $^3J$ = 5.4 Hz, 1H, PCHPy), [4.58/5.54 (d, $^3J$ = 4.3 Hz), 1H, PCHPy], 3.79/3.78 (q, $^3J$ = 6.6 Hz, 1H, C*H*$CH_3$), 3.17/3.00 (m, 3H, NMe), 2.64/2.93 (m, 3H, NMe), 2.53 (md, $^2J$ = 24.3 Hz, 1H, Cp–$CH_2$), 2.42 (md, $^2J$ = 24.3 Hz, 1H, Cp–$CH_2$); 2.02/2.01 (d, $^3J$ = 6.6 Hz, 3H, CHC*H*$_3$), 1.60–1.40 (m, 6H, $CH_3CCH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 51.3/52.0 [51.4/52.1] (s, 1P), −141.6 (sept, $^1J_{F-P}$ = 709.7 Hz, 1P, $PF_6$) ppm. MS (ESI) *m/z* (%): 637 (cation, 100). $C_{36}H_{40}F_6N_2P_2Pd$ (783.1): Calc. C 60.94, H 5.97, N 1.97. Found C 60.33, H 6.65, N 1.72%.

*5.8. {2-[(S)-1-N,N-Dimethylaminoethylphenylene-C,N]-2-[(R)-(1-diphenylphosphanyl-2-methylprop-1-yl)]-6-(1R,2S,5R)-menthoxypyridinepalladium(II)}-hexafluorophosphate* ***5b***

A suspension of the 1:1 mixture of the diastereomers of **4b** (3.0 g, 6.3 mmol) and (+)-bis{(μ-chloro)[2-(*S*)-1-dimethylaminoethylphenylene-*C,N*]palladium(II)} (2.1 g, 3.6 mmol) was stirred in methanol (50 ml). The solid dissolved giving a clear solution. The reaction mixture was stirred for 2 h at 20 °C. The mixture was filtered and the solvent was reduced to half. Addition of $NH_4PF_6$ (1.03 g, 6.3 mmol) in 10 ml of water followed slowly by another 20 ml of water precipitated the diastereomers of [($NMe_2$pea-$H^+$)Pd(**4b**)]$PF_6$. After washing with water, aqueous methanol and diethylether, the residue was recrystallized from acetone/hexane to give the pure diastereomer with (*R*)-configuration at the asymmetric carbon atom in the PN backbone. Yield 3.0 g (54%), m.p. 160–163 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.97 (t, $^3J$ = 8.1 Hz, 1H, Py–$H^4$), 7.81 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.4 Hz, 1H, Py–$H^{3/5}$), 7.78 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.4 Hz, 1H, Py–$H^{3/5}$), 7.54–7.39 (m, 4H, Ph), 7.28–7.20 (m, 5H, Ph), 7.04 (t, $J$ = 7.4 Hz, 1H, Ph), 6.97 (d, $J$ = 7.0 Hz, 1H, Ph), 6.96 (d, $^3J$ = 8.8 Hz, 1H, Ph), 6.82 (t, $^3J$ = 7.0 Hz, 1H, Ph), 6.68 (d, $^3J$ = 7.3 Hz, 1H, Ph), 4.80 (br q, $J$ = 6.6 Hz, 1H, C*H*$CH_3$), 4.14 (dt, $^3J$ = 10.9 Hz, $^3J$ = 3.8 Hz, 1H, OCH), 4.01 (dd, $^2J_{P-H}$ = 16.1 Hz, $^3J$ = 2.9 Hz, 1H, PCHPy), 2.92 (d, $^4J_{P-H}$ = 3.3 Hz, 3H, $NCH_3$), 2.60 (d, $^4J_{P-H}$ = 2.2 Hz, 3H, $NCH_3$), 2.29 (br d, $^3J$ = 12.1 Hz, 1H, Ment), 2.15–1.96 (m, 2H, Ment), 1.78–1.52 (m, 3H, Ment), 1.49 (d, $^3J$ = 7.0 Hz, 3H, $CH_3$), 1.46 (d, $^3J$ = 7.0 Hz, 3H, $CH_3$), 1.31–0.82 (m, 3H, Ment), 1.05 (d, $^3J$ = 7.0 Hz, 3H, $CH_3$), 0.99 (d, $^3J$ = 6.6 Hz, 3H, $CH_3$), 0.72 (d, $^3J$ = 7.3 Hz, 3H, $CH_3$), 0.30 (d, $^3J$ = 7.0 Hz, 3H, $CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 49.2 (s, 1P), −143.6 (sept, $^1J_{F-P}$ = 712.6 Hz, 1P, $PF_6$) ppm. MS (ESI): *m/z* (%) = 727 (cation, 100). $C_{41}H_{54}F_6N_2OP_2Pd$ (873.3): Calc. C 56.39, H 6.23, N 3.21. Found C 56.36, H 6.00, N 3.16%.

*5.9. ⟨[Chloro{2-(2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)-6-[(1R,2S,5R)-menthoxy]pyridine}rhodium(III)⟩-chloride* ($L_{Ment}$,$S_C$,$R_{Rh}$)-***7b***

($L_{Ment}$,$S_C$)-**3b** (1.00 g, 1.86 mmol) was dissolved in 25 ml of ethanol. $RhCl_3 \cdot 3H_2O$ (489 mg, 1.84 mmol), dissolved in 20 ml of ethanol, and $NaHCO_3$ (156 mg, 1.86 mmol) were added. After stirring at 20 °C for 24 h the solvent was removed. For purification a column chromatography with $SiO_2$ and petroleum ether (40/60):ethyl acetate (10:1) was carried out. Yield 1.06 g (81%), m.p. >200 °C. $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.57–7.51 (m, 1H, Ph), 7.41–7.13 (m, 6H, Ph, Py), 6.62 (dd, $^3J$ = 8.2 Hz, $^4J$ = 0.7 Hz, 1H, Py–$H^{3/5}$), 6.23 (m, 1H, Cp–H), 6.10 (m, 1H, Cp–H), 5.79 (dd, $^3J$ = 7.4 Hz, $^4J$ = 0.7 Hz, 1H, Py–$H^{3/5}$), 5.64 (m, 1H, Cp–H), 5.43 (m, 1H, Cp–H), 5.23 (dt, $^3J$ = 10.7 Hz, $^3J$ = 4.5 Hz, 1H, OCH), 5.14 (s, 1H, PCHPy), 2.35 (m, 1H, Ment), 2.23–2.15 (m, 1H, Ment), 2.01 (dsept, $^3J$ = 6.8 Hz, $^3J$ = 3.0 Hz, 1H, C*H*$(CH_3)_2$), 1.86–1.47 (m, 3H, Ment), 1.28 (s, 3H, $CH_3CCH_3$), 1.21 (s, 3H, $CH_3CCH_3$), 1.30–1.10 (m, 2H, Ment), 1.02–0.82 (m, 1H, Ment), 1.04 (d, $^3J$ = 6.5 Hz, 3H, Ment–$CH_3$), 0.92 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$), 0.77 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): diastereomer ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b**: $\delta$ = 72.6 (d, $^1J_{Rh-P}$ = 145 Hz, 1P), diastereomer ($L_{Ment}$,$R_C$,$S_{Rh}$)-**7b**: $\delta$ = 71.3 (d, $^1J_{Rh-P}$ = 145 Hz, 1P) ppm. MS (ESI, $CH_2Cl_2$): *m/z* (%) = 674 (cation, 100). Optical rotation of diastereomer ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** ($c$ = 1.1, $CHCl_3$): $[\alpha]_D^{RT} = -19$, $[\alpha]_{578}^{RT} = -23$, $[\alpha]_{546}^{RT} = -37$, $[\alpha]_{436}^{RT} = -43$. UV–Vis ($c = 2.1 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 271 ($\varepsilon = 1.4 \times 10^3$). CD ($c = 2.8 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 289 ($\Delta\varepsilon$ = −47.2), 382 ($\Delta\varepsilon$ = −5.3), 431

($\Delta\varepsilon$ = 8.7). $C_{36}H_{43}Cl_2NOPRh$ (710.5): Calc. C 60.86, H 6.10, N 1.97. Found C 60.88, H 6.18, N 1.72%.

### 5.10. Substitution of the Cl ligand in ($L_{Ment}$,$S_C$,$R_{Rh}$)-7b by halides (Br, I) and pseudohalides ($N_3$, CN, SCN) 8b–12b

The substitution of Cl in ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** by halides and pseudohalides involved metathesis of ($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** with the appropriate salts NaBr, NaI, $NaN_3$, KCN and NaSCN in methanol. The preparation of the bromo derivative ($L_{Ment}$,$S_C$,$R_{Rh}$)-**8b** is representative.

### 5.11. ($L_{Ment}$,$S_C$,$R_{Rh}$)-8b

($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** (0.20 g, 0.28 mmol) was dissolved in 10 ml of absolute methanol. To this solution NaBr (0.55 g, 0.53 mmol), dissolved in 20 ml of methanol, was added. The orange–red solution was stirred for 4 h. Then, $NH_4PF_6$ (48.5 mg, 0.28 mmol), dissolved in water, was added and the reaction mixture was stirred for 2 h. The solvent was removed and the product was extracted with $CH_2Cl_2$. The solution was passed over a short silica gel column with $CH_2Cl_2$ (red band). Removal of the solvent afforded an orange–red powder which was washed with hexane/ether. Yield: 185 mg (87%), m.p. 195–198 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.73–7.63 (m, 4H, Ph), 7.56–7.53 (m, 2H, Ph), 7.41–7.36 (m, 3H, Ph, Py), 7.29–7.25 (m, 2H, Ph), 6.63 (d, $^3J$ = 8.2 Hz, 1H, Py–H$^{3/5}$), 6.23 (m, 1H, Cp–H), 6.01 (m, 1H, Cp–H), 5.79 (d, $^3J$ = 7.6 Hz, 1H, Py–H$^{3/5}$), 5.71 (m, 1H, Cp–H), 5.55 (m, 1H, Cp–H), 5.25 (dt, $^3J$ = 10.3 Hz, $^3J$ = 4.5 Hz, 1H, OCH), 5.19 (d, $^2J_{P-H}$ = 11.3 Hz, 1H, PCHPy), 2.35 (m, 1H, Ment), 2.21–2.09 (m, 1H, Ment), 2.00 (dsept, $^3J$ = 6.8 Hz, $^3J$ = 3.0 Hz, 1H, C*H*$(CH_3)_2$), 1.89–1.61 (m, 3H, Ment), 1.25 (s, 3H, $CH_3CCH_3$), 1.21 (s, 3H, $CH_3CCH_3$), 1.30–1.10 (m, 2H, Ment), 1.02–0.82 (m, 1H, Ment), 1.04 (d, $^3J$ = 6.5 Hz, 3H, Ment–$CH_3$), 0.90 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$), 0.77 (d, $^3J$ = 7.0 Hz, 3H, Ment–$CH_3$) ppm. $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 66.6 (d, $^1J_{Rh-P}$ = 143 Hz, 1P, $PPh_2$), −142.0 (sept, 1P, $PF_6$) ppm. MS (ESI, $CH_2Cl_2$): *m*/*z* (%) = 718 (cation, 100). $C_{36}H_{43}BrF_6NOP_2Rh$ (864.5). UV–Vis ($c = 1.7\times10^{-4}$ mol l$^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 274 ($\varepsilon = 1.96\times10^3$), 410 ($\varepsilon = 0.4\times10^3$). CD ($c = 2.3\times10^{-4}$ mol l$^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 291 ($\Delta\varepsilon$ = −90.4), 381 ($\Delta\varepsilon$ = −11.3), 432 ($\Delta\varepsilon$ = 19.7).

### 5.12. ($L_{Ment}$,$S_C$,$R_{Rh}$)-9b

Yield 88%, m.p. 192–195 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.71–7.60 (m, 4H, Ph), 7.55–7.51 (m, 1H, Ph), 7.41–7.34 (m, 4H, Ph, Py), 7.29–7.25 (m, 2H, Ph), 6.63 (dd, $^3J$ = 8.2 Hz, $^4J$ = 0.7 Hz, 1H, Py–H$^{3/5}$), 6.23 (m, 1H, Cp–H), 6.11 (m, 1H, Cp–H), 5.80 (d, $^3J$ = 7.4 Hz, 1H, Py–H$^{3/5}$), 5.63 (m, 1H, Cp–H), 5.43 (m, 1H, Cp–H), 5.24 (dt, $^3J$ = 10.3 Hz, $^3J$ = 4.5 Hz, 1H, OCH), 5.16 (d, $^2J_{P-H}$ = 11.2 Hz, 1H, PCHPy), 2.21 (m, 1H, Ment), 2.20–2.15 (m, 1H, Ment), 2.01 (dsept, $^3J$ = 6.8 Hz, $^3J$ = 3.0 Hz, 1H, C*H*$(CH_3)_2$), 1.84–1.68 (m, 3H, Ment), 1.28 (s, 3H, $CH_3CCH_3$), 1.21 (s, 3H, $CH_3CCH_3$), 1.30–1.10 (m, 2H, Ment), 1.04 (d, $^3J$ = 6.5 Hz, 3H, Ment–$CH_3$), 1.02–0.82 (m, 1H, Ment), 0.92 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$), 0.77 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$) ppm. $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 70.9 (d, $^1J_{P-Rh}$ = 145 Hz, 1P), −144.0 (sept, 1P, $PF_6$) ppm. MS (ESI, $CH_2Cl_2$): *m*/*z* (%) = 766 (cation, 100). UV–Vis ($c = 1.65\times10^{-4}$ mol l$^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 275 ($\varepsilon = 2.0\times10^3$). CD ($c = 2.2\times10^{-4}$ mol l$^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 293 ($\Delta\varepsilon$ = −127.3), 397 ($\Delta\varepsilon$ = −10.3), 453 ($\Delta\varepsilon$ = 19.3). $C_{36}H_{43}F_6INOP_2Rh$ (911.5): Calc. C 47.44, H 4.76, N 1.54. Found C 46.96, H 4.69, N 1.30%.

### 5.13. ($L_{Ment}$,$S_C$,$R_{Rh}$)-10b

Yield 72%, m.p. 187–190 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.74–7.62 (m, 6H, Ph), 7.60 (m, 1H, Py–H$^4$), 7.49–7.45 (m, 2H, Ph), 7.39–7.33 (m, 2H, Ph), 6.62 (dd, $^3J$ = 8.2 Hz, $^4J$ = 0.7 Hz, 1H, Py–H$^{3/5}$), 6.23 (m, 1H, Cp–H), 6.00 (m, 1H, Cp–H), 5.78 (d, $^3J$ = 7.4 Hz, 1H, Py–H$^{3/5}$), 5.64 (m, 1H, Cp–H), 5.43 (br s, 1H, Cp–H), 5.20 (dt, $^3J$ = 10.3 Hz, $^3J$ = 4.5 Hz, 1H, OCH), 5.16 (d, $^2J_{P-H}$ = 11.2 Hz, 1H, PCHPy), 2.22 (m, 1H, Ment), 2.20–2.15 (br m, 1H, Ment), 2.00 (dsept, $^3J$ = 6.8 Hz, $^3J$ = 2.9 Hz, 1H, C*H*$(CH_3)_2$), 1.83–1.70 (m, 4H, Ment), 1.35 (s, 3H, $CH_3CCH_3$), 1.21 (s, 3H, $CH_3CCH_3$), 1.20–1.13 (m, 1H, Ment), 1.02 (d, $^3J$ = 6.5 Hz, 3H, Ment–$CH_3$), 1.00–0.89 (m, 1H, Ment), 0.87 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$), 0.75 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$) ppm. $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 73.5 (d, $^1J_{P-Rh}$ = 145.0 Hz, 1P), −143.0 (sept, 1P, $PF_6$) ppm. MS (ESI, $CH_2Cl_2$): *m*/*z* (%) = 681 (cation, 100). $C_{36}H_{43}F_6N_4OP_2Rh$ (826.6). IR (film): $\nu$ = 2180 s, 2060 s ($N_3$) cm$^{-1}$. UV–Vis ($c = 1.8\times10^{-4}$ mol l$^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 272 ($\varepsilon = 1.7\times10^3$). CD ($c = 2.8\times10^{-4}$ mol l$^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 311 ($\Delta\varepsilon$ = −68.7), 414 ($\Delta\varepsilon$ = −4.7).

### 5.14. ($L_{Ment}$,$S_C$,$R_{Rh}$)-11b

Yield 75%, m.p. 197–200 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.76–7.65 (m, 6H, Ph), 7.60 (m, 1H, Py–H$^4$), 7.55–7.47 (m, 2H, Ph), 7.39–7.33 (m, 2H, Ph), 6.61 (dd, $^3J$ = 8.2 Hz, $^4J$ = 0.7 Hz, 1H, Py–H$^{3/5}$), 6.23 (m, 1H, Cp–H), 6.11 (m, 1H, Cp–H), 5.83 (d, $^3J$ = 7.4 Hz, 1H, Py–H$^{3/5}$), 5.65 (m, 1H, Cp–H), 5.44 (br s, 1H, Cp–H), 5.23 (dt, $^3J$ = 10.3 Hz, $^3J$ = 4.5 Hz, 1H, OCH), 5.14 (d, $^2J_{P-H}$ = 11.2 Hz, 1H, PCHPy), 2.22 (m, 1H, Ment), 2.20–2.15 (m, 1H, Ment), 2.00 (dsept, $^3J$ = 6.8 Hz, $^3J$ = 2.9 Hz, 1H, C*H*$(CH_3)_2$), 1.83–1.70 (m, 4H,

Ment), 1.35 (s, 3H, $CH_3CCH_3$), 1.21 (s, 3H, $CH_3CCH_3$), 1.20–1.13 (m, 1H, Ment), 1.02 (d, $^3J$ = 6.5 Hz, 3H, Ment–$CH_3$), 1.00–0.89 (m, 1H, Ment), 0.87 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$), 0.75 (d, $^3J$ = 7.1 Hz, 3H, Ment–$CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 72.1 (d, $^1J_{P-Rh}$ = 143.0 Hz, 1P), −143.0 (sept, 1P, $PF_6$) ppm. MS (ESI, $CH_2Cl_2$): *m/z* (%) = 665 (cation, 100). $C_{37}H_{43}F_6N_2OP_2Rh$ (810.6). IR (film): $\nu$ = 2195 s (CN) $cm^{-1}$. UV–Vis ($c = 1.9 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 285 ($\varepsilon = 1.5 \times 10^3$). CD ($c = 2.9 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 292 ($\Delta\varepsilon$ = −76.3).

### 5.15. ($L_{Ment}$,$S_C$,$R_{Rh}$)-12b

Yield 80%, m.p. 191–193 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.79–7.59 (m, 2H, Ph), 7.52–7.42 (m, 4H, Ph), 7.41–7.34 (m, 1H, Py–$H^4$), 7.32–7.27 (m, 2H, Ph), 7.25–6.99 (m, 2H, Ph), 6.61 (d, $^3J$ = 8.3 Hz, 1H, Py–$H^{3/5}$), 6.21 (m, 1H, Cp–H), 6.06 (m, 1H, Cp–H), 5.71 (dd, $^3J$ = 7.4 Hz, $^4J$ = 0.7 Hz, 1H, Py–$H^{3/5}$), 5.50 (br s, 1H, Cp–H), 5.43 (m, 1H, Cp–H), 5.20 (dt, $^3J$ = 10.7 Hz, $^3J$ = 4.2 Hz, 1H, OCH), 5.16 (d, $^2J_{P-H}$ = 11.3 Hz, 1H, PCHPy), 2.22 (m, 1H, Ment), 2.20–2.15 (m, 1H, Ment), 2.00 (dsept, $^3J$ = 6.8 Hz, $^3J$ = 2.9 Hz, 1H, C*H*$(CH_3)_2$), 1.83–1.70 (m, 4H, Ment), 1.35 (s, 3H, $CH_3CCH_3$), 1.21 (s, 3H, $CH_3CCH_3$), 1.20–1.13 (m, 1H, Ment), 1.02 (d, $^3J$ = 6.5 Hz, 3H, Ment–$CH_3$), 1.00–0.85 (m, 1H, Ment), 0.92 (d, $^3J$ = 7.0 Hz, 3H, Ment–$CH_3$), 0.78 (d, $^3J$ = 6.9 Hz, 3H, Ment–$CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 70.2 (d, $^1J_{P-Rh}$ = 144.5 Hz, 1P), −145.0 (sept, 1P, $PF_6$) ppm. MS (ESI, $CH_2Cl_2$): *m/z* (%) = 697 (cation, 100). $C_{37}H_{43}F_6N_2OP_2SRh$ (842.7). IR (film): $\nu$ = 2115 s (SCN) $cm^{-1}$. UV–Vis ($c = 1.8 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 273 ($\varepsilon = 1.9 \times 10^3$). CD ($c = 2.7 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 291 ($\Delta\varepsilon$ = −125.3), 397 ($\Delta\varepsilon$ = −12.3), 452 ($\Delta\varepsilon$ = 18.1).

### 5.16. 13b

($L_{Ment}$,$S_C$,$R_{Rh}$)-**7b** (80.0 mg, 0.113 mmol) and $PPh_3$ (154 mg, 0.588 mmol) were dissolved in absolute methanol and stirred for 1.5 h at 20 °C. The solvent was evaporated. The residue was dissolved in $CH_2Cl_2$ and filtered to remove insoluble salts and excess $PPh_3$. The yellow solution was passed through a short silica gel column with $CH_2Cl_2$. Yield quant, m.p. 185–188 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.57−7.51 (m, 4H, Ph), 7.46–7.26 (m, 6H, Ph), 7.21–7.14 (m, 6H, Ph, Py–$H^4$), 7.10–6.99 (m, 8H, Ph), 6.87 (m, 2H, Ph), 6.47 (d, $^3J$ = 8.7 Hz, 1H, Py–$H^{3/5}$), 6.46 (br s, 1H, Cp–H), 6.32 (m, 1H, Cp–H), 6.10 (d, $^3J$ = 7.1 Hz, 1H, Py–$H^{3/5}$), 5.88 (br s, 1H, Cp–H), 5.55 (m, 1H, Cp–H), 5.22 (d, $^2J_{P-H}$ = 10.8 Hz, 1H, PCHPy), 4.50 (br t, $^3J$ = 9.7 Hz, 1H, OCH), 2.02 (br d, $^3J$ = 11.5 Hz, 1H, Ment), 1.97 (dsept, $^3J$ = 2.9 Hz, $^3J$ = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 1.88 (s, 3H, $CH_3$), 1.75–1.65 (m, 3H, Ment), 1.50–1.44 (m, 1H, Ment), 1.43 (s, 3H, $CH_3$), 1.17–1.05 (m, 1H, Ment), 0.96–0.80 (m, 2H, Ment), 0.89 (d, $^3J$ = 7.0 Hz, 3H, $CH_3$), 0.88 (d, $^3J$ = 6.6 Hz, 3H, $CH_3$), 0.69 (d, 3H, $^3J$ = 6.9 Hz, $CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 60.2 (dd, $^1J_{Rh-P}$ = 145.0 Hz, $^2J_{P-P}$ = 39.7 Hz, 1P, $PPh_2$), 34.5 (dd, $^1J_{Rh-P}$ = 129.7 Hz, $^2J_{P-P}$ = 39.7 Hz, 1P, $PPh_3$), −143.4 (sept, $^1J_{F-P}$ = 712.6 Hz, 1P, $PF_6$) ppm. MS (ESI, $CH_2Cl_2$): *m/z* (%) = 936 (cation, 100). UV–Vis ($c = 1.8 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 282 ($\varepsilon = 0.96 \times 10^3$), 350 ($\varepsilon = 0.58 \times 10^3$). CD ($c = 1.9 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 303 ($\Delta\varepsilon$ = −65.1), 415 ($\Delta\varepsilon$ = −27.6), 487 ($\Delta\varepsilon$ = 5.3). $C_{54}H_{58}ClF_6NOP_3Rh$ (1082.3): Calc. C 59.93, H 5.40, N 1.29, Cl 3.28. Found C 58.73, H 5.19, N 1.31, Cl 2.99%.

### 5.17. ($L_{Ment}$,$R_C$)-14b and ($L_{Ment}$,$S_C$)-14b

To a solution of a 1:1 mixture of ($L_{Ment}$,$R_C$)- and ($L_{Ment}$,$S_C$)-**4b** (374 mg, 0.788 mmol) in 2-propanol (40 ml) was added $[(Cp^*RhCl)_2(\mu\text{-}Cl)_2]$ (242 mg, 0.392 mmol) under nitrogen at 20 °C. The mixture was stirred for 4 h and then evaporated. Ether (40 ml) was added to the residue. The mixture was vigorously stirred and filtered. From the insoluble part ($L_{Ment}$,$R_C$)-**14b** was obtained in 53% (164 mg) yield based on ($L_{Ment}$,$R_C$)-**4b**. The filtrate was evaporated. The residue was chromatographed on silica gel using $CH_2Cl_2$/EtOAc (1:3) to give ($L_{Ment}$,$S_C$)-**14b** in 42% (129 mg) yield based on ($L_{Ment}$,$S_C$)-**4b**.

### 5.18. ($L_{Ment}$,$R_C$)-14b

Mp. 197.5–201 °C. $^1H$ NMR (400 MHz, 253 K, $CDCl_3$): $\delta$ = 8.45 (dd, $^3J$ = 7.2 Hz, $^3J$ = 9.6 Hz, 2H, Ph), 7.66–7.55 (m, 6H, Ph), 7.40 (t, $^3J$ = 7.8 Hz, 1H, Py–$H^4$), 7.18 (br t, $J$ = 6.6 Hz, 1H, Ph), 7.10 (br s, 1H, Ph), 7.00 (d, $^3J$ = 7.2 Hz, 1H, Py–$H^{3/5}$), 6.30 (d, $^3J$ = 8.2 Hz, 1H, Py–$H^{3/5}$), 5.08 (d, $^2J_{P-H}$ = 12.3 Hz, 1H, PCHPy), 4.82 (dt, $^3J$ = 4.3 Hz, $^3J$ = 10.7 Hz, 1H, OCH), 2.55 (sept, $^3J$ = 6.6 Hz, 1H, C*H*$(CH_3)_2$), 1.92–0.65 (m, 8H, Ment), 1.24 (d, $^4J_{P-H}$ = 3.3 Hz, 15H, Cp–$CH_3$), 0.99 (d, $^3J$ = 6.4 Hz, 3H, $CH_3$), 0.91 (d, $^3J$ = 6.4 Hz, 3H, $CH_3$), 0.81 (d, $^3J$ = 7.0 Hz, 3H, $CH_3$), 0.50 (d, $^3J$ = 6.9 Hz, 3H, $CH_3$), −0.01 (d, $^3J$ = 6.8 Hz, 3H, $CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, 253 K, $CDCl_3$): $\delta$ = 29.8 (d, $^1J_{Rh-P}$ = 140.3 Hz, 1P) ppm. MS (ESI, $CH_2Cl_2$): *m/z* (%) = 746 (M–Cl, 100). CD ($c = 2.3 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 272 ($\Delta\varepsilon$ = −5.7), 296 ($\Delta\varepsilon$ = 4.9), 337 ($\Delta\varepsilon$ = −0.2), 406 ($\Delta\varepsilon$ = 5.6), 492 ($\Delta\varepsilon$ = −1.7). $C_{41}H_{55}Cl_2NOPRh$ (782.7): Calc. C 62.92, H 7.08, N 1.79. Found C 62.38, H 6.59, N 1.67%.

### 5.19. ($L_{Ment}$,$S_C$)-14b

Mp. 229–231 °C. $^1H$ NMR (400 MHz, 253 K, $CDCl_3$): $\delta$ = 8.52 (dd, $^3J$ = 8.4 Hz, $^3J$ = 9.8 Hz, 2H,

Ph), 7.66–7.54 (m, 5H, Ph), 7.36 (t, $^3J$ = 7.6 Hz, 1H, Py–H$^4$), 7.18–7.05 (m, 3H, Ph), 6.98 (br d, $^3J$ = 7.2 Hz, 1H, Py–H$^{3/5}$), 6.29 (d, $^3J$ = 8.2 Hz, 1H, Py–H$^{3/5}$), 5.12 (d, $^2J_{P-H}$ = 13.3 Hz, 1H, PCHPy), 4.53 (dt, $^3J$ = 3.5 Hz, $^3J$ = 10.6 Hz, 1H, OCH), 2.68 (sept, $^3J$ = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$), 1.97–1.87 (m, 2H, Ment), 1.81–1.70 (m, 2H, Ment), 1.44–0.65 (m, 8H, Ment), 1.22 (d, $^4J_{P-H}$ = 3.3 Hz, 15H, Cp–CH$_3$), 0.94 (d, $^3J$ = 6.5 Hz, 3H, CH$_3$), 0.86 (d, $^3J$ = 6.4 Hz, 3H, CH$_3$), 0.74 (d, $^3J$ = 7.0 Hz, 3H, CH$_3$), 0.62 (d, $^3J$ = 7.0 Hz, 3H, CH$_3$), 0.10 (d, $^3J$ = 6.8 Hz, 3H, CH$_3$) ppm. $^{31}$P{$^1$H} NMR (162 MHz, 253 K, CDCl$_3$): $\delta$ = 29.5 (d, $^1J_{Rh-P}$ = 140.8 Hz, 1P) ppm. MS (ESI, CH$_2$Cl$_2$): *m*/*z* (%) = 746 (M–Cl, 100). CD ($c = 2.4 \times 10^{-4}$ mol l$^{-1}$, CH$_2$Cl$_2$): $\lambda_{max}$ (nm) = 263 ($\Delta\varepsilon = -2.3$), 301 ($\Delta\varepsilon = -5.6$), 340 ($\Delta\varepsilon$ = 0.63), 406 ($\Delta\varepsilon = -11.4$), 493 ($\Delta\varepsilon$ = 4.0). $C_{41}H_{55}Cl_2NOPRh$ (782.7): Calc. C 62.92, H 7.08, N 1.79. Found C 62.84; H 6.70, N 1.74%.

### 5.20. (*R*$_C$)(*R*$_{Rh}$)/(*S*$_C$)(*S*$_{Rh}$)- and (*R*$_C$)(*S*$_{Rh}$)/(*S*$_C$)-(*R*$_{Rh}$)-**15a**

To a solution of racemic **4a** (284 mg, 0.893 mmol) in ethanol (30 ml) was added [(Cp*RhCl)$_2$(μ-Cl)$_2$] (256 mg, 0.414 mmol) under nitrogen at 20 °C. The mixture was stirred for 5 h and then evaporated. The residue was washed with 10% dichloromethane/ether to give (*R*$_C$)(*R*$_{Rh}$)/(*S*$_C$)(*S*$_{Rh}$)- and (*R*$_C$)(*S*$_{Rh}$)/(*S*$_C$)(*R*$_{Rh}$)-**15a** in 94% (487 mg) yield. Orange powder, m.p. 168–174 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, major isomers (*R*$_C$)(*R*$_{Rh}$)/(*S*$_C$)(*S*$_{Rh}$), minor isomers (*S*$_C$)(*R*$_{Rh}$)/(*R*$_C$)(*S*$_{Rh}$) in brackets): $\delta$ = 8.66 (br d, $^3J$ = 5.8 Hz, 1H, Py–H$^6$), [8.87 (br d, $^3J$ = 6.4 Hz, 1H, Py–H$^6$)], 8.13–7.17 (m, 13H, Ph, Py–H$^{3-5}$), 3.99 (dd, $^3J_{P-H}$ = 15.2 Hz, $^3J$ = 5.3 Hz, 1H, PCHPy), [5.01 (br d, $J_{P-H}$ = 16.0 Hz, 1H, PCHPy)], 2.36–2.20 (m, 1H, C*H*(CH$_3$)$_2$), [2.56–2.42 (m, 1H, C*H*(CH$_3$)$_2$)], 1.41 (d, $^4J_{P-H}$ = 3.5 Hz, 15H, Cp–CH$_3$), [1.53 (d, $^3J$ = 3.7 Hz, 15H, Cp–CH$_3$)], 0.75 (d, $^3J$ = 6.8 Hz, 3H, CH$_3$), [1.11 (d, $^3J$ = 7.2 Hz, 3H, CH$_3$)], 0.32 (d, $^4J_{P-H}$ = 6.8 Hz, 3H, CH$_3$), [0.38 (d, $^3J$ = 7.0 Hz, 3H, CH$_3$) ppm. $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ = [73.9 (d, $^1J_{Rh-P}$ = 135.8 Hz, 1P, *R*$_C$,*S*$_{Rh}$/*S*$_C$,*R*$_{Rh}$-P)], 59.3 (d, $^1J_{Rh-P}$ = 141.9 Hz, 1P, *R*$_C$,*R*$_{Rh}$/*S*$_C$,*S*$_{Rh}$-P) ppm. MS (ESI, CH$_2$Cl$_2$): *m*/*z* (%) = 592 (cation, 100). $C_{31}H_{37}Cl_2NPRh$ (628.4): Calc. C 59.25, H 5.93, N 2.23. Found C 59.36, H 6.08, N 2.27%.

### 5.21. (*R*$_C$)(*R*$_{Rh}$)/(*S*$_C$)(*S*$_{Rh}$)- and (*R*$_C$)(*S*$_{Rh}$)/(*S*$_C$)-(*R*$_{Rh}$)-**16a**

(*R*$_C$)(*R*$_{Rh}$)/(*S*$_C$)(*S*$_{Rh}$)- and (*R*$_C$)(*S*$_{Rh}$)/(*S*$_C$)(*R*$_{Rh}$)-**15a** (174 mg, 0.277 mmol) were dissolved in THF (30 ml) under nitrogen at 20 °C. $NH_4PF_6$ (1.08 g, 6.63 mmol) was added. After stirring for 15 h the solvent was evaporated. Dichloromethane was added to the residue and the suspension was filtered. The filtrate was evaporated and the residue was washed with ether to give (*R*$_C$)(*R*$_{Rh}$)/(*S*$_C$)(*S*$_{Rh}$)- and (*R*$_C$)(*S*$_{Rh}$)/(*S*$_C$)(*R*$_{Rh}$)-**16a** in 80% (163 mg) yield. Isomer composition: (*R*$_C$)(*R*$_{Rh}$)/(*S*$_C$)(*S*$_{Rh}$):(*R*$_C$)(*S*$_{Rh}$)/(*S*$_C$)(*R*$_{Rh}$) = 74:26 by $^{31}$P{$^1$H} NMR integration at 300 K. Orange powder, m.p. 145–155 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, major isomers (*R*$_C$)(*R*$_{Rh}$)/(*S*$_C$)(*S*$_{Rh}$), minor isomers (*R*$_C$)(*S*$_{Rh}$)/(*S*$_C$)(*R*$_{Rh}$) in brackets): $\delta$ = 8.59 (br d, $^3J$ = 5.8 Hz, 1H, Py–H$^6$), [8.80 (br d, $^3J$ = 5.4 Hz, 1H, Py–H$^6$)], 8.06–7.17 (m, 13H, Ph, Py–H$^{3-5}$), 3.91 (dd, $^2J_{P-H}$ = 15.1 Hz, $^3J$ = 5.3 Hz, 1H, PCHPy), [4.99 (br d, $^2J_{P-H}$ = 15.0 Hz, 1H, PCHPy)], 2.37–2.21 (m, 1H, C*H*(CH$_3$)$_2$), [2.54–2.40 (m, 1H, C*H*(CH$_3$)$_2$)], 1.40 (d, $^4J_{P-H}$ = 3.7 Hz, 15H, Cp–CH$_3$), [1.51 (d, $^4J_{P-H}$ = 3.7 Hz, 15H, Cp–CH$_3$)], 0.74 (d, $^3J$ = 6.7 Hz, 3H, CH$_3$), [1.11 (d, $^3J$ = 7.2 Hz, 3H, CH$_3$)], 0.32 (d, $^3J$ = 6.9 Hz, 3H, CH$_3$), [0.38 (d, $^3J$ = 7.0 Hz, 3H, CH$_3$) ppm. $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ = 73.6 (d, $^1J_{Rh-P}$ = 135.8 Hz, 1P, *R*$_C$,*S*$_{Rh}$/*S*$_C$,*R*$_{Rh}$-P), 59.3 (d, $^1J_{Rh-P}$ = 143.5 Hz, 1P, *R*$_C$,*R*$_{Rh}$/*S*$_C$,*S*$_{Rh}$-P), −143.8 (sept, $^1J_{F-P}$ = 712.6 Hz, 1P, PF$_6$) ppm. MS (ESI, CH$_2$Cl$_2$): *m*/*z* (%) = 592 (cation, 100). $C_{31}H_{37}ClF_6NP_2Rh$ (737.9): Calc. C 50.46, H 5.05, N 1.90. Found C 50.59, H 5.65, N 1.86%.

### 5.22. (*L*$_{Ment}$,*R*$_C$)(*R*$_{Rh}$)- and (*L*$_{Ment}$,*R*$_C$)(*S*$_{Rh}$)-**16b**

(*L*$_{Ment}$,*R*$_C$)-**14b** (116 mg, 0.148 mmol) and $NH_4PF_6$ (1.26 g, 7.7 mmol) were dissolved in THF (30 ml) under nitrogen at 20 °C. The mixture was stirred for 16 h and then evaporated. Chloroform was added to the residue. The suspension was vigorously stirred and filtered. The filtrate was evaporated. The red residue was chromatographed on a short silica gel column using acetone as an eluent. The red fraction was evaporated and the residue was washed with ether to give the orange powder of (*L*$_{Ment}$,*R*$_C$)(*R*$_{Rh}$)-**16b**:(*L*$_{Ment}$,*R*$_C$)(*S*$_{Rh}$)-**16b** = 91:9 (by $^{31}$P{$^1$H} NMR integration at 300 K). Yield: 68.4 mg (51%), m.p. 164–166 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, major diastereomer (*L*$_{Ment}$,*R*$_C$)(*R*$_{Rh}$)-**16b**, minor diastereomer (*L*$_{Ment}$,*R*$_C$)(*S*$_{Rh}$)-**16b** in brackets): $\delta$ = 7.96 (t, $^3J$ = 7.4 Hz, 1H, Py–H$^4$), [8.17 (br t, $^3J$ = 8.5 Hz, 1H, Py–H$^4$)], 7.75–7.56 (m, 6H, Ph), 7.48–7.41 (m, 4H, Ph), 7.26 (d, $^3J$ = 7.4 Hz, 1H, Py–H$^{3/5}$), [7.04 (br d, $^3J$ = 8.5 Hz, 1H, Py–H$^{3/5}$)], 7.16 (d, $^3J$ = 8.4 Hz, 1H, Py–H$^{3/5}$), [7.02 (br d, $^3J$ = 8.5 Hz, 1H, Py–H$^{3/5}$)], 4.41 (br q, $^3J$ = 9.6 Hz, 1H, OCH), 4.01 (dd, $^2J_{P-H}$ = 13.5 Hz, $^3J$ = 3.1 Hz, 1H, PCHPy), 2.42–2.32 (m, 2H, C*H*(CH$_3$)$_2$), 1.97–0.95 (m, 8H, Ment), 1.30 (d, $^4J_{P-H}$ = 3.7 Hz, 15H, Cp–CH$_3$), [1.35 (d, $^4J_{P-H}$ = 3.9 Hz, 15H, Cp–CH$_3$)], 1.06 (d, $^3J$ = 7.0 Hz, 3H, CH$_3$), 1.03 (d, $^3J$ = 6.8 Hz, 6H, CH$_3$), 0.94 (d, $^3J$ = 6.4 Hz, 3H, CH$_3$), 0.36 (d, $^3J$ = 6.8 Hz, 3H, CH$_3$), [0.73 (d, $^3J$ = 7.0 Hz, 3H, CH$_3$)], 0.05 (d, $^3J$ = 6.8 Hz, 3H, CH$_3$), [0.43 (d, $^3J$ = 7.0 Hz, 3H, CH$_3$)] ppm. $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ = 55.8 (d, $^1J_{Rh-P}$ = 139.0 Hz, 1P), [61.6 (d, $^1J_{Rh-P}$ = 142.1 Hz, 1P)], −143.9 (sept, $^1J_{F-P}$ = 710.6 Hz, 1P, PF$_6$) ppm. CD

($c = 2.3 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 289 ($\Delta\varepsilon = -2.9$), 314 ($\Delta\varepsilon = 14.5$), 373 ($\Delta\varepsilon = -8.3$), 477 ($\Delta\varepsilon = 3.3$). MS (ESI, $CH_2Cl_2$): *m/z* (%) = 746 (cation, 100). HRMS (LSI, MeOH–glycerol): $C_{41}H_{55}ClOPRh$ (cation) Calc. 746.2758. Found 746.2744.

### 5.23. ($L_{Ment}$, $S_C$)($S_{Rh}$)-16b

In the above manner the reaction of ($L_{Ment}$,$S_C$)-**14b** (38.9 mg, 0.0497 mmol) with $NH_4PF_6$ (228 mg, 1.34 mmol) in THF (15 ml) gave ($L_{Ment}$,$S_C$)($S_{Rh}$)- and ($L_{Ment}$,$S_C$)($R_{Rh}$)-**16b** in 41% (18.6 mg) yield. Recrystallization of the mixture using acetone/petroleum ether 40/60 afforded pure ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** isolated as orange needles, m.p. 167–171 °C. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 7.96–7.90 (m, 3H, Ph, Py–$H^4$), 7.71–7.50 (m, 6H, Ph), 7.35–7.30 (m, 2H, Ph), 7.18 (d, $^3J$ = 7.2 Hz, 1H, Py–$H^{3/5}$), 7.03 (d, $^3J$ = 8.4 Hz, 1H, Py–$H^{3/5}$), 4.28 (dt, $^3J$ = 4.1 Hz, $^3J$ = 10.4 Hz, 1H, OCH), 3.93 (dd, $^2J_{P-H}$ = 13.3 Hz, $^3J$ = 4.3 Hz, 1H, PCHPy), 2.70 (dsept, $^3J$ = 2.4 Hz, $^3J$ = 6.8 Hz, 1H, Ment–C*H*($CH_3$)$_2$), 2.42–2.24 (m, 2H, Ment, PCHC*H*($CH_3$)$_2$), 1.81 (d, $^3J$ = 6.1 Hz, 3H, $CH_3$), 1.85–1.59 (m, 5H, Ment), 1.43–1.38 (m, 1H, Ment), 1.32 (d, $^4J_{P-H}$ = 3.9 Hz, 15H, Cp–$CH_3$), 1.11–1.01 (1H, m, Ment), 0.90 (d, $^3J$ = 6.8 Hz, 3H, $CH_3$), 0.80 (d, $^3J$ = 6.8 Hz, 3H, $CH_3$), 0.36 (d, $^3J$ = 6.8 Hz, 3H, $CH_3$), 0.11 (d, $^3J$ = 6.8 Hz, 3H, $CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta$ = 53.2 (d, $^1J_{Rh-P}$ = 142.3 Hz, 1P, PH), −143.9 (sept, $^1J_{F-P}$ = 710.6 Hz, 1P, $PF_6$) ppm. MS (ESI, $CH_2Cl_2$): *m/z* (%) = 746 (cation, 100). CD ($c = 2.4 \times 10^{-4}$ mol $l^{-1}$, $CH_2Cl_2$): $\lambda_{max}$ (nm) = 280 ($\Delta\varepsilon$ = 4.8), 316 ($\Delta\varepsilon = -29.7$), 373 ($\Delta\ \varepsilon = 14.6$), 465 ($\Delta\varepsilon = -3.91$). HRMS (LSI, MeOH–glycerol) $C_{41}H_{55}ClNOPRh$ (cation) Calc. 746.2758. Found 746.2747.

### 5.24. ($L_{Ment}$,$R_C$)($R_{Rh}$)-16b and ($L_{Ment}$,$S_C$)($S_{Rh}$)-16b as well as ($L_{Ment}$,$S_C$)($S_{Rh}$)-16b

As before a 1:1 mixture of ($L_{Ment}$,$R_C$)- and ($L_{Ment}$,$S_C$)-**14b** (87.4 mg, 0.111 mmol) was reacted with $NH_4PF_6$ (85.7 mg, 0.526 mmol). The residue was dissolved in ethanol. The ethanolic solution was diluted with ether and allowed to stand at room temperature to deposit a 1:1 mixture of the diastereomer ($L_{Ment}$,$R_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** (26.5 mg, 27%) as red–orange prisms. After filtration, further standing at room temperature afforded ($L_{Ment}$,$S_C$)($S_{Rh}$)-**16b** as orange needles in 40% (19.8 mg) yield.

### 5.25. ($L_{Ment}$,$R_C$)($R_{Rh}$)-, ($L_{Ment}$,$R_C$)($S_{Rh}$)-, ($L_{Ment}$,$S_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)-17b

To a 1:1 mixture of the diastereomers of **4b** (52.6 mg, 0.111 mmol) in THF (20 ml) was added [$(CpRhCl)_2(\mu$-$Cl)_2$] (32.6 mg, 0.0682 mmol) under nitrogen at 20 °C. The mixture was stirred for 2 h and then $NH_4PF_6$ (383 mg, 2.35 mmol) was added. The orange solution was stirred for 17 h and evaporated. Dichloromethane was added to the residue and the suspension was filtered to remove inorganic salts. The filtrate was evaporated and the residue was subjected to silica gel chromatography using 25% EtOH/benzene as an eluent to give a mixture of ($L_{Ment}$,$R_C$)($R_{Rh}$)-, ($L_{Ment}$,$R_C$)($S_{Rh}$)-, ($L_{Ment}$,$S_C$)($R_{Rh}$)- and ($L_{Ment}$,$S_C$)($S_{Rh}$)-**17b**. Yield 68.0 mg (75%). Isomer composition: $L_{Ment}$,$R_C$,$R_{Rh}$:$L_{Ment}$,$R_C$,$S_{Rh}$:$L_{Ment}$,$S_C$,$R_{Rh}$:$L_{Ment}$,$S_C$,$S_{Rh}$ = 20:25:5:50 by $^{31}P\{^1H\}$ NMR integration, m.p. 138–145 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.14−7.20 (m, 13H, Ph, Py–$H^{3-5}$), 5.36 (d, $^3J_{P-H}$ = 1.2 Hz, 5H, $L_{Ment}$,$S_C$,$S_{Rh}$-Cp–H), 5.67 (d, $^3J_{P-H}$ = 1.6 Hz, 5H, $L_{Ment}$,$S_C$,$R_{Rh}$-Cp–H), 5.63 (d, $^3J_{P-H}$ = 1.6 Hz, 5H, $L_{Ment}$,$R_C$,$S_{Rh}$-Cp–H), 5.38 (d, $^3J_{P-H}$ = 1.2 Hz, 5H, $L_{Ment}$,$R_C$,$R_{Rh}$-Cp–H), 4.35 (dt, $^3J$ = 3.9 Hz, $^3J$ = 11.0 Hz, 1H, $L_{Ment}$,$S_C$,$S_{Rh}$-OCH), 4.67–4.59 (m, 1H, $L_{Ment}$,$S_C$,$R_{Rh}$-OCH), 4.57–4.50 (m, 1H, $L_{Ment}$,$R_C$,$S_{Rh}$-OCH), 4.42 (dt, $^3J$ = 3.9 Hz, $^3J$ = 10.9 Hz, 1H, $L_{Ment}$,$R_C$,$R_{Rh}$-OCH), 4.10 (dd, $^2J_{P-H}$ = 16.8 Hz, $^3J$ = 5.3 Hz, 1H, $L_{Ment}$,$S_C$,$S_{Rh}$-PCHPy), 4.87 (br d, $^2J_{P-H}$ = 16.2 Hz, $L_{Ment}$,$S_C$,$R_{Rh}$-PCHPy), 4.79 (br d, $^2J_{P-H}$ = 16.2 Hz, $L_{Ment}$,$R_C$,$S_{Rh}$-PCHPy), 4.21 (dd, $^2J_{P-H}$ = 16.6 Hz, $^3J$ = 5.3 Hz, 1H, $L_{Ment}$,$R_C$,$R_{Rh}$-PCHPy), 2.65–0.80 (m, 10H, Ment, CHC*H*($CH_3$)$_2$), 1.04 (d, $^3J$ = 6.4 Hz, 3H, $L_{Ment}$,$S_C$, $S_{Rh}$-$CH_3$), 1.08 (d, $^3J$ = 6.4 Hz, 3H, $L_{Ment}$,$R_C$,$R_{Rh}$-$CH_3$), 1.17 (d, $^3J$ = 7.2 Hz, 3H, $L_{Ment}$,$R_C$,$S_{Rh}$-$CH_3$), 0.99 (d, $^3J$ = 7.0 Hz, 3H, $L_{Ment}$,$S_C$,$S_{Rh}$-$CH_3$), 0.98 (d, $^3J$ = 7.0 Hz, 3H, $L_{Ment}$,$R_C$,$R_{Rh}$-$CH_3$), 1.05 (d, $^3J$ = 7.0 Hz, 3H, $L_{Ment}$,$R_C$,$S_{Rh}$-$CH_3$), 0.74 (d, $^3J$ = 6.8 Hz, 3H, $L_{Ment}$,$S_C$,$S_{Rh}$-$CH_3$), 0.93 (d, $^3J$ = 6.4 Hz, 3H, $L_{Ment}$, $R_C$,$R_{Rh}$-$CH_3$), 0.91 (d, $^3J$ = 7.4 Hz, 3H, $L_{Ment}$,$R_C$,$S_{Rh}$-$CH_3$), 0.59 (d, $^3J$ = 6.8 Hz, 3H, $L_{Ment}$,$S_C$,$S_{Rh}$-$CH_3$), 0.92 (d, $^3J$ = 6.4 Hz, 3H, $L_{Ment}$,$S_C$,$R_{Rh}$-$CH_3$), 0.76 (d, $^3J$ = 7.4 Hz, 3H, $L_{Ment}$,$R_C$,$R_{Rh}$-$CH_3$), 0.91 (d, $^3J$ = 6.6 Hz, 3H, $L_{Ment}$,$R_C$,$S_{Rh}$-$CH_3$), 0.33 (d, $^3J$ = 6.8 Hz, 3H, $L_{Ment}$,$S_C$,$S_{Rh}$-$CH_3$), 0.39 (d, $^3J$ = 7.2 Hz, 3H, $L_{Ment}$, $S_C$,$R_{Rh}$-$CH_3$), 0.36 (d, $^3J$ = 6.8 Hz, 3H, $L_{Ment}$,$R_C$,$R_{Rh}$-$CH_3$), 0.48 (d, $^3J$ = 7.0 Hz, 3H, $L_{Ment}$,$R_C$,$S_{Rh}$-$CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 73.0 (d,$^1J_{Rh-P}$ = 125.1 Hz, 1P, $L_{Ment}$,$R_C$,$S_{Rh}$-P), 72.3 (d,$^1J_{Rh-P}$ = 123.6 Hz, 1P, $L_{Ment}$,$S_C$,$R_{Rh}$-P), 59.6 (d, $^1J_{Rh-P}$ = 131.24 Hz, 1P, $L_{Ment}$,$S_C$,$S_{Rh}$-P), 58.7 (d, $^1J_{Rh-P}$ = 129.7 Hz, 1P, $L_{Ment}$,$R_C$,$R_{Rh}$-P), −143.9 (sept, $^1J_{F-P}$ = 710.6 Hz, $PF_6$) ppm. MS (ESI, $CH_2Cl_2$): *m/z* (%) = 676 (cation, 100). $C_{36}H_{45}F_6ClNOP_2Rh \cdot (C_6H_6)_{1/2}$ (861.1): Calc. C 54.40, H 5.62, N 1.63. Found C 53.92, H 5.79, N 1.55%.

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