Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 4495–4505
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Optically active rhodium complexes with indenyl-linked phosphane ligands

Angelino Doppiu *, Ulli Englert, Vera Peters, Albrecht Salzer *

Institut für Anorganische Chemie, RWTH Aachen, Landoltweg 1, D-52056 Aachen, Germany

Received 13 February 2007; received in revised form 21 March 2007; accepted 21 March 2007
Available online 27 March 2007

Dedicated to Prof. Gerhard Erker on the occasion of his 60th birthday.

Abstract

The optically active indenyl-linked phosphane ligands (*S*)-[2-(3*H*-inden-1-yl)-1-phenylethyl]diphenylphosphane (**L_1**) and (*S*)-[2-(4,7-dimethyl-3*H*-inden-1-yl)-1-phenyl-ethyl]diphenylphosphane (**L_2**) were synthesized in three steps from (*R*)-1-phenylethane-1,2-diol in excellent yields. Their lithium salts reacted with $[Rh(\mu\text{-}Cl)(\eta^2\text{-}CH_2CH_2)_2]_2$ at −78 °C in THF affording the planar chiral complexes $(S,R_{pl}+S_{pl})$-$[Rh(\eta^5\text{-indenyl-}CH_2CH(Ph)PPh_2\text{-}kP)(\eta^2\text{-}CH_2CH_2)]$ and $(S,R_{pl}+S_{pl})$-$[Rh(\eta^5\text{-4,7-dimethylindenyl-}CH_2CH(Ph)PPh_2\text{-}kP)(\eta^2\text{-}CH_2CH_2)]$ as 61:39 and 15:85 mixtures of diastereomers. The complexes were isolated in optically pure form by column chromatography. The stereochemical configuration of one of the diastereomers was determined by X-ray crystallography. The complexation of **L_2** was studied in different solvents and with several Rh precursors and diastereomeric excesses up to 76% were achieved. The ability of the chiral ligands to control the stereochemistry at the metal center was tested by oxidative addition of methyl iodide. Diastereomeric excesses greater than 98% were observed.

Keywords: Rhodium; Constrained geometry ligands; P ligands; Chirality; Oxidative addition; X-ray diffraction

1. Introduction

Chelating ligands containing a cyclopentadienyl and a heteroatom connected by an appropriate spacer have received considerable attention in recent years. A special attraction of these ligands is the possibility to independently vary its three structural components, namely the cyclopentadienyl ring, the spacer and the heteroatom and its substituents in order to modify the chemical and physical properties of classical cyclopentadienyl metal complexes [1]. The additional coordination of the heteroatom leads to increased rigidity of the complex; accordingly, these chelating ligands are today referred to as constrained geometry ligands (CGLs). Comprehensive reviews on cyclopentadienyl ligands bearing pendant donor heteroatoms have appeared that focused on nitrogen, oxygen, phosphorus, arsenic and sulfur donors [2]. An additional feature of the CGLs is that the introduction of chirality elements in this system may assist in controlling the stereochemistry of reactions taking place at the metal center and therefore could eventually increase the stereoselection in asymmetric catalytic reactions, particularly if the chiral elements are in close proximity to the metal. Several attempts have been made to introduce chirality into the CGL-system [3]. In principle, there are four possible ways to achieve this goal: (i) chiral substituents in the Cp ring (*e.g.* menthyl group) or non-symmetric substitution pattern of the Cp ring; (ii) stereogenic center(s) in the connecting chain; (iii) stereogenic heteroatom or chiral substituents at the heteroatom; (iv) chiral ancillary ligands. In order to control the stereochemistry at the metal center, the

* Corresponding authors. Tel.: +49 241 80 94 646; fax: +49 241 80 92 288.
E-mail addresses: angelino.doppiu@ac.rwth-aachen.de (A. Doppiu), albrecht.salzer@ac.rwth-aachen.de (A. Salzer).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.03.030

incorporation of only one element of chirality in the CGL-system might probably not be enough, and a judicious combination of two or more types of chirality should be appropriate.

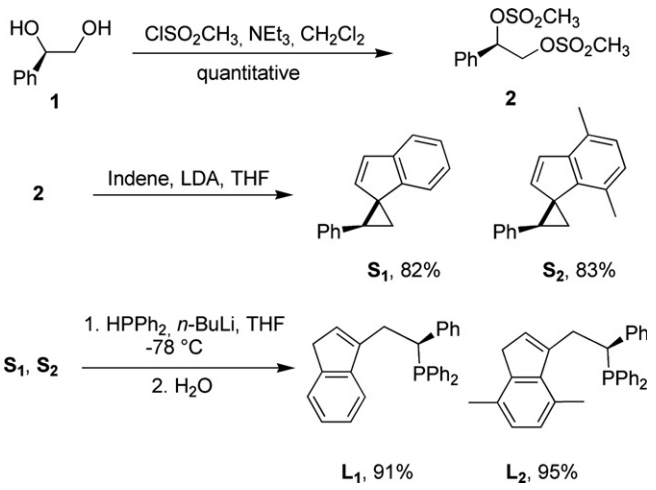
Rhodium compounds with CGLs are mostly limited to phosphinoalkyl-functionalized cyclopentadienyl ligands [4]. This fact is not surprising, if one considers the *soft* nature of the rhodium metal, which prefers to form strong bonds with *soft* ligands like phosphanes [5]. There is indeed an example of dialkylaminoalkyl-substituted Cp complex of rhodium, but according to the *hard* nature of the amino group, a hemilabile coordination has been observed [6]. Chiral rhodium complexes with CGLs have been reported by the groups of Hidai and coworkers [7], Tani and Kataoka [8], and Whitby and coworkers [9].These systems contain central chirality, planar chirality or even a combination of both.

In our group, we have concentrated on the investigation of chiral cyclopentadienyl metal compounds with a phosphane functionality tethered onto the Cp ring via an ethylene-spacer. We have developed a synthetic route to obtain optically active cyclopentadienyl-linked phosphane ligands from optically active vicinal diols, and we have already reported on the rhodium [10], iridium [11] and ruthenium [12] compounds derived from these ligands. As part of an ongoing study, we were prompted to find out whether the introduction of planar chirality into the ligand could better control the stereochemistry at the metal center. In this contribution, we describe the preparation and characterization of a series of planar chiral rhodium(I) complexes with optically active indenyl-phosphane ligands and report on the reactivity of such complexes in the oxidative addition of methyl iodide to afford rodium(III) compounds. The ability of the ligands in controlling the generation of metal chirality is also addressed.

2. Results and discussion

2.1. Synthesis of the ligands

The indenyl-linked phosphane ligands were obtained by a slight modification of the procedure developed by us for the synthesis of the cyclopentadienyl-containing ligands (Scheme 1) [12a]. Treatment of (*R*)-1-phenylethane-1,2-diol with methanesulfonyl chloride and triethylamine in CH_2Cl_2 affords in almost quantitative yields the bis-methanesulphonate ester **2**. Displacement of the methanesulphonate groups by indene or 4,7-dimethylindene in the presence of excess LDA in THF affords the spiro compounds $\mathbf{S_1}$ and $\mathbf{S_2}$, respectively, in excellent yields. This modified procedure requires the use of LDA instead of $NaNH_2$, otherwise the yields drop down due to the formation of elimination products of **2**. Interestingly, the two compounds were obtained as pure diastereomers [13]. The ring-opening reaction of $\mathbf{S_1}$ and $\mathbf{S_2}$ with lithium diphenylphosphide proceeds with complete regiospecificity by attack of the nucleophile at the activated benzylic position



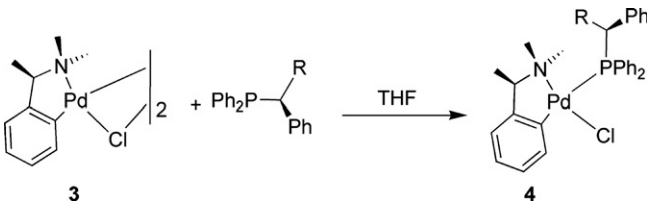
Scheme 1.

of the cyclopropane ring and with complete inversion of the configuration at the stereogenic center [9,10c], affording the ligands $\mathbf{L_1}$ and $\mathbf{L_2}$, which after quenching with water are isolated as slightly air-sensitive white crystalline solids. The overall yields on three steps (starting from the diols) are excellent (75–79%).

In order to ensure that no racemisation is occurring, the optical purity of the ligands was determined by diastereomeric derivatization [14]. $\mathbf{L_2}$ was reacted with the commercially available, optically pure binuclear Pd complex **3**. The chiral phosphane splits the dimer by coordination to the metal and forms the monomeric complexes **4**, which combine the stereogenic centers of both components (Scheme 2). As the derived complexes exhibit a single peak ascribed to a single diastereomer in ^{31}P NMR spectroscopy (48.6 ppm, CD_2Cl_2), the finding confirms an optical purity of the ligands of better than 98% *ee* (the diastereomers derived from the racemic ligand give rise to two well separated signals in the ^{31}P NMR spectra at 50.9 and 48.6 ppm).

2.2. Complexation of the ligands to rhodium

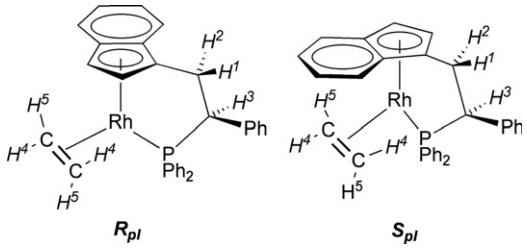
The ligands were deprotonated with *n*-BuLi and reacted in THF at −78 °C (dry ice/*i*-propanol) with the rhodium ethylene complex $[Rh(\mu\text{-}Cl)(\eta^2\text{-}CH_2CH_2)_2]_2$ (**5**). The reaction mixtures were slowly warmed up to room temperature overnight and then checked by ^{31}P NMR spectroscopy in order to determine the diastereomeric ratios. $\mathbf{L_1}$ afforded the diastereomers (S,R_{pl})-$\mathbf{Rh_1}$ and (S,S_{pl})-$\mathbf{Rh_2}$ in a 61:39



Scheme 2.

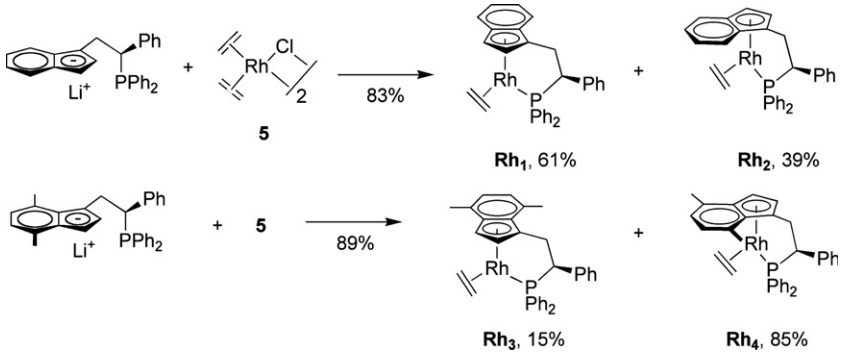
ratio, respectively ($de = 22\%$). Interestingly, Whitby obtained the related rhodium carbonyl complexes (S,R_{pl}) and (S,S_{pl}) in a 75:25 ratio, respectively (50% *de*), reacting $\mathbf{L_1}$ with the complex $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (**6**) [9]. He proposed that complexation of phosphane to rhodium precedes chloride displacement by the metalated indene, which takes place via a cyclic transition state, as already suggested by Poilblanc and coworkers [4b]. The real situation seems to be more complicated. In fact, the homochiral ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ show very different and, interestingly, opposite diastereoselectivity. The complexation of $\mathbf{L_2}$ to **5** affords the diastereomers (S,R_{pl})-$\mathbf{Rh_3}$ and (S,S_{pl})-$\mathbf{Rh_4}$ in a 15:85 ratio, respectively ($de = 70\%$); that is, the major diastereomer derived from $\mathbf{L_2}$ has the opposite planar configuration of the major diastereomer obtained from $\mathbf{L_1}$ (Scheme 3).

The two pairs of diastereomers were easily separated by column chromatography on alumina and were obtained in optically and analytically pure form. Some selected NMR data are reported in Table 1. Interestingly, the proton signals of the ethylene ligand are not broad at room temperature. Two well-separated multiplets are observed; each one integrates to two protons. The separation between the multiplets varies from 0.06 ppm to as much as 0.98 ppm. As a comparison, the ethylene ligand in (S)-[$Rh(\eta^5\text{-}C_5H_4CH_2CH(Ph)PPh_2\text{-}\kappa P)(\eta^2\text{-}CH_2CH_2)$] (**7**), gives rise to two very broad signals centered at 1.78 and 2.82 ppm [10c,15]. The different behavior could be ascribed to a rapid rotation of the ethylene ligand, causing its protons to interchange in pairs rapidly on NMR time scale. The ^{1}H NMR resonances of the bridge protons in the pairs $\mathbf{Rh_{1,3}}$ and $\mathbf{Rh_{2,4}}$ are very well comparable. This relationship should reflect the planar chirality of the complexes. Indeed, the same sign and the similar magnitude of the specific rotations suggest that $\mathbf{Rh_1}$ and $\mathbf{Rh_3}$ have the same chirality, as well as $\mathbf{Rh_2}$ and $\mathbf{Rh_4}$. The planar configuration of $\mathbf{Rh_3}$ was determined to be *R* by an X-ray structure analysis [16]. Thus, the configuration of the other complexes could be easily assigned (see Scheme 4).



Scheme 4.

X-ray-quality crystals of $\mathbf{Rh_3}$ were obtained by slow evaporation of a toluene/hexane solution. Details of the crystal structure determination are given in the experimental section, a displacement ellipsoid plot is shown in Fig. 1, important geometric parameters are compiled in Table 2. The introduction of planar chirality into the CGL does not significantly change the bonding geometry: the distances between the metal center and the ligand atoms C12 and P as well as the angle subtended at Rh are very similar to the values encountered for the Cp derived ligand [10c]. Comparable geometries with slightly smaller C–Rh–P angles have been found for two closely related complexes with a carbonyl instead of the ethylene ligand [9]. The bond length in the coordinated ethylene amounts to 1.386(8) Å and matches the mean value for this class of compounds: a search in the CSD data base [17] resulted in an average C–C bond length of 1.387 Å in 137 error-free observations of ethylene coordinated to rhodium.



Scheme 3.

Table 1
Selected NMR data[a] and specific rotations for $\mathbf{Rh_{1-4}}$

	H^1, td	H^2, ddd	H^3, m	H^4, H^5 [$\Delta\delta$], m	P	$[\alpha]_D$
(S,R_{pl})-$\mathbf{Rh_1}$	2.81 (14.0)	3.06 (59.5)	5.40	1.99, 1.93 [0.06]	87.0	−75
(S,S_{pl})-$\mathbf{Rh_2}$	3.13 (14.0)	2.80 (60.4)	4.93	2.10, 1.31 [0.79]	91.9	196
(S,R_{pl})-$\mathbf{Rh_3}$	2.83 (14.3)	3.17 (58.3)	5.46	2.04, 1.73 [0.31]	89.5	−90
(S,S_{pl})-$\mathbf{Rh_4}$	3.59 (14.0)	2.87 (60.7)	4.91	2.16, 1.18 [0.98]	92.7	139

[a] CD_2Cl_2, 500 MHz (^{1}H) and 202 MHz (^{31}P); J_{HP} in parentheses (Hz), δ in ppm. For the numbering system, see Scheme 4.

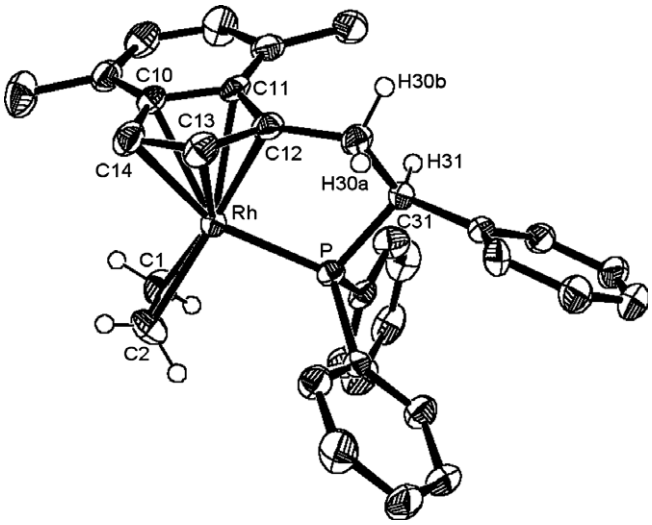


Fig. 1. ORTEP view of **Rh_3** with 50% displacement ellipsoid probability.

Table 2
Selected bond distances (Å) and angles (°) for **Rh_3**

C1–Rh	2.113(5)	C1–Rh–C2	38.3(2)
C2–Rh	2.113(5)	C1–Rh–P	98.27(18)
C10–Rh	2.346(5)	C2–Rh–P	97.78(19)
C11–Rh	2.323(5)	C12–Rh–P	86.62(12)
C12–Rh	2.129(4)	Rh–C11–C24	129.3(3)
C13–Rh	2.215(5)	Rh–C10–C21	125.8(3)
C14–Rh	2.262(4)	C14–Rh–C2	105.2(2)
P–Rh	2.1909(11)	C10–Rh–C1	105.6(2)
C10–C11	1.437(6)	C12–C30–C31	114.5(3)
C11–C12	1.457(6)	C30–C31–P	108.4(3)
C12–C13	1.411(7)	C31–P–Rh	104.95(15)
C13–C14	1.416(7)	P–C31–C30–H30b	157.0
C1–C2	1.386(8)	P–C31–C30–H30a	86.3

The difference in diastereoselectivity between the two ligands should be of kinetic origin as the complexation reaction is carried out at low temperature [18]. Subtle changes in the structure of indene give rise to very different results and the indenyl group seems to play a pivotal role in the complexation. The preferred formation of **Rh_4** is particularly remarkable: if one considers the steric hindrance of the methyl substituent at the C-7, one would expect the inverse diastereoselectivity than experimentally observed. Several variations of the ligand backbone could be conceived in order to improve the diastereoselectivity. As an example, Tani reported the 1-neoisomenthyl-3-(2-(diphenylphosphino)ethyl)indenyl ligand, where the chiral neoisomenthyl group on the indene directs the selective complexation of **6** affording the mixture of diastereomers in 87:13 ratio (74% *de*) [8c]. In contrast, a chiral center α at the indene, as in the (*R*)-[2-cyclohexyl-2-(3*H*-inden-1-yl)ethyl]diphenylphosphane ligand reported by Whitby [9], gives only minor improvements (56% *de*) in the coordination of **6**.

We preferred to concentrate on the reaction conditions and tested the coordination behavior of **L_2** in different solvents and with different rhodium precursors. The results are summarized in Table 3. When the reaction was performed in Et_2O, we observed the opposite diastereoselectivity to that one achieved in THF and the isomers **Rh_3** and **Rh_4** were obtained in an 85:15 ratio, respectively. This is likely due to the different aggregation state of the lithium salt of the ligand in the two solvents. Indeed, the diastereomers formed in almost equal amounts in a 1:1 THF/Et_2O mixture. When the reaction was performed in the presence of TMEDA, a complex mixture of unidentified species was obtained. The greatest diastereomeric ratio was obtained performing the reaction in DME (76% *de*). The same selectivity was achieved using as starting material the ethoxy-bridge ethylene complex $[Rh(\mu\text{-}EtO)(C_2H_4)_2]_2$ (**8**), which was generated in situ by the addition of sodium ethoxide to the chloro-bridge ethylene complex **5** [19]. The use of a monomeric rhodium precursor like [Rh(acac-κ*O*)(η^2-$CH_2CH_2)_2$] (**9**) did not provide any improvement.

2.3. Oxidative addition of methyl iodide

Oxidative addition is a fundamental organometallic reaction step, which plays a key role in many catalytic processes [20]. The oxidative addition of alkyl halides has attracted much academic attention as a result of the applications of this reaction in industrial processes. In particular, the addition of CH_3I to carbonyl rhodium and iridium complexes has been studied in mechanistic detail, since it is the key step in the catalyzed carbonylation of methanol on an industrial scale [21]. Oxidative addition of methyl iodide to a rhodium(I) center affords the corresponding iodo-methyl-rhodium(III) species; if this reaction is performed with a three-legged piano-stool metal complex, the resulting product will exhibit chirality at the

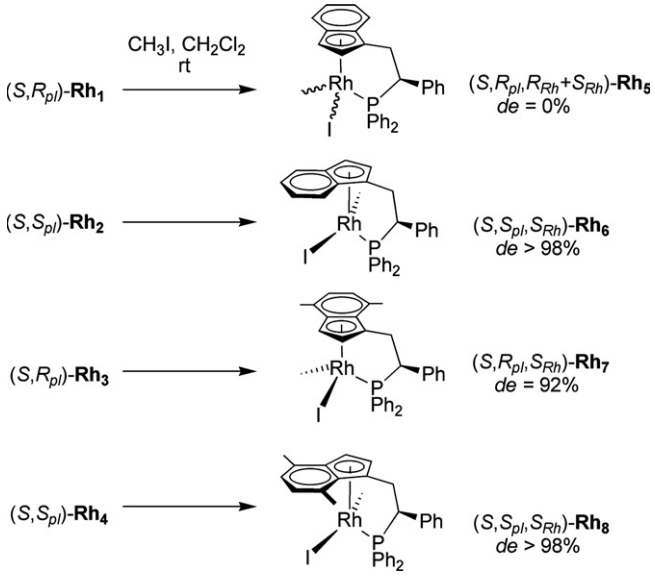
Table 3
Complexation of **L_2** in different reaction conditions[a]

Reagents	Solvent	(*S*,R_{pl})-**Rh_3** (%)	(*S*,S_{pl})-**Rh_4** (%)	***de*** (%)
5, **L_2**, *n*-BuLi	THF	15	85	70
5, **L_2**, *n*-BuLi	Et_2O	85	15	70
5, **L_2**, *n*-BuLi	THF/Et_2O, 1:1	43	57	14
5, **L_2**, *n*-BuLi	DME	12	88	76
8, **L_2**	THF/EtOH, 40:1	12	88	76
9, **L_2**, *n*-BuLi	THF	27	74	47

[a] The reaction mixtures were warmed from −78 °C to room temperature overnight.

metal. Much interest has been devoted to the controlled generation of metal-centered chirality. Some chiral transition metal complexes having a stereogenic center on the metal have been prepared and applied to asymmetric synthesis, but the controlled generation or resolution of the chiral center at the metal is still a challenging project [22]. A major goal in preparing our rhodium complexes with chiral chelating ligands was their application in stereoselective stoichiometric and catalytic reactions. With several optically pure rhodium complexes in hands that incorporate planar and central chirality, the first issue to be addressed was to determine the ability of the chiral scaffold to control the stereoselectivity of the reactions occurring at the metal. We chose the oxidative addition of methyl iodide as a model reaction. Treatment of the complexes with a 10-fold excess of CH_3I in CH_2Cl_2 at room temperature afforded the expected rhodium methyl iodide products in good yields. The results are depicted in Scheme 5.

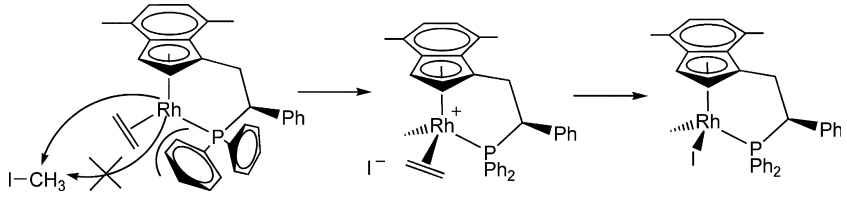
The diastereomeric ratios were determined on the crude reaction mixtures by ^1H and ^{31}P NMR. Interestingly, **Rh$_1$** showed no selectivity and **Rh$_5$** was obtained as an equimolar mixture of diastereomers. This might be due to a mismatch between the planar and the central chirality. On the contrary, **Rh$_3$**, which is homochiral to **Rh$_1$**, afforded



Scheme 5.

Rh$_7$ in 92% *de*; clearly, the methyl substituents on the indene play a crucial role. Complete control in the formation of the new stereogenic center at the rhodium could be achieved with the complexes **Rh$_2$** and **Rh$_4$**: only the signals of one diastereoisomer could be detected by ^{31}P and ^1H NMR. The configuration around the metal in the products **Rh$_{6-8}$** was unambiguously determined to be *S* by means of ^1H NMR NOE-difference experiments. For example, irradiation of the coordinated methyl group in **Rh$_6$** and **Rh$_8$** at $\delta = 1.30$ and 1.29, respectively, enhanced the signals ($\delta = 4.90$) of the benzylic H^3 proton of the linker and of a proton of the η^5-ring ($\delta = 5.15$ and 5.00). For the major diastereomer (S,S_{pl},S_{Rh})-**Rh$_7$**, irradiation of the methyl group at $\delta = -0.20$ enhanced the signals ($\delta = 5.17$) of the benzylic H^3 proton of the linker and of the protons of the methyl groups on the indene ($\delta = 2.29$ and 2.54). The *S* metal configuration can be rationalized looking at Fig. 1. From the figure, the chiral environment around the metal created by the phenyl groups of the phosphane can be appreciated; one phenyl group is almost parallel (dihedral angle = 26.7(2)°) to the phenyl substituent on the bridge and shelters a side of the metal.

On the basis of many studies, several mechanisms have been proposed for the oxidative addition reaction of alkyl halides. The most common mechanisms noted in the literature are the S_N2, the concerted *cis*-addition mechanisms, and mechanisms involving free alkyl radical intermediates [23]. We have shown that in (*S*)-[Rh(η^5-$C_5H_4CH_2CH$(Ph)PPh_2-κ*P*)(η^2-CH_2CH_2)] (**7**), the oxidative addition reaction of CH_3I follows a S_N2 mechanism and occurs via a two-step pathway involving (i) nucleophilic attack by the metal on the methyl carbon to displace iodide and form a metal carbon bond and (ii) coordination of iodide to the cationic methyl-ethylene intermediate [10a,24]. If we assume that the first step occurs from the less hindered side of the metal, the observed *S* metal configuration of the product can be thus explained for **Rh$_7$** [25] (Scheme 6). We might assume that for **Rh$_6$** and **Rh$_8$** a similar spatial arrangement of the phenyl groups is maintained. The arrangement influences the diastereoselectivity independently of the planar chirality present. In the case of **7**, the methyl-ethylene intermediate is also formed diastereomerically pure [10a], but then it epimerizes in the second step. On the contrary, no epimerization occurs in **Rh$_6$** and **Rh$_8$**. The higher rigidity of the ligand backbone and/or the ability of the indenyl group to switch from an η^5- to an η^1- or η^3-coordination could be responsible for this fact [26].



Scheme 6.

3. Conclusion

The results presented in this paper illustrate that the indenyl-linked phosphane ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ coordinate to rhodium in both oxidation states +I and +III as chelating (6 + 2)-electron donor ligands. The chiral center in the linking chain β to the indenyl group is able to discriminate between the enantiotopic faces of the indene. The result of the complexation is unpredictably controlled by several factors like ligand backbone, metal salt of the ligand [27], rhodium precursor and solvent. More experiments are necessary to find the right match. The ability of the chiral ligands in controlling the generation of a stereogenic center at the metal has been also tested. While the planar chirality appears to be an indispensable factor for inducing high stereoselectivity around the metal center, the stereochemistry seems to be governed by the chiral pocket around the metal generated by the phenyl groups.

4. Experimental

4.1. General remarks

All reactions, involving air- or moisture-sensitive compounds and subsequent work-up were carried out under nitrogen using standard Schlenk techniques. The solvents were dried and purified by standard methods. They were deoxygenated and stored under nitrogen. Reagents and solvents were transferred under nitrogen via syringe or cannula. Solutions of crude reaction mixtures were filtered through Celite (Fluka 535), neutral or basic alumina (ICN Alumina N, B, activity super I), deactivated with H_2O. Flash column chromatography of organic compounds was performed using silica gel 60 (230–400 mesh). Melting points were measured in a sealed capillary on a Büchi 510 melting point apparatus and are uncorrected. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity 500 (500 MHz, ^1H; 125 MHz, ^{13}C; 202 MHz, ^{31}P) at ambient temperature. ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to $Si(CH_3)_4$ and were referenced to the residual signals of the deuterated solvents. ^{31}P NMR chemical shifts were referenced to an 85% H_3PO_4 sample used as an external standard. ^1H and ^{13}C NMR signal assignments were confirmed by ^1H–^1H COSY, NOE-difference experiments, APT and ^1H–^{13}C HETCOR. Optical rotations were measured on a Perkin Elmer 341 Polarimeter at $\lambda = 589$ nm at 20 °C using CHROMASOLV® grade solvents. Mass spectra were obtained with a Finnigan MAT 95 spectrometer by electron impact (EI) or fast atom bombardment (FAB). Elemental analyses were performed by Institute of Organic Chemistry of the RWTH Aachen. 4,7-Dimethyl-1*H*-indene [28] and (*R*)-Phenyl-1,2-bis(methanesulfonyloxy)ethane [12a] were prepared following a published procedure. The complexes $[Rh(\mu\text{-}Cl)(C_2H_4)_2]_2$ and $[Rh(acac\text{-}\kappa O)(\eta^2\text{-}C_2H_4)_2]$ were prepared as described in the literature [29]. All other chemicals were purchased and used without further purification.

4.2. (1S,2S)-trans-2-Phenyl-spiro(cyclopropane-1,1′-indene) (S_1)

LDA (43 mL of a 2 M solution) was added dropwise to a solution of indene (4.34 g, 37.4 mmol) in THF (50 mL), cooled by an ice-water bath. The mixture was stirred for 30 min at room temperature and then cooled again to 0 °C. A solution of (*R*)-phenyl-1,2-bis(methanesulfonyloxy)ethane (10 g, 34 mmol) in THF (150 mL) was added dropwise and the mixture was allowed to reach room temperature overnight. A saturated solution of NH_4Cl was then added. The mixture was diluted with Et_2O and the layers were separated. The aqueous phase was washed with Et_2O (3×50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and treated with decolorizing charcoal. After filtration, the solvent was removed under reduced pressure and the oil obtained was purified by flash chromatography on silica gel with toluene/hexane 1:4 as eluent ($R_f = 0.4$). Yield: white crystalline powder, 7.6 g (82%). M.p.: 90–91 °C. ^1H NMR ($CDCl_3$): δ 2.04 (dd, 1H, $^2J_{HH} = 5.19$ Hz, $^3J_{HH} = 8.85$ Hz, CH_2), 2.36 (dd, 1H, $^2J_{HH} = 5.19$ Hz, $^3J_{HH} = 7.63$ Hz, CH_2), 3.25 (t, 1H, $^3J_{HH} = 8.24$ Hz, C*H*Ph), 6.01 (d, 1H, $^3J_{HH} = 5.49$ Hz, C*H*), 6.82 (d, 1H, $^3J_{HH} = 5.49$ Hz, C*H*), 7.09–7.40 (m, 9H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 19.26 (*C*H_2), 33.07 (*C*HPh), 40.84 (C_{spiro}), 117.43 (*C*H), 121.38 (*C*H), 124.32 (*C*H), 125.71 (*C*H), 126.59 (*C*H), 128.14 (*C*H), 128.26 (*C*H), 129.62 (*C*H), 137.34 (*C*H), 139.07 (*C*), 143.17 (*C*), 147.64 (*C*). $[\alpha]_D = +790$ ($c = 1$, $CHCl_3$). MS (EI): *m*/*z* 218 (M^+, 100%), 202 (50%). Anal. Calc. for $C_{17}H_{14}$: C, 93.52; H, 6.48. Found: C, 93.33; H, 6.42%.

4.3. (1S,2S)-trans-2-Phenyl-spiro(cyclopropane-1,1′-(4,7-dimethyl)indene) (S_2)

The title complex was prepared analogously to $\mathbf{S_1}$ from 10 g of (*R*)-phenyl-1,2- bis(methanesulfonyloxy)ethane and 5.4 g of 4,7-dimethyl-1*H*-indene. Yield: white crystalline powder, 7.0 g (83%). M.p.: 110 °C. ^1H NMR ($CDCl_3$): δ 2.19 (dd, 1H, $^2J_{HH} = 5.50$ Hz, $^3J_{HH} = 7.63$ Hz, CH_2), 2.38 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.52 (dd, 1H, $^2J_{HH} = 5.50$ Hz, $^3J_{HH} = 8.54$ Hz, CH_2), 3.81 (t, 1H, $^3J_{HH} = 8.24$ Hz, C*H*Ph), 5.83 (d, 1H, $^3J_{HH} = 5.49$ Hz, C*H*), 6.81 (d, 1H, $^3J_{HH} = 5.49$ Hz, C*H*), 6.84 (d, 1H, $^3J_{HH} = 7.63$ Hz, Ar*H*), 6.94 (d, 1H, $^3J_{HH} = 7.63$ Hz, Ar*H*), 7.18–7.30 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 14.97 (*C*H_2), 17.27 (*C*H_3), 18.10 (*C*H_3), 28.16 (*C*HPh), 42.27 (C_{spiro}), 126.51 (*C*H, Ar), 126.78 (*C*H, Ar), 126.83 (*C*H, Ar), 127.33 (*C*H), 128.16 (*C*), 128.23 (*C*H, Ar), 128.42 (*C*), 128.58 (*C*H, Ar), 138.21 (*C*H), 139.38 (*C*), 142.78 (*C*), 143.16 (*C*). $[\alpha]_D = +592$ ($c = 1$, $CHCl_3$). Anal. Calc. for $C_{19}H_{18}$: C, 92.63; H, 7.38. Found: C, 92.46; H, 7.28%.

4.4. (S)-[2-(3H-Inden-1-yl)-1-phenyl-ethyl]-diphenylphosphane (**L_1**)

$LiPPh_2$ was prepared by treating a solution of $HPPh_2$ (5.0 g, 26.7 mmol) in THF (50 mL) with *n*-BuLi (1.1 equiv.) at −78 °C. The deep orange solution thus formed was stirred for 15 min at room temperature and then cooled again to −78 °C. A solution of **S_1** (6.4 g, 29.3 mmol) in THF (10 mL) was added dropwise and the reaction mixture was allowed to reach room temperature overnight. The solvent was removed under reduced pressure and the oil left was washed several times with hexane until precipitation of the lithium salt of the ligand. The pale pink solid was dissolved with THF and degassed H_2O was added at room temperature. The ligand was extracted with CH_2Cl_2 (3×50 mL) and the combined organic extracts were dried over $MgSO_4$ and treated with decolorizing charcoal. The solution was filtered on a short column of basic alumina (activity I), and the solvent was removed under reduced pressure affording the analytical pure ligand. Yield: white crystalline solid, 9.9 g (91%). M.p.: 88–90 °C. ^{1}H NMR ($CDCl_3$): δ 3.10–3.29 (m, 2H, CH_2), 3.26 (br s, 2H, CH_2, Cp), 3.99 (m, 1H, C*H*Ph), 5.99 (br s, 1H, C*H*, Cp), 7.16–7.95 (m, 19H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 31.69 (d, $^2J_{CP} = 23.61$ Hz, *C*H_2), 37.71 (*C*H_2, Cp), 43.91 (d, $^1J_{CP} = 13.21$ Hz, *C*HPh), 118.71 (*C*H), 123.56 (*C*H), 124.33 (*C*H), 125.79 (*C*H), 126.06 (*C*H), 127.76 (d, $J_{CP} = 6.53$ Hz, *C*H), 128.00 (*C*H), 128.27 (*C*H), 128.58 (d, $J_{CP} = 7.04$ Hz, *C*H), 129.11 (d, $J_{CP} = 7.67$ Hz, *C*H), 129.41 (*C*H), 129.93 (*C*H, Cp), 133.15 (d, $J_{CP} = 17.46$ Hz, *C*H), 134.19 (d, $J_{CP} = 20.35$ Hz, *C*H), 136.73 (d, $J_{CP} = 14.82$ Hz, *C*), 141.02 (d, $J_{CP} = 7.66$ Hz, *C*), 141.58 (d, $J_{CP} = 13.06$ Hz, *C*), 144.14 (*C*), 145.15 (*C*). ^{31}P NMR ($CDCl_3$): δ 1.67 (s). $[\alpha]_D = -144$ ($c = 1$, toluene). MS (EI): *m*/*z* 404 (M^+, 10%). Anal. Calc. for $C_{29}H_{25}P$: C, 86.11; H, 6.24. Found: C, 85.96; H, 6.17%.

4.5. (S)-[2-(4,7-Dimethyl-3H-inden-1-yl)-1-phenyl-ethyl]-diphenylphosphane (**L_2**)

The title compound was prepared analogously to **L_1** from 5.1 g of **S_2** and 3.5 g of $HPPh_2$. Yield: white crystalline solid, 7.7 g (95%). M.p.: 99–101 °C. ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 3.06 (m, 2H, CH_2, Cp), 3.35–3.54 (m, 2H, CH_2), 3.78 (m, 1H, C*H*Ph), 6.12 (br s, 1H, C*H*, Cp), 6.95–7.95 (m, 17H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 18.16 (*C*H_3), 20.10 (*C*H_3), 34.11 (d, $^2J_{CP} = 23.0$ Hz, *C*H_2), 36.37 (*C*H_2, Cp), 43.67 (d, $^1J_{CP} = 13.82$ Hz, *C*HPh), 125.55 (*C*H), 125.94 (*C*H), 127.80 (*C*H), 128.01 (*C*H), 128.18 (*C*), 128.40 (d, $J_{CP} = 7.04$ Hz, *C*H), 128.99 (d, $J_{CP} = 7.16$ Hz, *C*H), 129.24 (*C*H), 130.14 (*C*H, Cp), 130.32 (*C*), 133.41 (d, $J_{CP} = 18.72$ Hz, *C*H), 133.82 (d, $J_{CP} = 19.72$ Hz, *C*H), 136.43 (d, $J_{CP} = 7.16$ Hz, *C*), 136.56 (d, $J_{CP} = 4.40$ Hz, *C*), 140.75 (d, $J_{CP} = 8.29$ Hz, *C*), 142.45 (*C*), 143.39 (d, $J_{CP} = 13.19$ Hz, *C*), 143.65 (*C*). ^{31}P NMR ($CDCl_3$): δ 3.60 (s). $[\alpha]_D = -178$ ($c = 1$, toluene). MS (EI): *m*/*z* 432 (M^+, 60%). Anal. Calc. for $C_{31}H_{29}P$: C, 86.08; H, 6.77. Found: C, 86.15; H, 6.73%.

4.6. (S,R_{pl})-[Rh(L_1)(ethylene)] (**Rh_1**) and (S,S_{pl})-[Rh(L_1)(ethylene)] (**Rh_2**)

L_1 (2.0 g, 4.9 mmol) was dissolved in THF (20 mL/g) and treated with *n*-BuLi (1.1 equiv.) at −78 °C. After stirring for 30 min at room temperature, this solution was added dropwise to a suspension of **5** (0.960 g, 2.45 mmol) in THF (10 mL) cooled at −78 °C. The mixture was allowed to slowly warm up to room temperature overnight. The solvent was removed under reduced pressure and the residue was dissolved in a hexane/toluene mixture (1:1) and filtered through a short pad of neutral alumina (activity IV). The solvent was evaporated and the product dried under high vacuum.

Rh_1 and **Rh_2** were obtained in a 61:39 diastereomeric ratio respectively (*de* = 22%). The two diastereomers were separated by chromatography on neutral alumina (activity IV) first eluting with hexane and then with toluene/hexane 1:1. **Rh_1** eluted first. The analytical data (elemental analysis and MS) were obtained on the mixture of the two diastereomers.

Rh_1. Yield: yellow solid, 1.4 g (52%) M.p.: 189–192 °C. ^{1}H NMR (CD_2Cl_2): δ 1.93 (m, 2H, C_2H_4), 1.99 (m, 2H, C_2H_4), 2.81 (td, 1H, $^3J_{HP(Rh)} = J_{HH} = 14.04$ Hz, $J_{HH} = 6.41$ Hz, CH_2), 3.06 (ddd, 1H, $^3J_{HP(Rh)} = 59.51$ Hz, $J_{HH} = 6.10$, 14.04 Hz, CH_2), 5.32 (m, 1H, *Ind*), 5.40 (m, 1H, C*H*Ph), 6.36 (m, 1H, *Ind*), 6.70 (m, 2H, Ar*H*), 7.00–7.75 (ms, 17H, Ar*H*). ^{13}C NMR (CD_2Cl_2): δ 30.29 (d, $^2J_{CP} = 8.67$ Hz, *C*H_2), 39.04 (d, $^1J_{CRh} = 14.45$ Hz, *C*$_2$H$_4$), 65.62 (d, $^1J_{CP} = 19.22$ Hz, *C*HPh), 73.87 (dd, $^2J_{CP} = 2.89$ Hz, $^1J_{CRh} = 14.45$ Hz, *C*H, *Ind*), 93.92 (t, $^1J_{CRh} = {}^2J_{CP} = 4.77$ Hz, C_{ipso}, *Ind*), 94.09 (t, $^1J_{CRh} = {}^2J_{CP} = 3.89$ Hz, *C*H, *Ind*), 109.45 (*C*), 117.32 (d, $J = 2.01$ Hz, *C*H), 117.65 (*C*), 118.55 (*C*H), 120.05 (*C*H), 123.26 (*C*H), 127.10 (d, $J = 1.88$ Hz, *C*H), 127.60 (d, $J = 9.55$ Hz, *C*H), 128.08 (d, $J = 2.01$ Hz, *C*H), 128.27 (d, $J_{CP} = 2.89$ Hz, *C*H), 128.45 (*C*H), 128.54 (*C*H), 129.11 (d, $J = 1.88$ Hz, *C*H), 130.73 (d, $J = 1.88$ Hz, *C*H), 131.07 (d, $J = 9.55$ Hz, *C*H), 133.73 (d, $J = 30.65$ Hz, *C*), 137.40 (d, $J = 12.56$ Hz, *C*H), 138.0 (d, $J = 8.54$ Hz, *C*). ^{31}P NMR (CD_2Cl_2): δ 86.95 (d, $^1J_{PRh} = 229.7$ Hz) $[\alpha]_D = -75$ ($c = 0.5$, toluene). MS (FAB): *m*/*z* 506 (M^+−(C_2H_4), 22%). Anal. Calc. for $C_{31}H_{28}PRh$: C, 69.67; H, 5.28. Found: C, 69.51; H, 5.57%.

Rh_2. Yield: yellow-orange solid, 0.84 g (31%). M.p.: 115–120 °C (dec.). ^{1}H NMR (CD_2Cl_2): δ 1.31 (m, 2H, C_2H_4), 2.10 (m, 2H, C_2H_4), 2.80 (ddd, 1H, $^3J_{HP(Rh)} = 60.43$ Hz, $J_{HH} = 6.10$, 14.04 Hz, CH_2), 3.13 (td, 1H, $^3J_{HP(Rh)} = J_{HH} = 14.04$ Hz, $J_{HH} = 6.72$ Hz, CH_2), 4.93 (m, 1H, C*H*Ph), 5.76 (m, 1H, *Ind*), 6.40 (m, 1H, *Ind*), 6.80 (m, 2H, Ar*H*), 7.0–7.45 (ms, 16H, Ar*H*). ^{13}C NMR (CD_2Cl_2): δ 26.89 (d, $^2J_{CP} = 7.66$ Hz, CH_2), 37.16 (d, $^1J_{CRh} = 14.45$ Hz, C_2H_4), 66.45 (d, $^1J_{CP} = 20.23$ Hz, C*H*Ph), 79.13 (d, $^1J_{CRh} = 12.44$ Hz, *C*H, *Ind*), 90.21 (t, $^1J_{CRh} =$

$^2J_{CP} = 2.89$ Hz, *C*H, *Ind*), 93.50 (t, $^1J_{CRh} = {}^2J_{CP} = 2.77$ Hz, C_{ipso}, *Ind*), 110.26 (*C*), 113.71 (*C*), 115.37 (*C*), 122.93 (d, $J = 1.88$ Hz, *C*H), 127.25 (*C*H), 127.37 (*C*H), 127.46 (*C*H), 128.14 (d, $J_{CP} = 2.01$ Hz, *C*H), 128.34 (*C*H), 128.43 (d, $J = 3.77$ Hz, *C*H), 128.50 (d, $J = 6.65$ Hz, *C*H), 131.06 (*C*H), 131.82 (d, $J = 9.54$ Hz, *C*H), 133.01 (d, $J = 35.42$ Hz, *C*), 138.98 (d, $J = 13.44$ Hz, *C*H). ^{31}P NMR (CD_2Cl_2): δ 91.93 (d, $^1J_{PRh} = 230.0$ Hz). $[\alpha]_D = +196$ ($c = 0.5$, toluene).

4.7. (*S,R*$_{pl}$)-[Rh(L$_2$)(ethylene)] (**Rh$_3$**) and (*S,S*$_{pl}$)-[Rh(L$_2$)(ethylene)] (**Rh$_4$**)

The title compounds were prepared according to the same procedure used to synthesize **Rh$_1$** and **Rh$_2$** from 1.8 g of **L$_2$** and 0.81 g of **5**. They were obtained in a 15:85 diastereomeric ratio respectively (*de* = 70%). The two diastereomers were separated by chromatography on neutral alumina (activity IV) first eluting with hexane and then with toluene/hexane 1:1. **Rh$_3$** eluted first. The analytical data (elemental analysis and MS) were obtained on the mixture of the two diastereomers.

Rh$_3$. Yield: brown-orange crystals, 0.32 g (14%). M.p.: 168–170 °C. ^{1}H NMR (CD_2Cl_2): δ 1.73 (m, 2H, C_2H_4), 2.04 (m, 2H, C_2H_4), 2.15 (s, 3H, CH_3), 2.83 (td, 1H, $^3J_{HP(Rh)} = J_{HH} = 14.34$ Hz, $J_{HH} = 5.80$ Hz, CH_2), 2.85 (s, 3H, CH_3), 3.17 (ddd, 1H, $^3J_{HP(Rh)} = 58.29$ Hz, $J_{HH} = 6.10$, 14.35 Hz, CH_2), 5.36 (m, 1H, *Ind*), 5.46 (m, 1H, C*H*Ph), 6.25 (m, 1H, *Ind*), 6.70 (m, 2H, Ar*H*), 6.76 (m, 2H, Ar*H*), 7.08-7.44 (m, 13H, Ar*H*). ^{13}C NMR (CD_2Cl_2): δ 18.60 (s, *C*H$_3$), 20.10 (s, *C*H$_3$), 32.80 (d, $^2J_{CP} = 8.67$ Hz, CH_2), 37.98 (d, $^1J_{CRh} = 13.44$ Hz, C_2H_4), 70.08 (d, $^1J_{CP} = 18.22$ Hz, C*H*Ph), 72.59 (dd, $^1J_{CRh} = 11.43$ Hz, $^2J_{CP} = 2.89$ Hz, *C*H, *Ind*), 93.85 (t, $^1J_{CRh} = {}^2J_{CP} = 3.89$ Hz, *C*H, *Ind*), 96.38 (t, $^1J_{CRh} = {}^2J_{CP} = 4.77$ Hz, C_{ipso}, *Ind*), 109.28 (*C*), 114.46 (*C*), 122.32 (*C*H), 122.96 (*C*H), 124.62 (d, $J_{CP} = 1.9$ Hz, *C*), 126.58 (*C*), 127.14 (*C*H), 127.56 (d, $J_{CP} = 9.55$ Hz, *C*H), 128.14 (d, $J_{CP} = 2.0$ Hz, *C*H), 128.39 (d, $J_{CP} = 2.89$ Hz, *C*H), 128.59 (d, $J_{CP} = 8.67$ Hz, *C*H), 128.98 (d, $J_{CP} = 2.89$ Hz, *C*H), 129.76 (d, $J_{CP} = 34.54$ Hz, *C*), 130.63 (d, $J_{CP} = 2.89$ Hz, *C*H), 131.20 (d, $J_{CP} = 9.67$ Hz, *C*H), 133.84 (d, $J_{CP} = 30.65$ Hz, *C*), 137.28 (d, $J_{CP} = 13.44$ Hz, *C*H), 137.93 (d, $J_{CP} = 8.67$ Hz, *C*). ^{31}P NMR (CD_2Cl_2): δ 89.50 (d, $^1J_{PRh} = 229.8$ Hz). $[\alpha]_D = -90$ ($c = 0.5$, toluene). MS (FAB): *m*/*z* 533 (M^+–(C_2H_4)–1, 60%). Anal. Calc. for $C_{33}H_{32}PRh$: C, 70.46; H, 5.69. Found: C, 69.98; H, 5.57%.

Rh$_4$. Yield: yellow-orange solid, 1.75 g (75%). M.p.: 175–180 °C. ^{1}H NMR (CD_2Cl_2): δ 1.18 (m, 2H, C_2H_4), 2.16 (m, 2H, C_2H_4), 2.17 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.87 (ddd, 1H, $^3J_{HP(Rh)} = 60.74$ Hz, $J_{HH} = 6.41$, 14.04 Hz, CH_2), 3.59 (td, 1H, $^3J_{HP(Rh)} = J_{HH} = 14.04$ Hz, $J_{HH} = 6.11$ Hz, CH_2), 4.91 (m, 1H, C*H*Ph), 5.81 (m, 1H, *Ind*), 6.28 (m, 1H, *Ind*), 6.66-7.45 (ms, 17H, Ar*H*). ^{13}C NMR (CD_2Cl_2): δ 18.60 (s, *C*H$_3$), 21.83 (s, *C*H$_3$), 29.15 (d, $^2J_{CP} = 7.66$ Hz, CH_2), 35.98 (d, $^1J_{CRh} = 14.32$ Hz, C_2H_4), 66.01 (d, $^1J_{CP} = 20.10$ Hz, C*H*Ph), 78.65 (dd, $^1J_{CRh} = 11.56$ Hz, $^2J_{CP} = 2.89$ Hz, *C*H, *Ind*), 89.66 (dd, $^1J_{CRh} = 4.77$ Hz, $^2J_{CP} = 2.89$ Hz, *C*H, *Ind*), 95.42 (t, $^1J_{CRh} = {}^2J_{CP} = 4.77$ Hz, C_{ipso}, *Ind*), 109.01 (*C*), 110.52 (d, $^1J_{CRh} = 4.77$ Hz,*C*), 122.20 (d, $J_{CP} = 2.01$ Hz, *C*H), 122.48 (*C*H), 124.75 (d, $J_{CP} = 2.89$ Hz, *C*), 127.24 (*C*H), 127.44 (*C*H), 128.16 (d, $J_{CP} = 1.88$ Hz, *C*H), 128.34 (d, $J_{CP} = 9.55$ Hz, *C*H), 128.58 (d, $J_{CP} = 2.89$ Hz, *C*H), 129,16 (*C*H), 129.90 (d, $J_{CP} = 29.67$ Hz, *C*), 131.10 (d, $J_{CP} = 2.89$ Hz, *C*H), 131.79 (d, $J_{CP} = 9.67$ Hz, *C*H), 133.40 (d, $J_{CP} = 35.43$ Hz, *C*), 137.95 (d, $J_{CP} = 13.32$ Hz, *C*H), 138.11 (d, $J_{CP} = 11.43$ Hz, *C*). ^{31}P NMR (CD_2Cl_2): δ 92.67 (d, $^1J_{PRh} = 227.3$ Hz). $[\alpha]_D = +139$ ($c = 0.5$, toluene).

4.8. (*S,R*$_{pl}$)-[Rh(L$_1$)(CH$_3$)I] (**Rh$_5$**)

0.509 g of **Rh$_1$** were dissolved in CH_2Cl_2 (10 mL) and excess amount of CH_3I (10 equiv.) was added. The progress of the reaction was monitored by ^{31}P NMR. After completion, the solvent was removed under reduced pressure and the compound was recovered as a crude product. It was dissolved in CH_2Cl_2 and filtered through neutral alumina (activity IV). Evaporation of the solvent afforded the pure compound. The two epimers (*S,R*$_{pl}$,*S*$_{Rh}$)-**Rh$_5$** and (*S,R*$_{pl}$,*R*$_{Rh}$)-**Rh$_5$** were obtained in a 1:1 ratio (*de* = 0%, checked by ^{31}P NMR of the crude reaction mixture). After filtration through alumina the *de* changed to 74%. Yield: dark-red solid, 0.60 g (98%). ^{1}H NMR (CD_2Cl_2): δ (major) −0.28 (dd, 3H, $^2J_{HRh} = 5.19$ Hz, $^3J_{HP} = 1.84$ Hz, CH_3), 2.72 (m, 1H, CH_2), 2.83 (m, 1H, CH_2), 4.96 (m, 1H, C*H*Ph), 5.98 (d, 1H, $J_{HH} = 2.74$ Hz, *Ind*), 6.71 (t, 1H, $J_{HH(Rh)} = 3.05$ Hz, *Ind*), 6.81 (d, 2H, $J_{HH} = 7.93$ Hz, Ar*H*), 7.02-7.65 (ms, 17H, Ar*H*); (minor) 1.14 (dd, 3H, $^2J_{HRh} = 5.80$ Hz, $^3J_{HP} = 2.75$ Hz, CH_3). ^{13}C NMR (CD_2Cl_2): δ (only the major diastereomer) 3.77 (dd, $^1J_{CRh} = 18.2$ Hz, $^2J_{CP} = 9.6$ Hz, *C*H$_3$), 20.80 (d, $^2J_{CP} = 5.78$ Hz, CH_2), 65.36 (d, $^1J_{CP} = 22.11$ Hz, *C*HPh), 92.90 (t, $J_{CP(Rh)} = 2.89$ Hz, *C*H, *Ind*), 93.08 (dd, $^1J_{CRh} = 7.66$ Hz, $^2J_{CP} = 1.88$ Hz, *C*H, *Ind*), 98.69 (m, *C*), 100.09 (dd, $^1J_{CRh} = 7.66$ Hz, $^2J_{CP} = 5.78$ Hz, *C*), 108.11 (d, $^1J_{CRh} = 6.66$ Hz, *C*), 117.44 (*C*H), 122.06 (d, $J_{CP} = 3.77$ Hz, *C*H), 124.85 (d, $J_{CP} = 2.76$ Hz, *C*H), 127.84 (d, $J_{CP} = 10.5$ Hz, *C*H), 127.94 (*C*), 127.98 (*C*H), 128.00 (*C*H), 128.12 (d, $J_{CP} = 9.5$ Hz, *C*H), 128.25 (d, $J_{CP} = 1.88$ Hz, *C*H), 128.32 (*C*H), 128.46 (*C*), 129.24 (d, $J_{CP} = 3.89$ Hz, *C*H), 130.40 (*C*H), 131.93 (*C*H), 132.48 (d, $J_{CP} = 7.66$ Hz, *C*H), 136.03 (*C*), 138.77 (d, $J_{CP} = 10.55$ Hz, *C*H). ^{31}P NMR (CD_2Cl_2): δ 86.09 (d, $^1J_{PRh} = 186.39$ Hz, major), 76.49 (d, $^1J_{PRh} = 171.57$ Hz, minor). MS (FAB): *m*/*z* 506 (M^+–CH_3I, 70%). Anal. Calc. for $C_{30}H_{27}IPRh$: C, 55.58; H, 4.20. Found: C, 56.01; H, 4.12%.

4.9. (*S,S*$_{pl}$,*S*$_{Rh}$)-[Rh(L$_1$)(CH$_3$)I] (**Rh$_6$**)

The title compound was prepared according to the general procedure used for **Rh$_5$** from 0.300 g of **Rh$_2$**. Only

one diastereomer could be observed ($de > 98\%$, checked by ^{31}P NMR of the crude reaction mixture). Yield: yellow solid, 0.345 g (95%). M.p.: 173–175 °C. ^{1}H NMR (CD_2Cl_2): δ 1.30 (dd, 3H, $^{2}J_{HRh} = 5.80$ Hz, $^{3}J_{HP} = 2.44$ Hz, CH_3), 2.65 (ddd, 1H, $^{3}J_{HP(Rh)} = 60.73$ Hz, $J_{HH} = 7.32$, 14.65 Hz, CH_2), 3.17 (td, 1H, $^{3}J_{HP(Rh)} = J_{HH} = 14.04$ Hz, $J_{HH} = 5.19$ Hz, CH_2), 4.90 (m, 1H, C*H*Ph), 5.15 (dd, 1H, $^{3}J_{HH} = 2.74$ Hz, $J_{HRh(P)} = 1.52$ Hz, *Ind*), 5.91 (dd, 1H, $^{3}J_{HH} = 2.74$ Hz, $J_{HRh(P)} = 7.93$ Hz, *Ind*), 7.01-7.57 (ms, 19H, Ar*H*). ^{13}C NMR (CD_2Cl_2): δ −9.98 (dd, $^{1}J_{CRh} = 23.12$ Hz, $^{2}J_{CP} = 7.66$ Hz, *C*H$_3$), 27.92 (d, $^{2}J_{CP} = 5.78$ Hz, *C*H$_2$), 65.70 (d, $^{1}J_{CP} = 21.11$ Hz, *C*HPh), 76.90 (dd, $^{1}J_{CRh} = 18.21$ Hz, $^{2}J_{CP} = 2.89$ Hz, *C*H, *Ind*), 89.87 (t, $J_{CP(Rh)} = 3.77$ Hz, *C*H, *Ind*), 99.12 (m, *C*), 108.90 (*C*), 120.40 (*C*H), 122.64 (*C*H), 124.14 (*C*), 125.59 (*C*H), 125.76 (*C*H), 127.48 (d, $J_{CP} = 10.55$ Hz, *C*H), 128.06 (*C*H), 128.14 (*C*H), 128.45 (*C*H), 128.51 (*C*H), 129.32 (*C*), 129.65 (*C*H), 130.35 (d, $J_{CP} = 2.89$ Hz, *C*H), 131.06 (*C*H), 132.07 (*C*H), 133.12 (d, $J_{CP} = 7.66$ Hz, *C*H), 136.37 (d, $J_{CP} = 10.55$ Hz, *C*), 139.26 (d, $J_{CP} = 10.55$ Hz, *C*H). ^{31}P NMR (CD_2Cl_2): δ 77.06 (d, $^{1}J_{PRh} = 171.31$ Hz). $[\alpha]_D = +8$ ($c = 0.5$, toluene). MS (FAB): m/z 506 (M^+−MeI, 70%). Anal. Calc. for $C_{30}H_{27}IPRh$: C, 55.58; H, 4.20. Found: C, 55.23; H, 4.32%.

4.10. (*S*,R_{pl})-[Rh(L$_2$)(CH$_3$)I] (**Rh$_7$**)

The title compound was prepared according to the general procedure from 0.150 g of **Rh$_3$**. The two diastereomers (*S*,R_{pl},S_{Rh})-**Rh$_7$** and (*S*,R_{pl},R_{Rh})-**Rh$_7$** were obtained in a 25:1 diastereomeric ratio respectively ($de = 92\%$, checked by ^{31}P NMR of the crude reaction mixture). Yield: dark-red solid, 0.170 g (95%). ^{1}H NMR (CD_2Cl_2): δ (major) −0.20 (dd, 3H, $^{2}J_{HRh} = 5.50$ Hz, $^{3}J_{HP} = 1.83$ Hz, CH_3), 2.29 (s, 3H, CH_3, *Ind*), 2.54 (s, 3H, CH_3, *Ind*), 2.81–2.98 (ms, 2H, CH_2), 5.17 (m, 1H, C*H*Ph), 5.91 (d, 1H, $^{3}J_{HH} = 3.35$ Hz, *Ind*), 6.68 (t, 1H, $J_{HH(Rh)} = 3.05$ Hz, *Ind*), 6.79 (m, 1H, Ar*H*), 6.90 (m, 2H, Ar*H*), 7.11 (m, 1H, Ar*H*), 7.13–7.63 (ms, 13H, Ar*H*); (minor) 1.16 (dd, 3H, $^{2}J_{HRh} = 6.10$ Hz, $^{3}J_{HP} = 2.44$ Hz, CH_3). ^{13}C NMR (CD_2Cl_2): δ (only the major diastereomer) 5.61 (dd, $^{1}J_{CRh} = 20.10$ Hz, $^{2}J_{CP} = 10.55$ Hz, *C*H$_3$), 19.00 (*C*H$_3$, *Ind*), 19.44 (*C*H$_3$, *Ind*), 32.68 (d, $^{2}J_{CP} = 5.78$ Hz, *C*H$_2$), 70.12 (d, $^{1}J_{CP} = 21.99$ Hz, *C*HPh), 93.16 (d, $^{1}J_{CRh} = 6.66$ Hz, *C*H, *Ind*), 94.45 (d, $^{1}J_{CRh} = 2.89$ Hz, *C*H, *Ind*), 97.77 (m, *C*), 105.24 (m, *C*), 122.83 (d, $J_{CP(Rh)} = 3.77$ Hz, *C*H), 123.69 (*C*), 127.78 (d, $J_{CP} = 9.67$ Hz, *C*H), 127.99 (*C*H), 128.08 (*C*H), 128.48 (*C*H), 129.30 (*C*), 129.48 (d, $J_{CP} = 3.89$ Hz, *C*H), 129.63 (*C*), 129.80 (*C*), 130.18 (d, $J_{CP} = 2.89$ Hz, *C*H), 130.29 (d, $J_{CP} = 2.89$ Hz, *C*H), 130.62 (d, $J_{CP} = 4.90$ Hz, *C*), 131.89 (*C*H), 132.80 (d, $J_{CP} = 7.66$ Hz, *C*H), 135.48 (d, $J_{CP} = 10.55$ Hz, *C*), 136.26 (d, $J_{CP} = 9.55$ Hz, *C*), 138.80 (d, $J_{CP} = 11.43$ Hz, *C*H). ^{31}P NMR (CD_2Cl_2): δ 88.05 (d, $^{1}J_{PRh} = 187.8$ Hz, major), 77.66 (d, $^{1}J_{PRh} = 170.50$ Hz, minor). MS (FAB): m/z 534 (M^+−CH$_3$I, 100%). Anal. Calc. for $C_{32}H_{31}IPRh$: C, 56.82; H, 4.62. Found: C, 56.51; H, 4.49.

4.11. (*S*,S_{pl},S_{Rh})-[Rh(L$_2$)(CH$_3$)I] (**Rh$_8$**)

The title compound was prepared according to the general procedure from 0.450 g of **Rh$_4$**. Only one diastereomer could be observed ($de > 98\%$, checked by ^{31}P NMR of the crude reaction mixture). Yield: yellow solid, 0.50 g (93%). M.p.: 179–180 °C. ^{1}H NMR (CD_2Cl_2): δ 1.29 (dd, 3H, $^{2}J_{HRh} = 6.10$ Hz, $^{3}J_{HP} = 2.75$ Hz, CH_3), 2.37 (s, 3H, CH_3, *Ind*), 2.39 (s, 3H, CH_3, *Ind*), 2.71 (ddd, 1H, $^{3}J_{HP(Rh)} = 59.81$ Hz, $J_{HH} = 7.93$, 14.65 Hz, CH_2), 3.61 (td, 1H, $^{3}J_{HP(Rh)} = J_{HH} = 14.34$ Hz, $J_{HH} = 4.27$ Hz, CH_2), 4.90 (dt, 1H, $^{2}J_{HP} = 13.12$ Hz, $^{3}J_{HH} = 7.93$ Hz, C*H*Ph), 5.00 (dd, 1H, $^{3}J_{HH} = 2.75$ Hz, $J_{HRh(P)} = 1.22$ Hz, *Ind*), 5.79 (dd, 1H, $^{3}J_{HH} = 2.75$ Hz, $J_{HRh(P)} = 7.93$ Hz, *Ind*), 6.86 (d, 1H, $J_{HH} = 6.72$ Hz), 7.03–7.55 (ms, 16H, Ar*H*). ^{13}C NMR (CD_2Cl_2): δ −10.73 (dd, $^{1}J_{CRh} = 22.24$ Hz, $^{2}J_{CP} = 7.79$ Hz, *C*H$_3$), 19.12 (*C*H$_3$, *Ind*), 22.35 (*C*H$_3$, *Ind*), 29.98 (d, $^{2}J_{CP} = 6.67$ Hz, *C*H$_2$), 66.64 (d, $^{1}J_{CP} = 21.11$ Hz, *C*HPh), 76.01 (dd, $^{1}J_{CRh} = 17.84$ Hz, $^{2}J_{CP} = 3.39$ Hz, *C*H, *Ind*), 88.38 (dd, $^{1}J_{CRh} = 6.66$ Hz, $^{2}J_{CP} = 4.39$ Hz, *C*H, *Ind*), 101.50 (m, *C*), 108.60 (*C*), 121.84 (*C*), 126.16 (*C*H), 127.58 (d, $J_{CP} = 11.06$ Hz, *C*H), 127.99 (*C*H), 128.06 (*C*H), 128.52 (*C*H), 129.55 (*C*H), 129.81 (*C*H), 129.85 (d, $J_{CP} = 6.66$ Hz, *C*H), 129.89 (*C*), 129.93 (*C*), 130.16 (*C*), 130.20 (d, $J_{CP} = 2.14$ Hz, *C*H), 132.12 (d, $J_{CP} = 2.26$ Hz, *C*H), 133.00 (*C*), 133.15 (d, $J_{CP} = 7.79$ Hz, *C*H), 136.68 (d, $J_{CP} = 8.92$ Hz, *C*), 139.17 (d, $J_{CP} = 12.19$ Hz, *C*H). ^{31}P NMR (CD_2Cl_2): δ 77.55 (d, $^{1}J_{PRh} = 171.30$ Hz). $[\alpha]_D = +11$ ($c = 0.5$, toluene). MS (FAB): m/z 661 (M^+−CH$_3$, 10%), 534 (M^+−CH$_3$I, 100%). Anal. Calc. for $C_{32}H_{31}IPRh$: C, 56.82; H, 4.62. Found: C, 56.61; H, 4.43%.

4.12. X-ray structure determination of **Rh$_3$**

Geometry and intensity data were collected with Mo Kα radiation at 213 K on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator ($\lambda = 0.71073$ Å). Crystal data: monoclinic space group $P2_1$ (no. 4), $a = 8.889(3)$ Å, $b = 13.3152(17)$ Å, $c = 11.3186(14)$ Å, $\beta = 99.27(2)°$, $V = 1322.1(5)$ Å^3, $Z = 2$, $d_{calc} = 1.413$ g cm^{-3}, $\mu = 0.726$ mm^{-1}, $F(000) = 580$. Nine thousand one hundred and eighty-eight intensity data were collected in the range $3.0 < \theta < 26.0°$ on an orange plate of approximate dimensions $0.38 \times 0.30 \times 0.03$ mm^3. A numerical absorption correction based on GAUSSIAN integration [30] was applied. The structure was solved by direct methods [31] and refined [32] on F^2 with anisotropic displacement parameters for all non-hydrogen atoms; H atoms of the coordinated olefin were refined isotropically, remaining hydrogen atoms were included as riding in standard geometry. 5149 independent data (4371 observations with $I > 2.0\sigma(I)$) for 334 variables resulted in $\omega R_2 = 0.0734$ ($R = 0.0382$), GOF = 0.0991, and an enantiomorph polarity parameter [33] of 0.03(3).

5. Supplementary material

CCDC 612001 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

The generous financial support by the Deutsche Forschungsgemeinschaft (DFG) within the Collaborative Research Centre (SFB 380) "Asymmetric Syntheses with Chemical and Biological Means" is acknowledged. V.P. thanks the DFG for a Ph.D. fellowship within its graduate training program "Methods in Asymmetric Synthesis" (GK 440).

References

[1] J. Okuda, Comm. Inorg. Chem. 16 (1994) 185.
[2] (a) H. Butenschön, Chem. Rev. 100 (2000) 1527;
(b) U. Siemeling, Chem. Rev. 100 (2000) 1495;
(c) H. Braunschweig, F.M. Breitling, Coord. Chem. Rev. 250 (2006) 2691;
(d) C. Müller, D. Vos, P. Jutzi, J. Organomet. Chem. 600 (2000) 127;
(e) A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.
[3] (a) G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermühle, C. Krüger, M. Nolte, S. Werner, J. Am. Chem. Soc. 115 (1993) 4590;
(b) L. Bell, R.J. Whitby, R.V.H. Jones, M.C.H. Standen, Tretrahedron Lett. 37 (1996) 7139;
(c) L. Bell, D.C. Brookings, G.J. Dawson, R.J. Whitby, R.V.H. Jones, M.C.H. Standen, Tetrahedron 54 (1998) 14617;
(d) Y. Kataoka, Y. Saito, K. Nagata, K. Kitamura, A. Shibahara, K. Tani, Chem. Lett. (1995) 833;
(e) Y. Kataoka, Y. Saito, K. Nagata, K. Kitamura, A. Shibahara, K. Tani, Chem. Lett. (1996) 577;
(f) A.A.H. van der Zeijden, J. Jimenez, C. Mattheis, C. Wagner, K. Merzweiler, Eur. J. Inorg. Chem. (1999) 1919;
(g) T.A. Mobley, R.G. Bergman, J. Am. Chem. Soc. 120 (1998) 3253;
(h) S.N. Paisner, G.G. Lavoie, R.G. Bergman, Inorg. Chim. Acta 334 (2002) 253;
(i) M.L.H. Green, N.M. Walker, J. Organomet. Chem. 344 (1988) 379.
[4] (a) M.P. Hogerheide, J. Boersma, G. van Koten, Coord. Chem. Rev. 155 (1996) 87;
(b) I. Lee, F. Dahan, A. Maisonnat, R. Poilblanc, Organometallics 13 (1994) 2743;
(c) L. Lefort, T.W. Crane, M.D. Farwell, D.M. Baruch, J.A. Kaeuper, R.J. Lachicotte, W.D. Jones, Organometallics 17 (1998) 3889;
(d) S.R. Klei, T.D. Tilley, R.G. Bergman, Organometallics 21 (2002) 4905;
(e) A.C. McConnell, P.J. Pogorzelec, A.M.Z. Slawin, G.L. Williams, P.I.P. Elliott, A. Haynes, A.C. Marr, D.J. Cole-Hamilton, Dalton Trans. 1 (2006) 91.
[5] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.
[6] P. Jutzi, M.O. Kristen, B. Neumann, H.-G. Stammler, Organometallics 13 (1994) 3854.
[7] Y. Nishibayashi, I. Takei, M. Hidai, Organometallics 16 (1997) 3091.
[8] (a) Y. Kataoka, Y. Saito, A. Shibahara, K. Tani, Chem. Lett. (1997) 621;
(b) Y. Kataoka, A. Shibahara, Y. Saito, T. Yamagata, K. Tani, Organometallics 17 (1998) 4338;
(c) Y. Kataoka, Y. Iwato, T. Yamagata, K. Tani, Organometallics 18 (1999) 5423;
(d) Y. Kataoka, A. Shibahara, T. Yamagata, K. Tani, Organometallics 20 (2001) 2431;
(e) Y. Kataoka, Y. Iwato, A. Shibahara, T. Yamagata, K. Tani, Chem. Commun. (2000) 841;
(f) Y. Kataoka, Y. Nakagawa, A. Shibahara, T. Yamagata, K. Mashima, K. Tani, Organometallics 23 (2004) 2095.
[9] D.C. Brookings, S.A. Harrison, R.J. Whitby, B. Crombie, R.V.H. Jones, Organometallics 20 (2001) 4574.
[10] (a) A. Doppiu, U. Englert, A. Salzer, Chem. Commun. (2004) 2166;
(b) S. Ciruelos, A. Doppiu, U. Englert, A. Salzer, J. Organomet. Chem. 663 (2002) 183;
(c) S. Ciruelos, U. Englert, A. Salzer, C. Bolm, A. Maischak, Organometallics 19 (2000) 2240.
[11] A. Doppiu, U. Englert, V. Peters, A. Salzer, Inorg. Chim. Acta 357 (2003) 1773.
[12] (a) A. Doppiu, A. Salzer, Eur. J. Inorg. Chem. (2004) 2244;
(b) E. Becker, K. Mereiter, M. Puchberger, R. Schmid, K. Kirchner, A. Doppiu, A. Salzer, Organometallics 22 (2003) 3164;
(c) A. Doppiu, U. Englert, A. Salzer, Inorg. Chim. Acta 350 (2003) 435.
[13] The absolute configuration of $\mathbf{S_1}$ was also determined by X-ray analysis. Chunhua Hu, personal communication.
[14] S.B. Wild, Coord. Chem. Rev. 166 (1997) 291.
[15] (a) J.W. Faller, Adv. Organomet. Chem. 16 (1977) 211;
(b) For a discussion on the ethylene ligand in $[Rh(C_5H_5)(C_2H_4)_2]$ see:R. Cramer, J. Am. Chem. Soc. 86 (1964) 217.
[16] The planar chirality in the complexes is assigned *R* or *S* based on the Cahn–Ingold–Prelog configuration of the position 1 of the ligand where the metal is treated as being individually bonded to all five C-atoms of the cyclopentadienyl part of the indenyl group. The position 1 chosen is that at the carbon bearing the linker.
[17] F. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
[18] When the reaction was carried out at room temperature, the two diastereomers were obtained in equimolar amount. The isolated pure diastereomers do not interconvert when left for several days in THF-solution at room temperature, nor under reflux for several hours in THF or benzene.
[19] C. Köcher, W.A. Herrmann, J. Organomet. Chem. 532 (1997) 261.
[20] (a) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987;
(b) Ch. Elschenbroich, Organometallics, Wiley-VCH, Weinheim, Germany, 2006.
[21] (a) D. Forster, Adv. Organomet. Chem. 17 (1979) 255;
(b) M.J. Howard, M.D. Jones, M.S. Roberts, S.A. Taylor, Catal. Today 18 (1993) 325;
(c) A. Haynes, B.E. Mann, G.E. Morris, P.M. Maitlis, J. Am. Chem. Soc. 115 (1993) 4093;
(d) P.M. Maitlis, A. Haynes, G.J. Sunley, M.J. Howard, J. Chem. Soc., Dalton Trans. (1996) 2187;
(e) G.J. Sunley, D.J. Watson, Catal. Today 58 (2000) 293.
[22] (a) For detailed comprehensive review see: C. Ganter, Chem. Soc. Rev. 32 (2003) 130, and references cited therein;
(b) H. Brunner, Eur. J. Inorg. Chem. (2001) 905;
(c) H. Brunner, A. Köllnberger, A. Mehmood, T. Tsuno, M. Zabel, Organometallics 23 (2004) 4006;
(d) F. Morandini, G. Pilloni, G. Consiglio, A. Sironi, M. Moret, Organometallics 12 (1993) 3495.
[23] (a) M. Feliz, Z. Freixa, P.W.N.M. Van Leeuwen, C. Bo, Organometallics 24 (2005) 5718;
(b) S. Henderson, R.A. Henderson, Adv. Phys. Org. Chem. 23 (1987) 1;
(c) J.A. Labinger, J.A. Osborn, Inorg. Chem. 19 (1980) 3230;
(d) J.A. Venter, J.G. Leipoldt, R. van Eldik, Inorg. Chem. 30 (1991) 2207;

(e) T.L. Hall, M.F. Lappert, P.W. Lednor, J. Chem. Soc., Dalton Trans. (1980) 1448.
[24] (a) T.R. Griffin, D.B. Cook, A. Haynes, J.M. Pearson, D. Monti, G.E. Morris, J. Am. Chem. Soc. 118 (1996) 3029;
(b) F.M. Bickelhaupt, T. Ziegler, P. Von Ragué Schleyer, Organometallics 14 (1995) 2288.
[25] The intermediate methyl-ethylene species (diastereomerically pure) have been spectroscopically observed for **Rh_2** and **Rh_4** but they could not be isolated. No intermediate species could be detected for **Rh_1** and **Rh_3**.
[26] (a) M.J. Calhorda, L.F. Veiros, Comm. Inorg. Chem. 22 (2001) 375;
(b) J.M. O'Connor, C.P. Casey, Chem. Rev. 87 (1987) 307.
[27] W.H. Bosch, U. Englert, B. Pfister, R. Stauber, A. Salzer, J. Organomet. Chem. 506 (1996) 273.
[28] G. Erker, C. Psiorz, R. Fröhlich, M. Grehl, C. Krüger, R. Noe, M. Nolte, Tetrahedron 51 (1995) 4347.
[29] R. Cramer, Inorg. Synth. 15 (1973) 14.
[30] P. Coppens, L. Leiserowitz, D. Rabinovich, Acta Crystallogr. 18 (1965) 1035.
[31] G.M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of Göttingen, 1997.
[32] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
[33] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.