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New optically active 'constrained-geometry' cyclopentadienyl-phosphine ligands and their metal complexes

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Dedicated to Professor Pascual Royo Gracia.

Abstract

Optically active cyclopentadienyl-phosphine ligands were prepared by stereoselective ring opening of spirocyclopentadienes. Optically active metal complexes were made from these new bidentate ligands. A new stereogenic center at rhodium was generated by oxidative addition reactions with high stereoselectivity. The absolute configuration of the major isomer of one rhodium complex was determined by a X-ray structure analysis.

Keywords: Constrained-geometry; Cyclopentadienyl-phosphine ligands; Rhodium

1. Introduction

Chelating ligands containing both a cyclopentadienyl and a heteroatom have received considerable attention in recent years. A special attraction of this kind of ligand is the possibility to vary its three structural components independently, namely the cyclopentadienyl ring, the hydrocarbon linker and the heteroatom and its substituents. The heteroatom can be a hard nucleophile such as oxygen and nitrogen, but also a soft nucleophile such as phosphorus, arsenic or sulfur. Both classes of bidentate ligands and their metal complexes have recently been reviewed [1,2]. The increased interest in these ligands is in part due to their application as so-called 'constraint-geometry' catalysts (CGC) in industrial Ziegler–Natta catalysis [3]. Among the possible heteroatoms, phosphorus has been receiving growing interest in view of the general importance of phosphine ligands in organometallic chemistry and homogeneous catalysis. A cyclopentadienyl-phosphine ligand, connected by an appropriate linker, acts as a 6+2 electron ligand and forms a stable chelate ring with both early and late transition metals [2].

Additionally, chirality introduced into systems in which phosphorus is coordinated to the metal may assist in controlling the stereochemistry of reactions at the metal center, ultimately leading to an increase in stereoselection in stoichiometric and catalytic reactions. This may be dependent on the spatial proximity of the stereogenic center(s) to the metal, the rigidity of the chelate ring as well as the shape of the chiral 'pocket' created by it.

Although recent reports of such compounds have appeared in the literature in which the highly selective formation of new stereogenic centers at the transition metal have been presented [4,5], there still remains a dearth of general procedures to prepare suitable ligands by a method that allows their modular construction by independent variation of the three components. We have recently reported such a route in a preliminary communication [6] by adapting the method of Kauffmann for ring-opening substituted spiro[2,4]hepta-4,6-dienes [7].

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2. Discussion

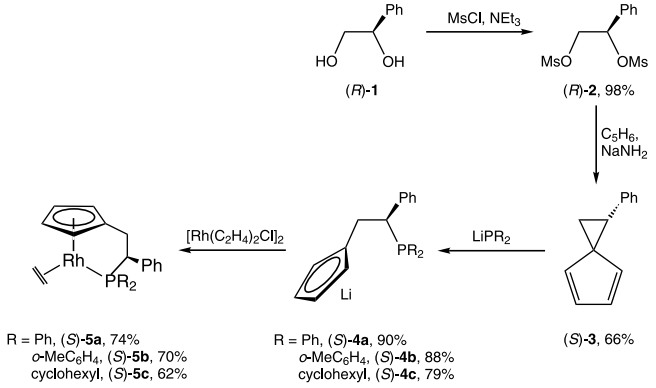
A convenient approach to chiral derivatives of spirocyclopentadienes starts from optically active 1,2-diols. We started our investigation with (*R*)-1-phenylethane-1,2-diol, [(*R*)-**1**], which was converted into the bismethansulfonate ester (*R*)-**2** in quantitative yield. Displacement of the methansulfonate groups by cyclopentadiene–$NaNH_2$ formed the spiroannulated diene (*S*)-**3**. Both carbons in (*R*)-**2** undergo inversion. The ring opening reaction of (*S*)-**3** with $LiPPh_2$ proceeds with complete regioselectivity at the substituted carbon atom of the cyclopropane ring, bringing the stereogenic center close to the phosphorus atom.

A related route, starting from chiral styrene epoxide, which was ring-opened with indenyllithium, has also recently been reported by Whitby [8]. As fas as we know, the only precedent for a similar ring opening of a chiral (but racemic) substituted spiro[2,4]hepta-4,6-diene was reported by Rieger in a reaction sequence to synthesize unsymmetrical *ansa*-indenyl and -fluorenyl ligands with chiral ethylene bridges [9].

The ring-opening reaction of (*S*)-**3** with $LiPPh_2$ proceeds with complete inversion of configuration at the stereogenic center as was proven by an X-ray structure of the rhodium complex (*S*)-**5a** [6] (Scheme 1).

This synthetic pathway is very general and should allow the synthesis of a wide variety of derivatives for the following reasons:

a) The chiral precursors, e.g. monosubstituted ethane-1,2-diols, are easily available in large quantities by the general Jacobsen route [10].
b) The lithium salt can be used directly for the synthesis of metal complexes [6] or quenched with water to the corresponding cyclopentadiene or with $(CH_3)_3SiCl$ to the trimethylsilylderivative [2]. If desired, the phosphine can at that stage be protected by the BH_3 group.
c) The method can be combined with other ways to introduce chirality into the ligands. Ring opening of a spiroannelated indene as reported by Rieger [9] should lead to ligands combining both central and planar chirality. Alternatively, opening reactions with chiral nucleophiles might produce ligands which contain additional chiral information within the nucleophile.
d) According to Kauffmann's protocol, the length of the spacer between cyclopentadienyl ring and phosphorus can also be modified by changing the length of the diol-precursor. The scope of the nucleophile should also allow for considerable variation as many secondary phosphines are available.



Scheme 1.

We have reacted the lithium salt (*S*)-**4** with some metal precursors, as reported in the preliminary communication. In particular, we have prepared the rhodium complexes (*S*)-**5** and (*S*)-**7**. We have also treated (*S*)-**3** with $LiP(o\text{-tolyl})_2$ and $LiP(cyclohexyl)_2$ to give (*S*)-**4b** and (*S*)-**4c**, respectively. These were treated with $[Rh(C_2H_4)_2Cl]_2$ and gave (*S*)-**5b** and (*S*)-**5c**.

A major goal in preparing these complexes with chiral chelating ligands was their application in stereoselective stoichiometric and catalytic reactions. As a model reaction to explore the efficiency in which the chiral ligand controlled the stereochemistry at the metal center we chose the oxidative addition of methyl iodide. It had been shown in several examples that almost complete control of diastereoselectivity was achieved by chiral Cp-linked phosphines [11,12]. We reacted the rhodium complexes (*S*)-**5a**–(*S*)-**5c** and (*S*)-**7** with methyl iodide at room temperature (Scheme 2).

The best diastereoselectivity was observed with (*S*)-**6a** and (*S*)-**6b**, which both gave a diastereomeric ratio of 93:7. This value is somewhat lower than that reported by Tani for his 'third generation' Cp′–P ligands [11]. This may possibly be due to the fact that the Tani ligands exhibit planar chirality as they are derived from indene and have in some cases additional neomenthyl substituents. Indenyl ligands, however, have the serious disadvantage that metal complexation invariably leads to diastereomers which have to be separated.

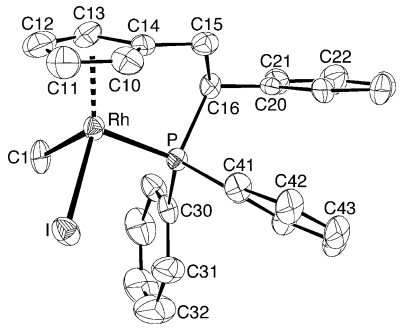
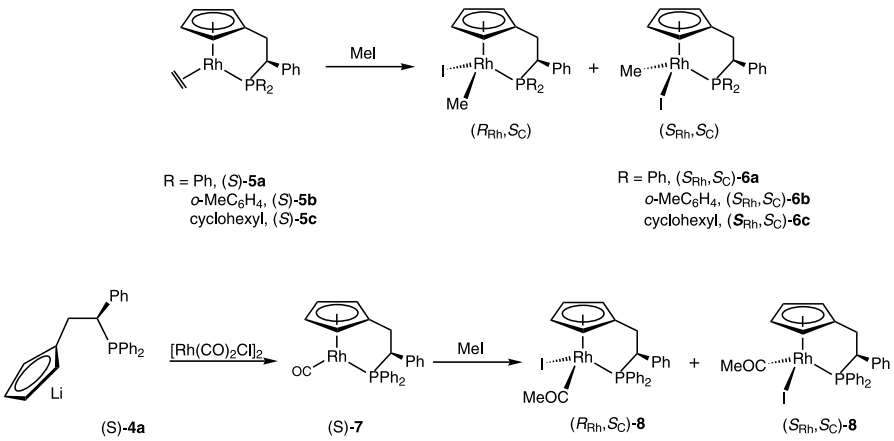


Fig. 1. Displacement ellipsoid plot of (S_{Rh},S_C)-**6a** (Platon98, A.L. Spek, University of Utrecht; 50% probability, H atoms omitted).



Scheme 2.

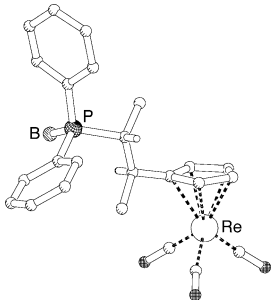


Fig. 2. Graphical summary of one of the two independent molecules of (*R*,*R*)-**12**.

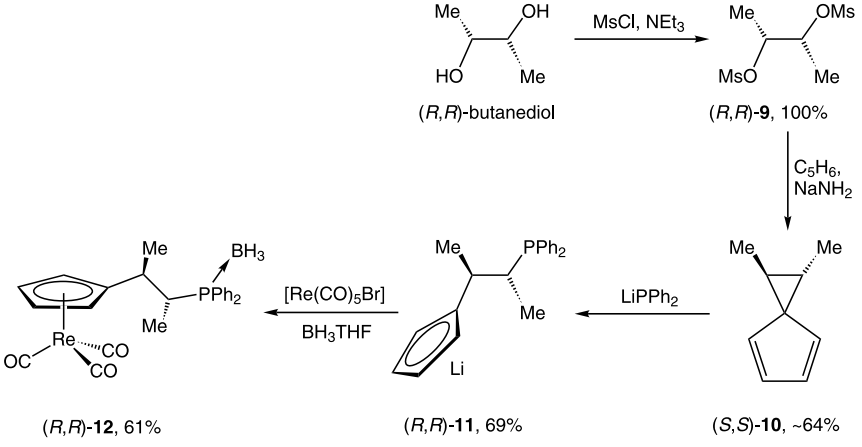
The major isomer of (*S*′)-**6a** was isolated in pure form by recrystalization and single crystals were grown from CH_2Cl_2–hexane. The X-ray structure is shown in Fig. 1 and confirms the stereochemical assignment as (S_{Rh},S_C).

We also prepared the carbonyl complex (*S*)-**7** from $[Rh(CO)_2Cl]_2$ to (*S*)-**4a**. Reaction with methyl iodide gave the acetyliodo complex (S_{Rh},S_C)-**8** and its diastereomer (R_{Rh},S_C)-**8** in a ratio of 91:9. Again, the major isomer could be isolated in pure form by recrystalization. We are as yet unable to assign the configuration of the major isomer.

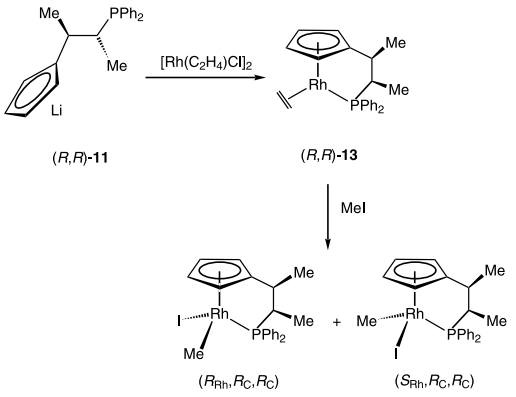
To explore further routes into Cp-linked phosphines, we also prepared a spiro-cyclopentadiene with a doubly substituted linker from commercially available (*R*,*R*)-butanediol. Treatment of the dimesylate (*R*,*R*)-**9** with cyclopentadiene–$NaNH_2$ gave good yields of (*S*,*S*)-**10**, which was ring-opened with $LiPPh_2$ to give the lithium salt (*R*,*R*)-**11**. Treatment with $Re(CO)_5Br$ gave good yields of the rhenium complex (*R*,*R*)-**12**, which was protected with BH_3 (Scheme 3).

Unfortunately, the single crystals obtained after recrystalization from hexane were of relatively poor quality and no details of the structure will be reported or deposited. A graphical summary of one of the two similar independent molecules is shown in Fig. 2.

(*R*,*R*)-**11** was also reacted with $[Rh(C_2H_4)_2Cl]_2$ to produce complex (*R*,*R*)-**13** and reacted with methyl iodide (Scheme 4). The two isomers were formed in a ratio of 90:10, de = 80%. The major isomer could be obtained in pure form by recrystalization. It was not possible to assign a definite configuration to both diastereomers.



Scheme 3.



Scheme 4.

Our experiments with the oxidative addition of methyl iodide have shown that a very good diastereoselectivity can be achieved with the chelating ligands developed by us. Further experiments will be necessary to optimize them. We are currently preparing spiro compounds based on indene and fluorene and will introduce other more bulky phosphorus nucleophiles to optimize the chiral environment of our ligands to such an extend that complete control of the chiral metal center becomes possible.

3. Experimental

All reactions were carried out under nitrogen using standard Schlenck techniques. Solvents were dried and deoxygenated by standard methods. NMR spectra were recorded on a Varian Mercury 200 (200MHz, ^{1}H; 50 MHz, ^{13}C; 81 MHz, ^{31}P) and a Varian Unity 500 (500 MHz, ^{1}H; 125 MHz, ^{13}C; 202 MHz, ^{31}P) at ambient temperature. ^{1}H and ^{13}C Chemical shifts (δ) are given in ppm relative to $SiMe_4$, ^{31}P relative to H_3PO_4. Mass spectra were obtained with a Finnigan MAT 95 spectrometer. Elemental analyses were obtained on a Carlo Erba Strumentazione element analyzer, Model 1106. (*R*,*R*)-2,3-butanediol (Strem), methanesulfonyl chloride (Fluka), $NaNH_2$ (Merck), Li^{n}Bu (1.6 M in hexane, Aldrich), BH_3·THF (1.0 M in THF, Aldrich), PPh_2H, PCy_2H, and P(*o*-Tol)$_2$H (Strem) were used as purchased. Monomeric C_5H_6 was obtained from commercial dicyclopentadiene (Fluka) by dropping into hot decaline and distilling off through a Vigreux column and was stored under nitrogen at −80 °C. NEt_3 (Merck) was distilled before use and stored over 4 Å molecular sieves. The syntheses of the compounds (*R*)-**1**, (*R*)-**2**, (S)-**3** and (S)-**4a** was published in the preliminary communication previous to this paper [6]. [Re(CO)$_5$Br] [13], [Rh(C$_2$H$_4$)$_2$Cl]$_2$[14] and [Rh(CO)$_2$Cl]$_2$[14] were prepared by published methods.

3.1. (*S*)-[Rh(η^2-C_2H_4)(η^5-η^1-$C_5H_4CH_2CHPhPPh_2$)] (**5a**)

A suspension of [Rh(C$_2$H$_4$)$_2$Cl]$_2$ (205 mg, 0.53 mmol) in 15 ml of Et$_2$O was treated with (*S*)-**4a** (382 mg, 1.06 mmol) dissolved in 20 ml of THF. The reaction mixture was stirred for 1 h, leading to a red–brownish solution which was evaporated to dryness. Then the residue, dissolved in a hexane–toluene mixture (1:1) was eluted and filtered through a 5 cm pad of alumina. The solvent was evaporated and the product (*S*)-**5a** was obtained by cooling a saturated hexane solution at −40 °C (378 mg, 0.78 mmol, 74%). ^{31}P-NMR (202 MHz, C_6D_6): δ +92.4 (d, $^{1}J_{P-Rh} = 216.7$ Hz, *P*Ph$_2$). ^{1}H-NMR (500 MHz, C_6D_6): δ 1.78 (br, 2H, C$_2$*H*$_4$), 2.33 (m, 1H, C*H*$_2$), 2.43 (m, 1H, C*H*$_2$), 2.82 (br, 2H, C$_2$*H*$_4$), 4.60 (m, 1H, C*H*Ph), 4.99 (m, 1H, *Cp*), 5.34 (m, 1H, *Cp*), 5.80 (m, 1H, *Cp*), 5.83 (m, 1H, *Cp*), 6.48–7.61 (m, 15H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6): δ 27.7 (br, *C*$_2$H$_4$), 29.75 (d, $^{2}J_{C-P} = 7.7$ Hz, *C*H$_2$), 31.9 (br, *C*$_2$H$_4$), 66.25 (dd, $^{1}J_{C-P} = 20.3$ Hz, $^{2}J_{C-Rh} = 2.2$ Hz, *C*HPh), 81.44 (*C*H, Cp), 85.36 (*C*H, Cp), 85.57 (*C*H, Cp), 91.60 (*C*H, Cp), 103.31 (*C*$_{ipso}$, Cp), 126.80 (d, $J_{C-P} = 2.2$ Hz, *C*H, Ph), 127.22 (d, $J_{C-P} = 9.9$ Hz, *C*H, Ph), 128.91 (d, $J_{C-P} = 2.2$ Hz, *C*H, Ph), 129.14 (dd, $^{1}J_{C-P} = 35.1$ Hz, $^{2}J_{C-Rh} = 1.7$ Hz, *C*$_{ipso}$, P*Ph*$_2$), 130.52 (d, $J_{C-P} = 1.6$ Hz, *C*H, Ph), 131.95 (d, $J_{C-P} = 9.3$ Hz, *C*H, Ph), 133.15 (dd, $^{1}J_{C-P} =$ 34.5 Hz, $^{2}J_{C-Rh} = 1.6$ Hz, *C*$_{ipso}$, P*Ph*$_2$), 137.97 (d, $J_{C-P} = 13.2$ Hz, *C*H, Ph), 138.12 (*C*$_{ipso}$, CH*Ph*), (other signals in the aryl area are overlapped by the C_6D_6). Anal. Calc. for $C_{27}H_{26}PRh$: C, 66.95; H, 5.41. Found: C, 67.17; H, 5.50%. MS: *m*/*z* [assignment, R_{int} (%)]: 484 [M$^+$, 18]; 456 [(M−C$_2$H$_4$)$^+$, 100]; 270 [(M−C$_2$H$_4$−PPh$_2$H)$^+$, 42].

3.2. (S_{Rh},S_C)-[Rh(CH$_3$)(η^5-η^1-$C_5H_4CH_2CHPhPPh_2$)I] (**6a**)

Excess amount of methyl iodide (78 μl, 1.24 mmol) was added to a solution of (*S*)-**5a** (101 mg, 0.21 mmol) in 20 ml of THF. The reaction mixture was stirred for 12 h, leading to a deep red solution which was evaporated to dryness. Then the residue, dissolved in CH_2Cl_2, was eluted and filtered through a 5 cm pad of alumina. The solvent was evaporated to afford a diastereomeric mixture (115 mg, 92% yield, major–minor = 93:7, 86% de; the ratio was determined by ^{31}P-NMR). Recrystalization of the crude product from CH_2Cl_2–hexane gave crystals of the title compound in 34% yield. ^{31}P-NMR (202 MHz, $CDCl_3$): δ +84.3 (d, $^{1}J_{P-Rh} = 168.5$ Hz, *P*Ph$_2$, major), +81.9 (d, $^{1}J_{P-Rh} = 170.3$ Hz, *P*Ph$_2$, minor). ^{1}H-NMR (500 MHz, $CDCl_3$, only the major diastereoisomer): δ 0.94 (m, 3H, Rh*Me*), 2.53 (m, 1H, C*H*$_2$), 2.68 (m, 1H, C*H*$_2$), 4.65 (m, 1H, C*H*Ph), 4.85 (m, 1H, *Cp*), 5.58 (m, 1H, *Cp*), 5.72 (m, 1H, *Cp*), 6.15 (m, 1H, *Cp*), 6.57–7.53 (m, 15H, *Ph*). ^{13}C{^{1}H}-NMR (125

MHz, $CDCl_3$, only the major diastereoisomer): δ −13.70 (dd, $^1J_{C-Rh} = 20.6$ Hz, $^2J_{C-P} = 9.9$ Hz, Rh*Me*), 29.69 (d, $^2J_{C-P} = 6.1$ Hz, *C*H$_2$), 63.54 (d, $^1J_{C-P} = 23.6$ Hz, *C*HPh), 76.48 (*C*H, Cp), 85.98 (*C*H, Cp), 93.82 (*C*H, Cp), 100.11 (*C*H, Cp), 111.38 (C_{ipso}, Cp), 127.40 (d, $J_{C-P} = 2.2$ Hz, *C*H, Ph), 127.49 (d, $J_{C-P} = 2.3$ Hz, *C*H, Ph), 127.92 (d, $J_{C-P} = 1.6$ Hz, *C*H, Ph), 128.12 (d, $J_{C-P} = 9.5$ Hz, *C*H, Ph), 128.71 (d, $J_{C-P} = 3.8$ Hz, *C*H, Ph), 129.14 (dd, $^1J_{C-P} = 35.1$ Hz, $^2J_{C-Rh} = 1.7$ Hz, C_{ipso}, P*Ph*$_2$), 130.24 (d, $J_{C-P} = 2.2$ Hz, *C*H, Ph), 131.43 (d, $J_{C-P} = 2.7$ Hz, *C*H, Ph), 132.28 (d, $J_{C-P} = 7.7$ Hz, *C*H, Ph), 135.69 (dd, $^1J_{C-P} = 34.5$ Hz, $^2J_{C-Rh} = 1.6$ Hz, C_{ipso}, P*Ph*$_2$), 138.11 (d, $J_{C-P} = 11.0$ Hz, *C*H, Ph), 139.02 (C_{ipso}, CH*Ph*). Anal. Calc. for $C_{26}H_{25}PIRh$: C, 52.20; H, 4.21. Found: C, 51.97; H, 4.37%. MS: *m*/*z* [assignment, R_{int} (%)]: 598 [M^+, 28]; 583 [$(M-CH_3)^+$, 52]; 456 [$(M-CH_3I)^+$, 100].

3.3. (*S*)-[*Li*(*C*$_5$*H*$_4$*CH*$_2$*CHPhP*(*o*-*Tol*)$_2$)] (**4b**)

A flask was charged with 40 ml of THF and cooled to −60 °C. At this temperature P(*o*-Tol)$_2$H (0.47 g, 2.19 mmol) and Li^{n}Bu (1.4 ml, 1.6 M in hexane, 2.23 mmol) were added. After the reaction mixture had warmed to room temperature (r.t.), (*S*)-**3** (0.37 g, 2.19 mmol) was added by syringe. The mixture was stirred overnight. The solvent was removed and the product (*S*)-**4b** was washed with cold hexane (3 × 20 ml) and Et_2O (2 × 20 ml) and dried in vacuum (0.85 g, 88% yield) and was used immediately for the preparations described below.

3.4. (*S*)-[*Rh*(*η*^{2}-*C*$_2$*H*$_4$)(*η*^{5}-*η*^{1}-*C*$_5$*H*$_4$*CH*$_2$*CHPhP*(*o*-*Tol*)$_2$)] (**5b**)

The same procedure described to prepare (*S*)-**5a** using (*S*)-**4b** (540 mg, 1.39 mmol) and $[Rh(C_2H_4)_2Cl]_2$ (155 mg, 0.39 mmol) gave (*S*)-**5b** as an orange crystalline solid (498 mg, 70% yield). ^{31}P-NMR (202 MHz, C_6D_6): δ +89.7 (d, $^1J_{P-Rh} = 216.1$ Hz, *P*Ph$_2$). ^{1}H-NMR (500 MHz, C_6D_6): δ 1.90 (br, 2H, C_2H_4), 1.97 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), 2.39 (m, 1H, C*H*$_2$), 2.49 (m, 1H, C*H*$_2$), 3.00 (br, 2H, C_2H_4), 4.62 (m, 1H, C*H*Ph), 5.03 (m, 1H, *Cp*), 5.37 (m, 1H, *Cp*), 5.84 (m, 1H, *Cp*), 5.88 (m, 1H, *Cp*), 6.58–7.59 (m, 13H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6): δ 21.15 (*Me*), 21.25 (*Me*), 27.5 (br, C_2H_4), 29.77 (d, $^2J_{C-P} = 7.1$ Hz, *C*H$_2$), 31.5 (br, C_2H_4), 66.40 (d, $^1J_{C-P} = 20.9$ Hz, *C*HPh), 81.38 (*C*H, Cp), 85.32 (*C*H, Cp), 85.63 (*C*H, Cp), 91.50 (*C*H, Cp), 103.31 (C_{ipso}, Cp), 125.95 (d, $^1J_{C-P} = 35.7$ Hz, C_{ipso}, P*Ph*$_2$), 126.71 (d, $J_{C-P} = 1.6$ Hz, *C*H, Ph), 128.43 (d, $J_{C-P} = 2.8$ Hz, *C*H, Ph), 129.04 (d, $J_{C-P} = 9.3$ Hz, *C*H, Ph), 129.89 (d, $^1J_{C-P} = 36.2$ Hz, C_{ipso}, P*Ph*$_2$), 132.20 (d, $J_{C-P} = 9.3$ Hz, *C*H, Ph), 138.15 (d, $J_{C-P} = 13.1$ Hz, *C*H, Ph), 138.36 (d, $^2J_{C-P} = 9.9$ Hz, C_{ipso}, CH*Ph*), 138.85 (d, $^2J_{C-P} = 2.7$ Hz, *C*Me, Ph), 140.62 (d, $^2J_{C-P} = 2.2$ Hz, *C*Me, Ph) (other signals in the aryl area are overlapped by the C_6D_6). Anal. Calc. for $C_{29}H_{30}PRh$: C, 67.97; H, 5.90. Found: C, 67.17; H, 5.86%. MS: *m*/*z* [assignment, R_{int} (%)]: 512 [M^+, 15]; 484 [$(M-C_2H_4)^+$, 100]; 270 [$(M-C_2H_4-P(o\text{-Tol})_2H)^+$, 37].

3.5. (*S*$_{Rh}$,*S*$_C$)-[*Rh*(*CH*$_3$)(*η*^{5}-*η*^{1}-*C*$_5$*H*$_4$*CH*$_2$*CHPhP*(*o*-*Tol*)$_2$)*I*] (**6b**)

The same procedure described to prepare (R_{Rh},S_C)-**6a** using (*S*)-**5b** (121 mg, 0.24 mmol) and excess MeI (89 μl, 1.44 mmol) afforded a diastereomeric mixture (136 mg, 92% yield, major–minor = 93:7, 86% de; the ratio was determined by ^{31}P-NMR). Recrystalization of the crude product from CH_2Cl_2–hexane gave crystals of the title compound in 38% yield. ^{31}P-NMR (202 MHz, $CDCl_3$): δ +83.3 (d, $^1J_{P-Rh} = 166.6$ Hz, *P*Ph$_2$, major), +80.7 (d, $^1J_{P-Rh} = 170.3$ Hz, *P*Ph$_2$, minor). ^{1}H-NMR (500 MHz, $CDCl_3$, only the major diastereoisomer): δ 0,93 (m, 3H, Rh*Me*), 2.32 (s, 3H, Ph*Me*), 2.38 (s, 3H, Ph*Me*), 2.60 (m, 1H, C*H*$_2$), 4.58 (m, 1H, C*H*Ph), 4.80 (m, 1H, *Cp*), 5.53 (m, 1H, *Cp*), 5.65 (m, 1H, *Cp*), 6.10 (m, 1H, *Cp*), 6.61–7.44 (m, 13H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$, only the major diastereoisomer): δ −13.49 (dd, $^1J_{C-Rh} = 20.6$ Hz, $^2J_{C-P} = 9.9$ Hz, Rh*Me*), 23.17 (Ph*Me*), 23.45 (Ph*Me*), 29.12 (d, $^2J_{C-P} = 7.1$ Hz, *C*H$_2$), 64.48 (d, $^1J_{C-P} = 19.5$ Hz, *C*HPh), 78.48 (*C*H, Cp), 84.35 (*C*H, Cp), 89.67 (*C*H, Cp), 97.23 (*C*H, Cp), 109.16 (C_{ipso}, Cp), 126.83 (d, $^1J_{C-P} = 32.6$ Hz, C_{ipso}, P*Ph*$_2$), 127.35 (d, $J_{C-P} = 2.2$ Hz, *C*H, Ph), 128.99 (d, $J_{C-P} = 2.3$ Hz, *C*H, Ph), 129.77 (d, $J_{C-P} = 8.8$ Hz, *C*H, Ph), 130.43 (d, $^1J_{C-P} = 36.2$ Hz, C_{ipso}, P*Ph*$_2$), 131,16 (d, $^1J_{C-P} = 36.2$ Hz, C_{ipso}, P*Ph*$_2$), 131.57 (d, $J_{C-P} = 1.6$ Hz, *C*H, Ph), 132.67 (d, $J_{C-P} = 10.4$ Hz, *C*H, Ph), 139.03 (d, $J_{C-P} = 12.5$ Hz, *C*H, Ph), 139.67 (d, $^2J_{C-P} = 10.2$ Hz, C_{ipso}, CH*Ph*), 138.85 (d, $^2J_{C-P} = 2.5$ Hz, *C*Me, Ph), 140.62 (d, $^2J_{C-P} = 2.3$ Hz, *C*Me, Ph). Anal. Calc. for $C_{28}H_{29}PIRh$: C, 53.69; H, 4.67. Found: C, 53.17; H, 4.73%. MS: *m*/*z* [assignment, R_{int} (%)]: 626 [M^+, 11]; 611 [$(M-CH_3)^+$, 40]; 484 [$(M-CH_3I)^+$, 100].

3.6. (*S*)-[*Li*(*C*$_5$*H*$_4$*CH*$_2$*CHPhPCy*$_2$)] (**4c**)

The same procedure described to prepare (*S*)-**4b** using 0.68 g of PCy_2H (3.4 mmol), 2.2 ml of Li^{n}Bu (3.5 mmol) and 0.57 g of (*S*)-**3** (3.4 mmol) gave (*S*)-**4c** as a white solid (1.00 g, 79% yield).

3.7. (*S*)-[*Rh*(*η*^{2}-*C*$_2$*H*$_4$)(*η*^{5}-*η*^{1}-*C*$_5$*H*$_4$*CH*$_2$*CHPhPCy*$_2$)] (**5c**)

A suspension of $[Rh(C_2H_4)_2Cl]_2$ (155 mg, 0.39 mmol) in 15 ml of Et_2O was treated with (*S*)-**4c** (293 mg, 0,78 mmol) dissolved in 20 ml of THF. The reaction mixture was stirred for 1 h, leading to a red–brownish solution which was evaporated to dryness. Then the residue, dissolved in a hexane–toluene mixture (1:1) was eluted

and filtered through a 5 cm pad of alumina. The solvent was evaporated and the product (*S*)-**5c** was obtained by cooling a saturated hexane solution at −40 °C (304 mg, 0.61 mmol, 78%). ^{31}P-NMR (202 MHz, C_6D_6): δ +88.2 (d, $^1J_{P-Rh}$ = 210.6 Hz, *P*Ph$_2$). ^{1}H-NMR (500 MHz, C_6D_6): δ 1.00–1.30 (m, 10H, *Cy*), 1.50–1.68 (m, 10H, *Cy*), 1.91 (m, 1H, *Cy*), 2.02 (m, 1H, *Cy*), 2.12 (br, 2H, C_2H_4), 2.36 (m, 1H, CpCH_2), 2.53 (m, 1H, CpCH_2), 2.86 (br, 2H, C_2H_4), 3.93 (m, 1H, CpCH$_2$C*H*), 4.75 (m, 1H, *Cp*), 5.29 (m, 1H, *Cp*), 5.62 (m, 1H, *Cp*), 5.78 (m, 1H, *Cp*), 6.98 (m, 2H, *Ph*), 7.02 (m, 1H, *Ph*), 7.09 (m, 2H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6): δ 24.8 (br, C_2H_4), 25.7 (br, C_2H_4), 26.84 (d, J_{C-P} = 12.0 Hz, CH_2, *Cy*), 27.11 (d, J_{C-P} = 9.8 Hz, CH_2, *Cy*), 27.65 (d, J_{C-P} = 21.4 Hz, CH_2, *Cy*), 27.66 (CH_2, *Cy*), 27.94 (d, J_{C-P} = 11.5 Hz, CH_2, *Cy*), 28.07 (CH_2, *Cy*), 28.27 (d, J_{C-P} = 1.6 Hz, CH_2, *Cy*), 28.77 (CH_2, *Cy*), 31.02 (CH_2, *Cy*), 32.39 (d, $^2J_{C-P}$ = 5.5 Hz, CH_2Cp), 32.69 (d, $^1J_{C-P}$ = 14.8 Hz, *C*H, *Cy*), 35.62 (d, $^1J_{C-P}$ = 14.8 Hz, *C*H, *Cy*), 61.92 (d, $^1J_{C-P}$ = 15.4 Hz, *C*HPh), 80.71 (*C*H, Cp), 84.29 (*C*H, Cp), 84.65 (*C*H, Cp), 91.60 (*C*H, Cp), 103.89 (C_{ipso}, Cp), 126.90 (d, J_{C-P} = 1.6 Hz, *C*H, *Ph*), 128.45 (d, J_{C-P} = 2.8 Hz, *C*H, *Ph*), 128.55 (d, J_{C-P} = 1.1 Hz, *C*H, *Ph*), 140.04 (d, $^2J_{C-P}$ = 7.6 Hz, C_{ipso}, *Ph*), (other signals in the aryl area are overlapped by the C_6D_6). Anal. Calc. for $C_{27}H_{38}$PRh: C, 65.32; H, 7.72. Found: C, 65.93; H, 7.83%. MS: *m*/*z* [assignment, R_{int} (%)]: 496 [M$^+$, 14]; 466 [(M−C_2H_4)$^+$, 100].

3.8. (*S*$_{Rh}$,*S*$_C$)-[Rh(CH$_3$)(η^5-η^1-C$_5$H$_4$CH$_2$CHPhPCy$_2$)I] (**6c**)

The same procedure described to prepare (R_{Rh},S_C)-**6a** and (R_{Rh},S_C)-**6b** using (*S*)-**5b** (100 mg, 0.20 mmol) and excess MeI (76 μl, 1.21 mmol) afforded a diastereomeric mixture (98 mg, 80% yield, major–minor = 66:34, 32% de; the ratio was determined by ^{31}P-NMR). In this case, attempts to obtain the pure diastereomer by repeated recrystalization failed. ^{31}P-NMR (202 MHz, $CDCl_3$): δ +84.9 (d, $^1J_{P-Rh}$ = 152.0 Hz, *P*Ph$_2$, major), +82.0 (d, $^1J_{P-Rh}$ = 166.6 Hz, *P*Ph$_2$, minor). ^{1}H-NMR (500 MHz, $CDCl_3$, only the major diastereoisomer): δ 0.89 (m, 3H, Rh*Me*), 1.08–1.41 (m, 10H, *Cy*), 1.53–1.97 (m, 10H, *Cy*), 2.03 (m, 1H, *Cy*), 2.16 (m, 1H, *Cy*), 2.42 (m, 1H, CpCH_2), 2.65 (m, 1H, CpCH_2), 3,77 (m, 1H, CpCH$_2$C*H*), 4.85 (m, 1H, *Cp*), 5.28 (m, 1H, *Cp*), 5.43 (m, 1H, *Cp*), 5.97 (m, 1H, *Cp*), 7.14 (m, 2H, *Ph*), 7.29–7.43 (m, 3H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$, only the major diastereoisomer): δ −13.56 (dd, $^1J_{C-Rh}$ = 19.5 Hz, $^2J_{C-P}$ = 9.1 Hz, Rh*Me*), 26.42 (d, J_{C-P} = 11.4 Hz, CH_2, *Cy*), 26.76 (d, J_{C-P} = 10.3 Hz, CH_2, *Cy*), 26.93 (d, J_{C-P} = 19.4 Hz, CH_2, *Cy*), 27.05 (CH_2, *Cy*), 27.12 (d, J_{C-P} = 10.4Hz, CH_2, *Cy*), 28.03 (CH_2, *Cy*), 28.56 (d, J_{C-P} = 2.2 Hz, CH_2, *Cy*), 29.11 (CH_2, *Cy*), 31.19 (CH_2, *Cy*), 32.57 (d, $^2J_{C-P}$ = 5.5 Hz, CH_2Cp), 33.45 (d, $^1J_{C-P}$ = 14.4 Hz, *C*H, *Cy*), 36.74 (d, $^1J_{C-P}$ = 13.2 Hz, *C*H, *Cy*), 63.37 (d, $^1J_{C-P}$ = 13.6 Hz, *C*HPh), 79.12 (*C*H, Cp), 85.57 (*C*H, Cp), 86.62 (*C*H, Cp), 93.45 (*C*H, Cp), 107.76 (C_{ipso}, Cp), 127.43 (d, J_{C-P} = 2.2 Hz, *C*H, *Ph*), 128.67 (d, J_{C-P} = 3.3 Hz, *C*H, *Ph*), 128.78 (d, J_{C-P} = 1.6 Hz, *C*H, *Ph*), 129.35 (d, J_{C-P} = 8.8 Hz, *C*H, *Ph*), 131.15 (d, J_{C-P} = 3.3 Hz, *C*H, *Ph*), 140.04 (d, $^2J_{C-P}$ = 7.6 Hz, C_{ipso}, *Ph*). Anal. Calc. for $C_{26}H_{37}$PIRh: C, 51.16; H, 6.11. Found: C, 50.65; H, 6.19%. MS: *m*/*z* [assignment, R_{int} (%)]: 610 [M$^+$, 13]; 595 [(M−CH_3)$^+$, 26]; 468 [(M−CH_3I)$^+$, 100].

3.9. (*S*)-[Rh(CO)(η^5-η^1-C$_5$H$_4$CH$_2$CHPhPPh$_2$)] (**7**)

A suspension of $[Rh(CO)_2Cl]_2$ (101 mg, 0.26 mmol) in 15 ml of Et_2O was treated with (*S*)-**4a** (192 mg, 0.53 mmol) dissolved in 20 ml of THF. The reaction mixture was stirred for 2 h, leading to a dark orange solution which was evaporated to dryness. Then the residue, dissolved in a hexane–toluene mixture (1:1) was eluted and filtered through a 5 cm pad of alumina. The solvent was evaporated and the product (*S*)-**7** was obtained by cooling a saturated hexane solution at −40 °C (179 mg, 71%). ^{31}P-NMR (202 MHz, C_6D_6): δ +89.4 (d, $^1J_{P-Rh}$ = 206.9 Hz, *P*Ph$_2$). ^{1}H-NMR (500 MHz, C_6D_6): δ 2.19 (m, 1H, CH_2), 2.26 (m, 1H, CH_2), 4.52 (m, 1H, C*H*Ph), 5.51 (m, 1H, *Cp*), 5.56 (m, 1H, *Cp*), 5.59 (m, 1H, *Cp*), 5.75 (m, 1H, *Cp*), 6.44–7.60 (m, 15H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6): δ 30.14 (d, $^2J_{C-P}$ = 7.7 Hz, CH_2), 68.35 (d, $^1J_{C-P}$ = 19.7 Hz, *C*HPh), 85.13 (*C*H, Cp), 85.41 (*C*H, Cp), 89.32 (*C*H, Cp), 91.00 (*C*H, Cp), 101.90 (C_{ipso}, Cp), 127.26 (d, J_{C-P} = 2.2 Hz, *C*H, Ph), 127.41 (d, J_{C-P} = 10.4 Hz, *C*H, Ph), 128.45 (d, J_{C-P} = 3.3 Hz, *C*H, Ph), 130.24 (d, $^1J_{C-P}$ = 40.6 Hz, C_{ipso}, P*Ph*$_2$), 130.96 (d, J_{C-P} = 2.1 Hz, *C*H, Ph), 132.60 (d, J_{C-P} = 10.9 Hz, *C*H, Ph), 135.24 (dd, $^1J_{C-P}$ = 44.7 Hz, $^2J_{C-Rh}$ = 1.6 Hz, C_{ipso}, P*Ph*$_2$), 137.63 (C_{ipso}, CH*Ph*), 137.74 (d, J_{C-P} = 13.7 Hz, *C*H, Ph), (other signals in the aryl area are overlapped by the C_6D_6), 193.88 (dd, $^1J_{C-Rh}$ = 88.8 Hz, $^2J_{C-P}$ = 19 Hz, *C*O). Anal. Calc. for $C_{26}H_{22}$OPRh: C, 64.48; H, 4.58. Found: C, 64.62; H, 4.58%. MS: *m*/*z* [assignment, R_{int} (%)]: 484 [M$^+$, 41]; 456 [(M−CO)$^+$, 100]; 270 [(M−CO−PPh_2H)$^+$, 59].

3.10. [Rh(COMe)(η^5-η^1-C$_5$H$_4$CH$_2$CHPhPPh$_2$)I] (**8**)

Excess amount of methyl iodide (177 μl, 2.82 mmol) was added to a solution of (*S*)-**7** (226 mg, 0.47 mmol) in CH_2Cl_2 at r.t. The reaction mixture was stirred for 5 h and then the solvent was removed in vacuo to afford a diastereomeric mixture (263 mg, 90% yield, major–minor = 91:9, 82% de; the ratio was determined by ^{31}P-NMR). Recrystalization of the crude product from CH_2Cl_2–hexane gave crystals of the title compound in 41% yield. ^{31}P-NMR (202 MHz, $CDCl_3$): δ +86.6 (d, $^1J_{P-Rh}$ = 184.9 Hz, *P*Ph$_2$, major), +80.9 (d, $^1J_{P-Rh}$ =

170.3 Hz, PPh_2, minor). ^{1}H-NMR (500 MHz, C_6D_6, only the major diastereoisomer): δ 1.95 (m, 1H, CH_2), 2.01 (m, 1H, CH_2), 2.75 (s, 3H, CO*Me*), 4.63 (m, 1H, C*H*Ph), 5.22 (m, 2H, *Cp*), 6.33 (m, 1H, *Cp*), 6.34 (m, 1H, *Cp*), 6.70–7.76 (m, 15H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6, only the major diastereoisomer): δ 28.33 (d, $^2J_{C-P} = 4.7$ Hz, *C*H_2), 30.49 (CO*C*H_3), 65.90 (d, $^1J_{C-P} = 23.1$ Hz, *C*HPh), 81.01 (*C*H, Cp), 85.08 (*C*H, Cp), 95.13 (*C*H, Cp), 105.18 (*C*H, Cp), 116.73 (*C*$_{ipso}$, Cp), 127.67 (d, $J_{C-P} = 2.3$ Hz, *C*H, Ph), 127.99 (d, $J_{C-P} = 9.3$ Hz, *C*H, Ph), 128.88 (d, $J_{C-P} = 1.6$ Hz, *C*H, Ph), 130.20 (d, $^1J_{C-P} = 40.4$ Hz, *C*$_{ipso}$, P*Ph*$_2$), 131.16 (d, $J_{C-P} = 1.6$ Hz, *C*H, Ph), 132.77 (d, $J_{C-P} = 9.9$ Hz, *C*H, Ph), 132.16 (dd, $^1J_{C-P} = 44.4$ Hz, $^2J_{C-Rh} = 1.6$ Hz, *C*$_{ipso}$, P*Ph*$_2$), 137.65 (*C*$_{ipso}$, CH*Ph*), 138.43 (d, $J_{C-P} = 13.7$ Hz, *C*H, Ph), (other signals in the aryl area are overlapped by the C_6D_6), 226.03 (dd,, $^1J_{C-Rh} = 28.8$ Hz, $^2J_{C-P} = 7.7$ Hz, *C*O). Anal. Calc. for $C_{27}H_{25}OPIRh$: C, 51.78; H, 4.02. Found: C, 51.11; H, 4.12%. MS: *m*/*z* [assignment, R_{int} (%)]: 626 [M^+, 2]; 583 [$(M-COMe)^+$, 8]; 498 [$(M-I)^+$, 51]; 456 [$(M-COMe-I)^+$, 100].

3.11. (*R*,*R*)-2,3-butanediol bis(methanesulfonate) (**9**)

To a solution of (*R*,*R*)-2,3-butanediol (10.0 g, 110.9 mmol) in 200 ml of CH_2Cl_2 was added NEt_3 (31.0 ml, 223.6 mmol). The solution was cooled to 0 °C, and methanesulfonyl chloride (18.0 ml, 231.8 mmol) in CH_2Cl_2 (50 ml) was added dropwise over 1 h. Upon complete addition, the mixture containing precipitated salts was allowed to stir at 0 °C for 1 h and then at r.t. for 2 h. The mixture was then poured into 1 N HCl (250 ml). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic layers were washed successively with 1N HCl (50 ml), saturated $NaHCO_3$ (50 ml) and brine (100 ml). After drying ($MgSO_4$) the solvent was pumped off to obtain a pale yellow solid (24.5 g, ca. 100%). This crude product thus obtained was sufficiently pure to be used in the next step. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.46 (m, 6H, CH_3), 3.23 (s, 6H, SCH_3), 4.78 (m, 2H, C*H*).

3.12. (*S*,*S*)-1,2-Dimethyl-spiro[2,4]hepta-4,6-diene (**10**)

To a suspension of $NaNH_2$ (9.50 g, 243.5 mmol) in 200 ml of THF was added dropwise at r.t. freshly cracked cyclopentadiene (15.0 ml, 181.5 mmol). The addition of the diene was adjusted so as to maintain gentle reflux (some care needs to be exercised at this point since occasionally an induction period in the anion formation was observed). Upon complete addition, the pink mixture was stirred 1 h and then a solution of compound (*R*,*R*)-**9** (24.5 g, 114.4 mmol) in 200 ml of THF was added dropwise. This addition was accompanied by heat evolution. After the reaction mixture had cooled to r.t. overnight, 20 ml of methanol were carefully added to quench any excess of $NaNH_2$ or NaCp and then 300 ml of water were added. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 100 ml). The combined organic fraction was dried over $MgSO_4$ and then the solvent was pumped off on a rotovap. The residue was distilled (38–42 °C/17 mbar) to yield (*S*,*S*)-**10** as a colorless liquid (8.5 g, 64%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.06 (m, 1H, CH_2), 2.31 (m, 1H, CH_2), 3.32 (m, 1H, C*H*Ph), 1.32 (m, 6H, CH_3), 2.00 (m, 2H,C*H*), 6.25 (m, 1H, *Cp*), 6.50 (m, 2H, *Cp*). These analytical data are in agreement with those reported for the racemic form of (*S*,*S*)-**10** [15].

3.13. (*R*,*R*)-[*Li*(C_5H_4*CHMeCHMePPh*$_2$)] (**11**)

The same procedure described to prepare (*S*)-**4a** using 0.9 ml of PPh_2H (5.17 mmol), 3.2 ml of Li^{n}Bu (5.2 mmol) and 646 mg of (*S*,*S*)-**10** (5.3 mmol) gave (*R*,*R*)-**11** as a white solid (1.12 g, 69% yield).

3.14. (*R*,*R*)-[*Re*(*CO*)$_3$(η^5-C_5H_4*CHMeCHMePPh*$_2$·*BH*$_3$)] (**12**)

[$Re(CO)_5Br$] (349 mg, 0.86 mmol) was dissolved in 30 ml of THF and heated to reflux for 4 h. After cooling this mixture to 0 °C, (*R*,*R*)-**11** (269 mg, 0.86 mmol), dissolved in 20 ml of THF, was slowly added. The resulting solution was stirred 2 h at ambient temperature and then refluxed for 1 h. After removing of the solvent in vacuo, the yellow residue was extracted with 25 ml of toluene, and the extract was filtered over celite. BH_3·THF (1.5 ml, 1.5 mmol, 1.0 M solution in THF) was added to the filtrate. The mixture was stirred at ambient temperature overnight. The solvent was evaporated and the product (*R*,*R*)-**12**·BH_3 was obtained by cooling a saturated hexane solution at −40 °C (309 mg, 61%). ^{31}P-NMR (202 MHz, $CDCl_3$): δ +20.6 (br, *P*Ph_2·BH_3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.8–1.2 (br, 3H, B*H*$_3$), 1.08 (m, 3H, CpC*Me*), 1.17 (m, 3H, C*Me*PPh_2), 2.72 (m, 1H, C*H*PPh_2), 3,03 (m, 1H, CpC*H*), 5.05 (m, 2H, *Cp*), 5.26 (m, 2H, *Cp*), 7.41–7.50 (m, 6H, *Ph*), 7.77 (m, 4H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 12.81 (CpC*Me*), 24.16 (d, $^2J_{C-P} = 7.1$ Hz, C*Me*PPh_2), 33.23 (d, $^2J_{C-P} = 4.4$ Hz, Cp*C*Me), 35.89 (d, $^1J_{C-P} = 32.4$ Hz, *C*PPh2), 81.08 (*C*H, Cp), 83.28 (*C*H, Cp), 84.60 (*C*H, Cp), 86.96 (*C*H, Cp), 111.99 (d, $^3J_{C-P} = 5.5$ Hz, *C*$_{ipso}$, Cp), 128.33 (*C*$_{ipso}$, Ph), 128.75 (d, $J_{C-P} = 9.9$ Hz, *C*H, Ph), 128.79 (d, $J_{C-P} = 10.5$ Hz, *C*H, Ph), 128.93 (d, $J_{C-P} = 9.3$ Hz, *C*H, Ph), 129.26 (*C*$_{ipso}$, Ph), 131.28 (d, $J_{C-P} = 2.2$ Hz, *C*H, Ph), 131.33 (d, $J_{C-P} = 2.2$ Hz, *C*H, Ph), 132.42 (d, $J_{C-P} = 8.3$ Hz, *C*H, Ph), 132.98 (d, $J_{C-P} = 8.8$ Hz, *C*H, Ph), 194.16 (*C*O). Anal. Calc. for $C_{24}H_{25}BO_3PRe$: C, 48.90; H, 4.28. Found: C, 48.86; H, 4.32%. MS: *m*/*z* [assignment, R_{int} (%)]: 590 [M^+, 2]; 562 [$(M-CO)^+$, 8]; 548 [$(M-CO-BH_3)^+$, 100].

3.15. (*R*,*R*)-[Rh(η^2-C_2H_4)(η^5-η^1-C_5H_4CHMeCHMePPh$_2$)] (**13**)

The same procedure described to prepare (*S*)-**5a** and (*S*)-**5b** using (*R*,*R*)-**11** (270 mg, 0.86 mmol) and $[Rh(C_2H_4)_2Cl]_2$ (164 mg, 0.42 mmol) gave (*R*,*R*)-**13** as a spectroscopically pure, orange oil (258 mg, 70% yield) that failed to crystallize. ^{31}P-NMR (202 MHz, C_6D_6): δ +79.0 (d, $^1J_{P-Rh} = 212.4$ Hz, *P*Ph$_2$). ^{1}H-NMR (500 MHz, C_6D_6): δ 0.72 (m, 3H, CpC*Me*), 0.95 (m, 3H, C*Me*PPh$_2$), 1.9 (br, 2H, C_2H_4), 2.40 (m, 1H, C*H*PPh$_2$), 2.9 (br, 2H, C_2H_4), 3.39 (m, 1H, CpC*H*), 4.94 (m, 1H, *Cp*), 5.27 (m, 1H, *Cp*), 5.56 (m, 1H, *Cp*), 5.83 (m, 1H, *Cp*), 6.96–7.15 (m, 8H, *Ph*), 8.05 (m, 2H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6): δ 13.00 (CpC*Me*), 14.27 (d, $^2J_{C-P} = 6.9$ Hz, C*Me*PPh$_2$), 30.41 (d, $^2J_{C-P} = 13.3$ Hz, Cp*C*Me), 58.53 (d, $^1J_{C-P} = 25.2$ Hz, *C*PPh2), 81.32 (*C*H, Cp), 81.67 (*C*H, Cp), 84.86 (*C*H, Cp), 90.58 (*C*H, Cp), 112.98 (C_{ipso}, Cp), 128.60 (d, $J_{C-P} = 2.3$ Hz, *C*H, Ph), 130.25 (d, $J_{C-P} = 2.7$ Hz, *C*H, Ph), 130.67 (d, $J_{C-P} = 8.7$ Hz, *C*H, Ph), 132.84 (d, $^1J_{C-P} = 30.7$ Hz, C_{ipso}, Ph), 134.81 (d, $^1J_{C-P} = 35.2$ Hz, C_{ipso}, Ph), 137.44 (d, $J_{C-P} = 8.8$ Hz, *C*H, Ph), (other signals in the aryl area are overlapped by the C_6D_6). (It was impossible to obtain a consistent elemental analysis and MS of the compound due to the fact that it failed to crystallize).

3.16. [Rh(CH$_3$)(η^5-η^1-C_5H_4CHMeCHMePPh$_2$)I] (**14**)

Excess amount of methyl iodide (194 μl, 3.1 mmol) was added to a solution of (*R*,*R*)-**13** (271 mg, 0.62 mmol) in 20 ml of THF. The reaction mixture was stirred for 12 h, leading to a deep red solution which was evaporated to dryness. Then the residue, dissolved in CH_2Cl_2, was eluted and filtered through a 5 cm pad of alumina. The solvent was evaporated to afford a diastereomeric mixture (287 mg, 84% yield, major–minor = 90:10, 80% de; the ratio was determined by ^{31}P-NMR). Recrystalization of the crude product from CH_2Cl_2–hexane gave crystals of the title compound in 29% yield. ^{31}P-NMR (202 MHz, $CDCl_3$): δ +75.6 (d, $^1J_{P-Rh} = 164.8$ Hz, *P*Ph$_2$, major), +65.6 (d, $^1J_{P-Rh} = 168.5$ Hz, *P*Ph$_2$, minor). ^{1}H-NMR (500 MHz, $CDCl_3$, only the major diastereoisomer): δ 0.84 (m, 3H, CpC*Me*), 0.89 (m, 3H, Rh*Me*), 1.23 (m, 3H, C*Me*PPh$_2$), 2.64 (m, 1H, C*H*PPh$_2$), 3.65 (m, 1H, CpC*H*), 4.67 (m, 1H, *Cp*), 5.49 (m, 1H, *Cp*), 5.56 (m, 1H, *Cp*), 6.10 (m, 1H, *Cp*), 7.25–7.55 (m, 8H, *Ph*), 8.01 (m, 2H, *Ph*). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$, only the major diastereoisomer): δ −13.05 (dd, $^1J_{C-Rh} = 20.8$ Hz, $^2J_{C-P} = 10.4$ Hz, Rh*Me*), 12.64 (CpC*Me*), 14.63 (d, $^2J_{C-P} = 6.6$ Hz, C*Me*PPh$_2$), 33.60 (d, $^2J_{C-P} = 3.3$ Hz, Cp*C*Me), 57.53 (d, $^1J_{C-P} = 26.9$ Hz, *C*PPh2), 78.15 (*C*H, Cp), 81.74 (*C*H, Cp), 90.97 (*C*H, Cp), 100.50 (*C*H, Cp), 121.60 (C_{ipso}, Cp), 127.56 (d, $J_{C-P} = 10.4$ Hz, *C*H, Ph), 128.26 (d, $J_{C-P} = 9.9$ Hz, *C*H, Ph), 128.64 (d, $^1J_{C-P} = 30.7$ Hz, C_{ipso}, Ph), 129.36 (d, $^1J_{C-P} = 29.9$ Hz, C_{ipso}, Ph), 129.97 (d, $J_{C-P} = 2.8$ Hz, *C*H, Ph), 131.23 (d, $J_{C-P} = 2.7$ Hz, *C*H, Ph), 131.70 (d, $J_{C-P} = 7.1$ Hz, *C*H, Ph), 138.12 (d, $J_{C-P} = 11.0$ Hz, *C*H, Ph). Anal. Calc. for $C_{22}H_{25}$IPRh: C, 48.02; H, 4.58. Found: C, 48.57; H, 4.63%. MS: *m*/*z* [assignment, R_{int} (%)]: 550 [M^+, 19]; 408 [$(M-CH_3)^+$, 44]; 408 [$(M-CH_3I)^+$, 100].

4. X-ray structure determination

Intensity data for ($S_{Rh}S_C$)-**6a** were collected on an ENRAF–Nonius CAD4 diffractometer, Mo–K_α radiation equipped with incident beam graphite monochromator ($\lambda = 0.71073$ Å), $T = 243$ K. A red platelet of ca. dimensions $0.46 \times 0.36 \times 0.10$ mm^3 was mounted in a stream of dinitrogen on a glass fiber. Crystal data: $C_{26}H_{25}$IPRh, orthorhombic space group $P2_12_12_1$, $a = 10.339(1)$, $b = 12.621(2)$, $c = 18.051(2)$ Å, $V = 2355.3(6)$ Å^3, $Z = 4$. 5370 reflections in the ω–2θ scan mode with $\theta < 26°$, 4456 independent data, empirical absorption correction by azimuthal scans [16] (minimum relative transmission 0.734, maximum relative transmission 0.996). Solution with direct methods (SHELXS97 [17]), refinement on F^2 (SHELXL97 [18]) with anisotropic displacement parameters for all non-hydrogen atoms and H atoms in riding geometry. 263 variables, wR_2 (all data) = 0.1550, R_1 (for data with $I > 2\sigma(I)$) = 0.0637, max/min electron density from final Difference Fourier 1.87 and −2.11 e Å^{-3} (close to the halogen atom). The absolute structure of **6a** was unambiguously determined; a Flack enantiomorph polarity parameter of 0.03(5) was obtained [19].

In the case of (*R*,*R*)-**12** the crystal quality was low, and no details of the structure will be reported or deposited. A graphical summary of one of two similar independent molecules is provided by Fig. 2.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 187573. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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