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Synthesis of rhodium(III) complexes with the chiral phosphine (*S*)-$Ph_2PCH_2CHMeCH_2OH$. Crystal structure of (S_{Rh},S_C)-[(η^5-C_5Me_5)RhCl(η^2-$PPh_2CH_2CHMeCH_2OH$–P,O)]BF_4

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Abstract

Reaction of dinuclear complex [{(η^5-C_5Me_5)RhCl}$_2$(μ-Cl)$_2$] with the chiral phosphine (S)-$Ph_2PCH_2CHMeCH_2OH$ leads to the complex [(η^5-C_5Me_5)$RhCl_2$(η^1-$PPh_2CH_2CHMeCH_2OH$–P)] (**1**). Complex **1** reacts with NaH and $TlBF_4$ affording the chiral-at-metal rhodium compounds [(η^5-C_5Me_5)RhCl(η^2-$PPh_2CH_2CHMeCH_2O$–P,O)] (**2**) and [(η^5-C_5Me_5)RhCl(η^2-$PPh_2CH_2CHMeCH_2OH$–P,O)]BF_4(**3**), respectively. Complex **2** has been alternatively prepared by reaction of [{(η^5-C_5Me_5)RhCl}$_2$(μ-Cl)$_2$] with the sodium salt $Ph_2PCH_2CHMeCH_2ONa$. Complex **2** reacts with HBF_4 to give **3**. The reaction of **3** with an excess of NaI affords the neutral complex [(η^5-C_5Me_5)RhI_2(η^1-$PPh_2CH_2CHMeCH_2OH$–P)] (**4**). All the complexes have been characterised by elemental analyses and multinuclear NMR spectroscopy. The crystal structure of complex **3** has been determined by X-ray diffraction.

Keywords: Rhodium; Chiral-at-metal complexes; Chiral bidentate ligand; Chiral phosphine; Crystal structures

1. Introduction

Transition metal compounds with chiral ligands have been extensively studied because of their potential applications in stoichiometric or catalytic asymmetric reactions [1,2]. In particular, organometallic half-sandwich complexes containing stereogenic metal centres and chiral ligands, with three or four-legged piano stool structures, have been tools in the elucidation of the stereochemical course of reactions [3]. These type of complexes, showing an η^6-$MeC_6H_4Pr^i$ or η^5-C_5Me_5 groups and optically active chelate ligands such as diphosphines, bis(oxazolines), phosphino-oxazolines or imines, are recently reported as catalysts in enantioselective Diels–Alder reactions [4].

As tertiary phosphines are highly efficient ligands in many catalytic reactions, the design and synthesis of new chiral phosphines and principally chelating diphosphines have received a considerable attention [5]. Of particular interest is the behaviour of chiral chelating phosphino-amine and phosphino-ether ligands, considering that the combination of soft and hard donor atoms can provide free co-ordination sites by the deco-ordination of the most labile bound atom [6]. Recently, Börner et al. describes the synthesis of the chiral phosphino-alcohol ligand (*R*,*R*)-1,4-bis(diphenylphosphino)butane-2,3-diol and its rhodium(I) complex, showing that the interaction of the hemilabile coordinating OH groups with the metal centre is strongly dependent upon the characteristics of the ancillary ligands and solvent employed [7].

We are interested in preparing new chiral polydentate ligands containing both strong and weak donor groups and their potential use in asymmetric catalysis. In this paper we describe the synthesis and properties of new (η^5-C_5Me_5)Rh(III) complexes containing the chiral monophosphine ligand $Ph_2PCH_2CHMeCH_2OH$ as monodentate (P-donor), anionic chelate (P,O-donor) and neutral chelate (P,O-donor) ligand. The molecular structure of complex (S_{Rh},S_C)-[(η^5-C_5Me_5)RhCl(η^2-$PPh_2CH_2CHMeCH_2OH$–P,O)]BF_4, determined by single-crystal X-ray diffraction, is also described.

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2. Experimental

2.1. General procedures

All reactions were routinely performed under a purified nitrogen atmosphere, by using standard Schlenk-tube techniques. Solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting complex $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ and the ligand (*S*)-$PPh_2CH_2CHMeCH_2OH$ were prepared by published procedures [8,9]. Carbon and hydrogen analyses were performed using a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. ^{1}H- (200 MHz), ^{13}C- (50 MHz) and ^{31}P- (81 MHz) NMR spectra were recorded on a Bruker AC-200P spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (^{31}P, positive shifts downfield) as internal and external standards, respectively. Specific rotation, circular dichroism (CD) and optical rotatory dispersion (ORD) spectra were determined in $CHCl_3$ in a 1.0 cm path length cell by using a Jovin Yvon DC6 instrument (CEPEDEQ, Universidad de Chile).

2.2. Synthesis of compounds

2.2.1. (S)-$PPh_2CH_2CHMeCH_2OH$

The monophosphine ligand was prepared but not isolated in the described synthesis of (*S*)-3-(diphenylphosphinyl)-2-methyl-1-propanol [9]. A pure sample was obtained as pale yellow oil. δ_H ($CDCl_3$, 295 K) 1.09 [d, ^2J(HH) = 6.6 Hz, 3H, Me], 1.7–1.85 [m, br, 1H, CHMe], 1.85–2.0 [m, 1H, PCH], 2.2–2.3 [m, 1H, PCH], 3.58 [dd, 2H, ^3J(HH) = 6 Hz, ^4J(PH) = 1.5 Hz, CH_2O], 7.3–7.6 [m, 10H, Ph]. δ_P ($CDCl_3$, 295 K) −21.9 (s).

2.2.2. $[(\eta^5\text{-}C_5Me_5)RhCl_2(\eta^1\text{-}PPh_2CH_2CHMeCH_2OH\text{-}P)]$ (1)

$[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ (433 mg; 0.7 mmol) was dissolved in dichloromethane (25 cm^3) under nitrogen. (*S*)-$PPh_2CH_2CHMeCH_2OH$ (363 mg; 1.4 mmol), dissolved in tetrahydrofuran (25 cm^3), was added dropwise and the reaction mixture was stirred at room temperature (r.t.) for 12 h. The reaction mixture was evaporated to dryness and the solid residue formed was extracted with diethyl ether. Careful addition of *n*-hexane caused the precipitation of a red solid, which was filtered off, washed with cold *n*-hexane (3 × 5 cm^3), and dried under vacuum. Red crystals were obtained from dichloromethane–*n*-hexane. Yield 703 mg, 89% (Anal. Found: C, 55.3; H, 6.2. $C_{26}H_{34}Cl_2OPRh$ requires: C, 55.0; H, 6.0%). ν_{max} (cm^{-1}) (KBr): 3442 (OH). δ_H ($CDCl_3$, 295 K) 0.46 [d, 3H, ^2J(HH) = 6.4 Hz, Me], 1.33 [d, 15H, ^3J(PH) = 3.5 Hz, C_5Me_5], 2.2–2.4 [m, 2H, CHMe, PCH], 3.0–3.3 [m, 3H, PCH, CH_2O], 7.6–7.9 [m, 10H, Ph]. δ_P ($CDCl_3$, 295 K) 25.5 [d, ^1J(RhP) = 141 Hz].

2.2.3. $[(\eta^5\text{-}C_5Me_5)RhCl(\eta^2\text{-}PPh_2CH_2CHMeCH_2O\text{-}P,O)]$ (2)

The complex can be prepared by the two methods described below.

(a) A slight excess of NaH (63 mg, dispersion in mineral oil, 80% w/w, 2.0 mmol) was added to a solution of (*S*)-$PPh_2CH_2CHMeCH_2OH$ (418 mg; 1.62 mmol) in tetrahydrofuran (25 cm^3) at r.t. The mixture was stirred for 8 h and the excess of NaH was filtered off through Kieselguhr. The solution obtained was added dropwise to a solution of $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ (500 mg; 0.81 mmol) in dichloromethane (20 cm^3) and the reaction mixture was stirred for 12 h. The solution obtained was concentrated to a small volume and the complex precipitated by adding *n*-hexane. The red solid was filtered off, washed with cold *n*-hexane and dried under vacuum. Red crystals were obtained from dichloromethane–*n*-hexane. Yield 736 mg, 86%.

(b) A slight excess of NaH (3.3 mg, dispersion in mineral oil, 80% w/w, 0.125 mmol) was added to a solution of complex **1** (60 mg; 0.1 mmol) in tetrahydrofuran (15 cm^3). The reaction mixture was stirred for 8 h at r.t. The excess of solid NaH was filtered off and the solution evaporated to dryness. The solid residue was extracted with acetone and the complex precipitated by adding *n*-hexane. Yield 34 mg, 60%.

(Anal. Found: C, 58.7; H, 6.2. $C_{26}H_{33}ClOPRh$ requires: C, 58.8; H, 6.3%). δ_H ($CDCl_3$, 295 K) 0.44 [d, 3H, ^2J(HH) = 6.4 Hz, Me], 1.32 [d, 15H, ^3J(PH) = 3.5 Hz, C_5Me_5], 2.1–2.35 [m, 3H, PCH_2, CHMe], 2.9–3.2 [m, 2H, CH_2O], 7.3–8.0 [m, 10H, Ph]. δ_P [$CDCl_3$, 295 K] 25.4 [d, ^1J(RhP) = 143 Hz]. $[\alpha]_D^{22} = +90°$ (c 0.1, $CHCl_3$). CD ($CHCl_3$, 2.13×10^{-4} mol l^{-1}): 339 ($\Delta\varepsilon = +0.08$), 406 ($\Delta\varepsilon = -0.3$) and 498 nm ($\Delta\varepsilon = +0.20$ mol^{-1} cm^{-1}).

2.2.4. $[(\eta^5\text{-}C_5Me_5)RhCl(\eta^2\text{-}PPh_2CH_2CHMeCH_2OH\text{-}P,O)]BF_4$ (3)

The complex can be prepared by the two methods described below.

(a) $TlBF_4$ (102 mg; 0.35 mmol) was added to a solution of complex **1** (200 mg; 0.35 mmol) in acetone (20 cm^3). After heating the reaction mixture under reflux for 4 h, the precipitated thallium chloride was removed by filtration through Kieselguhr. The solution obtained was evaporated to a small volume and the complex precipitated by adding diethyl ether. The orange solid was filtered off, washed with cold diethyl ether and dried under vacuum. Red crystals were obtained from acetone–diethyl ether. Yield 358 mg, 89%.

(b) A mixture of the rhodium complex [{(η^5-C_5Me_5)RhCl}$_2$(μ-Cl)$_2$] (204 mg; 0.33 mmol) and $AgBF_4$ (128 mg; 0.66 mmol) in acetone (15 cm^3), was stirred for 1 h at r.t. The precipitated silver chloride was removed by filtration through Kieselguhr and, to the resulting solution, (*S*)-$PPh_2CH_2CHMeCH_2OH$ (170 mg; 0.66 mmol) dissolved in tetrahydrofuran (10 cm^3) was added dropwise. After stirring for 2 h, the solution was evaporated to a small volume and the complex precipitated by adding diethyl ether. The solid was filtered off, washed with diethyl ether and dried under vacuum. Yield 358 mg, 89%.

(Anal. Found: C, 50.9; H, 5.7. $C_{26}H_{34}BClF_4OPRh$ requires C, 50.5; H, 5.5%). ν_{max} (cm^{-1}) (KBr): 3355 (OH), 1100 and 520 (BF_4). δ_H ($CDCl_3$, 295 K) 0.73 [dd, 3H, ^3J(HH) = 6.7 Hz, ^4J(PH) = 2.3 Hz, Me], 1.45 [d, 15H, ^3J(PH) = 3.5 Hz, C_5Me_5], 1.7–1.9 [m, 1H, CH], 2.0–2.2 [m, 1H, PCH], 2.74 [dt, 1H, ^2J(HH) = 12 Hz, ^2J(PH) = 5.9 Hz, PCH], 3.5–3.9 [m, 2H, CH_2O], 5.4 [s, br, 1H, OH], 7.6–7.9 [m, 10H, Ph]. δ_P ($CDCl_3$, 295 K) 25.3 [d, ^1J(RhP) = 141 Hz]. δ_C ($CDCl_3$, 295 K) 8.9 [s, C_5Me_5], 19.7 [d, ^3J(PC) = 16.3 Hz, $CHCH_3$], 31.0 [d, ^2J(PC) = 7.3 Hz, $CHCH_3$], 34.0 [d, ^1J(PC) = 25 Hz, CH_2P], 66.0 [s, CH_2OH], 99.7 [dd, ^1J(PC) = 2.6 Hz, ^1J(RhC) = 7.5 Hz, C_5Me_5]. $[\alpha]_D^{22} = -226°$ (c 0.1, $CHCl_3$). CD ($CHCl_3$, 1.58×10^{-4} mol l^{-1}): 352 ($\Delta\varepsilon = +0.10$), 400 ($\Delta\varepsilon = -2.40$), 469 ($\Delta\varepsilon = +0.10$) and 512 nm ($\Delta\varepsilon = -0.20$ mol^{-1} cm^{-1}).

Table 1
Crystal data and refinement parameters for complex **3**

Empirical formula	$C_{26}H_{34}BClF_4OPRh$
Formula weight	618.67
Temperature (K)	297(2)
Wavelength (Å)	Mo–K_α (0.71073)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	9.365(2)
b (Å)	16.074(3)
c (Å)	17.961(4)
Volume (Å^3)	2781.7(10)
Z	4
D_{calc} (Mg m^{-3})	1.477
Absorption coefficient (mm^{-1})	0.812
F(619)	1264
Index ranges	$0 \le h \le 10$, $-20 \le k \le 20$, $-23 \le l \le 23$
Reflections collected	12 951
Independent reflections	6193 ($R_{int} = 0.0267$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6193/1/310
Goodness-of-fit on F^2	0.995
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0389$, $wR_2 = 0.1014$
R indices (all data)	$R_1 = 0.0463$, $wR_2 = 0.1051$
Absolute structure parameter	−0.06(4)
Largest difference peak and hole (e Å^{-3})	0.722 and −0.594

2.2.5. [(η^5-C_5Me_5)RhI_2(η^1-$PPh_2CH_2CHMeCH_2OH$–P)] (4)

An excess of sodium iodide (96 mg; 0.64 mmol) was added to a solution of complex **3** (100 mg; 0.16 mmol) in acetone (15 cm^3). The solution, which immediately changed from orange to dark violet, was stirred for 4 h. It was concentrated to a small volume and the complex precipitated by addition of *n*-hexane. The dark violet solid obtained was filtered off, washed with *n*-hexane and dried under vacuum. Yield 98 mg, 82% (Anal. Found: C, 41.9; H, 4.6. $C_{26}H_{34}I_2OPRh$ requires: C, 41.6; H, 4.6%). ν_{max} (cm^{-1}) (KBr) 3483 (OH). δ_H ($CDCl_3$, 295 K) 0.55 [d, 3H, ^2J(HH) = 6.7 Hz, Me], 1.68 [d, 15H, ^3J(PH) = 3.4 Hz, C_5Me_5], 2.1–2.3 [m, 1H, CHMe], 2.7–2.9 [m, H, PCH], 3.1–3.4 [m, 3H, PCH, CH_2O], 7.3–8.0 [m, 10H, Ph]. δ_P ($CDCl_3$, 295 K) 24.2 [d, ^1J(RhP) = 147 Hz].

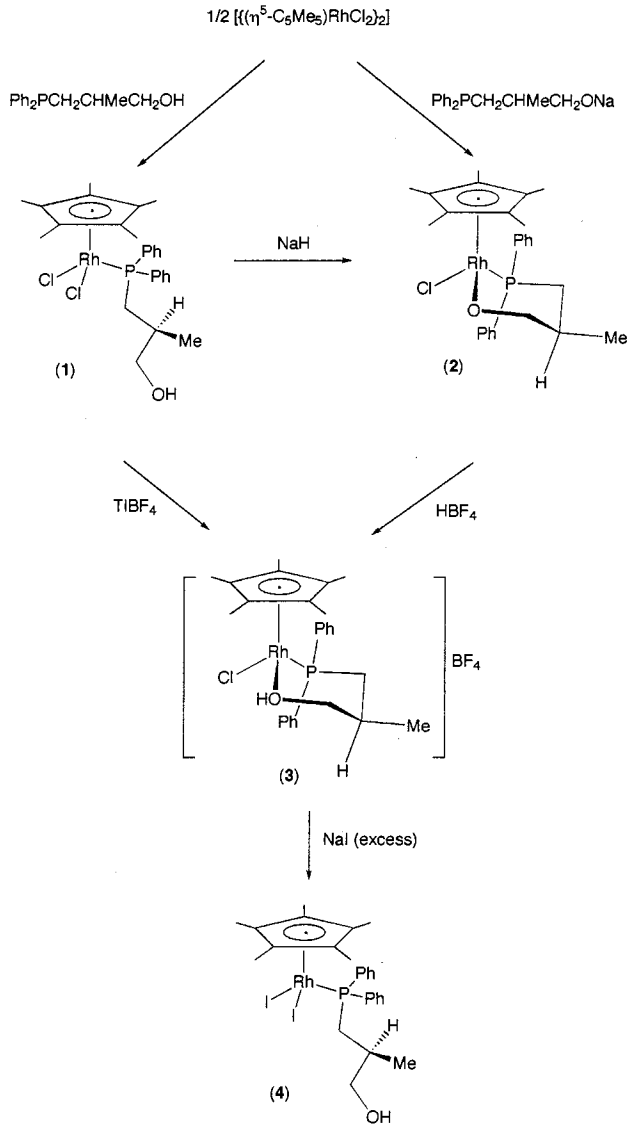
2.2.6. X-ray structure determination of complex 3

A red polyhedron of approximate dimensions of $0.30 \times 0.28 \times 0.14$ mm, obtained by slow diffusion of diethyl ether into an acetone solution, was selected for structure determination by X-ray diffraction. Intensity data were collected on a Siemens R3m/V diffractometer in $\theta/2\theta$ scan mode, using graphite-monochromated Mo–K_α radiation. Empirical corrections, via psi-scans, were applied for absorption.

A summary of crystal data and relevant refinement parameters are given in Table 1. The structure was solved by direct methods and refined by least-squares procedures with SHELX-97 [10]. Hydrogen bonded to oxygen atom was obtained from a difference synthesis and allowed to refine with O–H distance restrained to the value of 0.82(1) Å. A riding model was applied to all other H atoms which were placed at geometrically idealised positions with C–H = 0.96 Å. Isotropic thermal parameters were considered for all hydrogen equal to 1.2 times the equivalent isotropic thermal parameters of the corresponding parent atom. The BF_4 anion was restrained to be a regular tetrahedron with B–F = 1.37 Å and refined as a rigid group. The absolute structure was determined using the SHELX-97 routine to refine the Flack parameter which converged to −0.06(4).

3. Results and discussion

The monophosphine (*S*)-$Ph_2PCH_2CHMeCH_2OH$ was prepared by reaction of (*S*)-(+)-$BrCH_2CHMeCH_2OH$ with Ph_2PK in tetrahydrofuran solution in the presence of lithium diisopropylamide and characterised by ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy (see Section 2). This compound is an intermediate in the synthesis of the described compound $Ph_2P(O)CH_2CHMeCH_2OH$ [9]. The treatment of the monophosphine with the dinuclear complex [{(η^5-



Scheme 1.

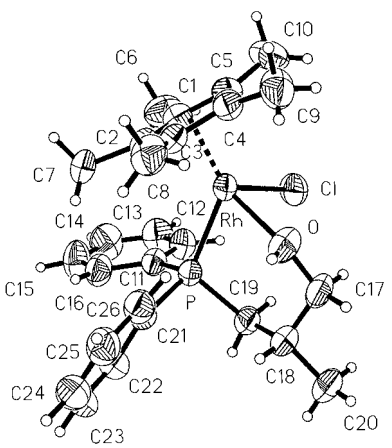


Fig. 1. Molecular view of the cation of complex **3**, together with the numbering scheme used.

$C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ in dichloromethane solution, in a 2:1 molar ratio, afforded the neutral compound $[(\eta^5\text{-}C_5Me_5)RhCl_2(\eta^1\text{-}PPh_2CH_2CHMeCH_2OH\text{–}P)]$ (**1**). Complex **1** reacted with sodium hydride in tetrahydrofuran solution deprotonating the alcohol group. The alkoxo group formed displaced a chloride ligand to give the complex $[(\eta^5\text{-}C_5Me_5)RhCl(\eta^2\text{-}PPh_2CH_2CHMeCH_2O\text{–}P,O)]$ (**2**). A similar synthetic result was obtained by reaction of the dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ with the sodium salt $Ph_2PCH_2CHMeCH_2ONa$ in tetrahydrofuran solution.

On the other hand, reflux of complex **1** with thallium tetrafluoroborate in acetone gave the cationic complex $[(\eta^5\text{ - }C_5Me_5)RhCl(\eta^2\text{ - }PPh_2CH_2CHMeCH_2OH\text{–}P,O)]\text{-}BF_4$ (**3**), that contains the neutral monophosphine bound in its bidentate form. This compound can be alternatively prepared by reaction of complex **2** with HBF_4 in diethyl ether solution. All reactions are summarised in Scheme 1.

All compounds were isolated as stable microcrystalline solids. The IR spectrum of complex **1** shows a strong absorption band at 3442 cm^{-1} corresponding to the OH group. As expected, complex **3** exhibits the ν(OH) stretching, shifted to lower frequencies (3355 cm^{-1}) relative to complex **1**, together with the characteristic bands of the uncoordinated anion (BF_4^-: ca. 1100, 520 cm^{-1}). Its ^{1}H-NMR spectrum in $CDCl_3$ exhibited the expected doublets resonances assigned to methyl groups of C_5Me_5 ring together with multiplet signals corresponding to the CH_2 and CH protons of the carbon chain. In complexes **1** and **2**, the methyl group bound to the asymmetric carbon appears as a doublet signal due to H–H coupling. However, for complex **3** the methyl group appears as a doublet of doublets due to P–H coupling [$^3J(HH) = 6.7$, $^4J(PH) = 2.3$ Hz]. The $^{31}P\{^1H\}$-NMR spectra show in all cases a doublet resonance at δ 25–26 with a ^1J(RhP) coupling in the range 141–143 Hz.

In order to determine the absolute configuration of complex **3**, its molecular structure was elucidated by diffractometric means. Single crystals were grown by slow diffusion of diethyl ether into an acetone solution. Molecular representation of the cation of complex **3** is shown in Fig. 1. Relevant bond distances and angles are given in Table 2.

In the cation, the rhodium atom shows a 'three-legged piano stool configuration', with the pentamethylcyclopentadienyl ligand occupying three fac positions, the bidentate phosphine–alcohol ligand bonded through the phosphorus and oxygen atoms and a chlorine atom completing the co-ordination sphere of the metal. The six-membered metallacycle ring adopts a chair-like conformation. In the complex the absolute configuration of the rhodium centre is *S* according to the following ligand priority $\eta^5\text{-}C_5Me_5 > Cl > P > O$ [11].

The Rh–C(ring) distances span the range 2.114(4)–2.229(4) Å and compare well with those found in other pentamethylcyclopentadienyl rhodium(III) complexes, $[(\eta^5\text{-}C_5Me_5)Rh\{(SePPh_2)_2CH\}]ClO_4$ [2.166(6)–2.188(7) Å] [12], $[(\eta^5\text{-}C_5Me_5)Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-}C_3H_3N_2)Ru(C_6H_6)]ClO_4{\cdot}CH_2Cl_2$ [2.175(12)–2.285(9) Å] [13] and $[(\eta^5\text{-}C_5Me_5)Rh(OH_2)(prophos)]SbF_6$ [2.165(9)–2.232(9) Å] [4a]. The Rh–P [2.328(1) Å], Rh–Cl [2.395(1) Å] and Rh–O [2.193(3) Å] distances are similar to those found in other related rhodium complexes, such as $[(\eta^5\text{-}C_5Me_5)RhCl(prophos)]BF_4$ [Rh–P, 2.325(1) and Rh–Cl, 2.393(1) Å] [4b] and $[(\eta^5\text{-}C_5Me_5)Rh(OH_2)(prophos)]SbF_6$ [Rh–P, 2.324(2) and Rh–O, 2.187(5) Å] [4a].

Variable temperature NMR experiments (213–333 K) of complex **3** show no evidence of the presence of two possible diastereomers in solution [$CDCl_3$, $(CD_3)_2CO$]. This result suggests that the formation of complex **3** is stereoselective and that the configuration at rhodium is retained in solution. However, although we have no evidence, we can not exclude definitively the fact that two diastereomers could be present in rapid exchange also at low temperature.

On the other hand, the circular dichroism spectra of complexes **2** and **3** in chloroform solution show negative Cotton effect centred at 406 and 400 nm, respectively. These results give evidence that both complexes present a similar configuration at rhodium centre (*S*). It is noteworthy that the proposed diastereoselectivity of the formation of complexes **2** and **3**, do not depend on the preparation method. In both cases, using the two preparative methods we observe identical spectroscopic properties.

Treatment of complex **3** with sodium iodide or triphenylphosphine in acetone solution led to the opening of the metallacycle ring by displacing the co-ordinated OH group of the metal centre. Thus, the reaction with an excess of sodium iodide gives the diiodo-complex $[(\eta^5\text{-}C_5Me_5)RhI_2(\eta^1\text{-}PPh_2CH_2CHMeCH_2OH\text{–}P)]$ (**4**) in high yield. However, after 10 h at reflux temperature, the reaction with PPh_3 gives a mixture of starting complex **3** and the cationic compound $[(\eta^5\text{-}C_5Me_5)RhCl(PPh_3)(\eta^1\text{ - }PPh_2CH_2CHMeCH_2OH\text{–}P)]^+$, which was characterised only by $^{31}P\{^1H\}$-NMR spectrum [$CDCl_3$, δ 19.48 {dd, $^1J(RhP) = 132$ Hz, $^2J(PP) = 52$ Hz, PPh_3}; δ 25.69 {dd, $^1J(RhP) = 140$ Hz, $-PPh_2$}].

Table 2
Selected bond lengths (Å) and angles (°) for complex **3**

Rh–C(1)	2.114(4)	Rh–C(2)	2.167(4)
Rh–C(3)	2.188(4)	Rh–C(4)	2.220(4)
Rh–C(5)	2.229(4)	Rh–P	2.328(1)
Rh–O	2.193(3)	Rh–Cl	2.395(1)
P–Rh–Cl	89.32(4)	O–Rh–Cl	86.14(10)
P–Rh–O	83.38(10)	Rh–O–C(17)	126.4(3)
Rh–P–C(19)	110.5(2)	P–C(19)–C(18)	104.3(3)
O–C(17)–C(18)	104.7(4)	C(17)–C(18)–C(19)	112.7(4)
C(11)–P–C(21)	106.5(2)		

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 145430 for compound **3**. 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; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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