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Rhodium (II) compounds with functionalized metalated phosphines as bridging ligands

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Abstract

The reaction of $Rh_2(O_2CCH_3)_4 \cdot 2CH_3OH$ with the phosphine $P(4\text{-}BrC_6H_4)_2(C_6H_5)$, **2**, results in the formation of the monometalated compound $Rh_2(O_2CCH_3)_3[PC] \cdot 2CH_3CO_2H$ (PC representing a metalated $P(4\text{-}BrC_6H_4)_2(C_6H_5)$). The reaction involves selective metalation of the phosphine at one Br-substituted ring (12:1 isomer ratio). The reaction of $Rh_2(O_2CCH_3)_3[(4\text{-}BrC_6H_3)\text{-}P(4\text{-}BrC_6H_4)(C_6H_5)] \cdot 2CH_3CO_2H$, **4**, with one additional mol of triphenylphosphine yields a mixture of two main stereoisomers $Rh_2(O_2CCH_3)_2[(4\text{-}BrC_6H_3)P(4\text{-}BrC_6H_4)(C_6H_5)]\ [(C_6H_4)P(C_6H_5)_2] \cdot 2CH_3CO_2H$, **5a** and **5b**, that were isolated as pure compounds. These two compounds were resolved in the corresponding ***M*** and ***P*** enantiomers as trifluoroacetate derivatives that show good enantioselectivities in catalytic transformation of α-diazocarbonyl compounds.

Keywords: Rhodium; P ligands; Chirality; Catalysis; Enantioselectivity

1. Introduction

Aryl phosphines undergo orthometalation in a process that is well documented [1,2]. Compounds of the general formula $Rh_2(O_2CR)_2[PC]_2$, representing dirhodium (II) compounds with two metalated aryl phosphines, [PC], with head to tail configuration are accessible by direct thermal reaction of the corresponding phosphine with dirhodium tetracarboxylate [3–7]. They are a family of dirhodium (II) compounds and show good activity and selectivity in the catalytic transformation of α-diazocarbonyl compounds. The inherent backbone chirality of these compounds has been explored for enantioselective reactions [8–12] since the racemic mixture can be separated by standard resolution methods in the ***M*** and ***P*** enantiomers [11,13].

New chiral orthometalated rhodium (II) catalysts have been synthesized using chiral phosphine ligands and their catalytic behaviour has been studied [14].

The good catalytic behaviour of these dirhodium (II) compounds prompted us to study the supporting of these homogenous catalysts and the catalytic behaviour under heterogeneous conditions. The first approach tested involved the linkage of the dirhodium units via carboxylate groups introduced in a mesoporous material. The catalytic selectivities of the resulting compounds were considerably lower than those observed for the analogous homogeneous catalysts and important leaching was also observed [15]. This result is consistent with the facility of exchange of the carboxylate groups with free carboxylic acid shown by these metalated compounds [16].

A similar exchange between the metalated and free phosphine has never been observed. Consequently, we consider, as an alternative strategy, the linkage of the

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catalyst to the inert material via one phenyl group of the phosphine.

Until now, we have studied to some extent the reaction of dirhodium (II) carboxylates with several substituted aryl phosphines. However, most of the phosphines used, contained groups (CH_3, F, Cl, CF_3, OCH_3) that are not reactive enough to allow further catalyst linkage [17,18]. The functional groups attached to the phosphine ligand should not be affected by the acid medium during the metalation process. Considering that the best catalytic selectivities have been obtained with catalysts containing triphenylphosphine or tris *p*-tolylphosphine, functional groups with strong electron-withdrawing substituents should be avoided.

Our first choice was the *p*-bromoarylphosphines. P(4-$BrC_6H_4)(C_6H_5)_2$, **1** and P(4-$BrC_6H_4)_2(C_6H_5)$, **2**. We report here some preliminary studies on the reactivity of rhodium (II) acetate and **1** and **2**. Two new isomeric compounds of the formula $Rh_2(O_2CCH_3)_2$[(4-BrC_6H_3)-P(4-BrC_6H_4)(C_6H_5)][(C_6H_4)P($C_6H_5)_2$] · $2CH_3CO_2H$, **5a** and **5b**, have been isolated and characterized by X-ray crystallography. The trifluoroacetate derivative compounds, isolated as pure ***M*** and ***P*** enantiomers, have been studied in catalytic processes, inter- and intramolecular cyclopropanation reactions.

2. Results and discussion

We explored first the regioselectivity of the metalation reaction using the phosphine **1** that can be activated at the ortho C–H bond of the substituted phenyl group or at one of the C–H bonds of the phenyl groups. In the last case the P atom becomes a center of chirality.

The reaction of rhodium (II) tetraacetate and **1**, under thermal or photochemical conditions, is not selective and gave the two mono metalated compounds, Rh_2-$(O_2CCH_3)_3$[(4-BrC_6H_3)P($C_6H_5)_2$] and $Rh_2(O_2CCH_3)_3$-[(C_6H_4)P(4-BrC_6H_4)(C_6H_5)] in approximately 1:1 ratio. The ^{31}P NMR spectrum of the reaction mixture shows two doublets of doublets centred at 18.5 ($^1J_{Rh-P}$ = 152 Hz, $^2J_{Rh-P}$ = 7 Hz) and 18.9 ppm ($^1J_{Rh-P}$ = 151 Hz, $^2J_{Rh-P}$ = 6 Hz). All the efforts to separate the pure compounds by chromatography and crystallization techniques were unsuccessful. A detailed NMR study allowed us to assign the signals centred at 18.9 ppm to $Rh_2(O_2CCH_3)_3$[(4-BrC_6H_3)P($C_6H_5)_2$] compound.

We also studied whether the phosphine **1** can undergo more selective metalation when it reacts with a monometalated compound. $Rh_2(O_2CCH_3)_3$[(4-$CH_3C_6H_3$)-P(4-$CH_3C_6H_4)_2$] · $2CH_3CO_2H$ was reacted with **1** under thermal or photochemical conditions, and in both conditions, the reaction yielded several compounds. The photochemical reaction was relatively cleaner and according to the ^{31}P NMR of the crude of the reaction three compounds were formed in a 4:1:1 ratio. By a combination of chromatography and crystallization, the major stereoisomer was isolated in low yield, as an analytically pure compound, **3**. All the efforts to obtain single crystals of this compound in order to perform the full structural characterization were unsuccessful, but according to further studies with the phosphine P(4-$BrC_6H_4)_2(C_6H_5)$, included in this paper, we assume that compound **3** contains the phosphine metalated through the 4-Br phenyl group, $Rh_2(O_2CCH_3)_3$[(4-BrC_6H_3)-P($C_6H_5)_2$][(4-$CH_3C_6H_3$)P(4-$CH_3C_6H_4)_2$] · $2CH_3CO_2H$.

Similar results were obtained in the reaction under photochemical conditions of the monometalated compound $Rh_2(O_2CCH_3)_3$[(C_6H_4)P($C_6H_5)_2$] · $2CH_3CO_2H$ with **1**.

The poor selectivity observed in the metalation reactions with the phosphine **1**, prompted us to use the phosphine P(4-$BrC_6H_4)_2(C_6H_5)$, **2**, as an alternative functionalized phosphine. By refluxing for 4 h, rhodium (II) acetate and **2** (1:1.1 molar ratio) in a mixture of toluene and acetic acid (3:1), the monometalated compound $Rh_2(O_2CCH_3)_3$[PC] · $2CH_3CO_2H$ was formed in high yield (>80%). The ^{31}P NMR spectrum of the purified compound indicated that the metalation reaction was highly regioselective as the two possible isomers were formed in the 12:1 ratio.

As phosphine **1**, P(4-$BrC_6H_4)_2(C_6H_5)$ can undergo orthometalation by activation of C–H bond in the phenyl or 4-Br substituted aryl group. A center of chirality is created at the P atom when one of the 4-Br substituted rings is activated.

Detailed NMR study let us identify the major product as $Rh_2(O_2CCH_3)_3$[(4-BrC_6H_3)P(4-BrC_6H_4)(C_6H_5)] · $2CH_3CO_2H$, **4**, the minor compound is assigned to $Rh_2(O_2CCH_3)_3$[(C_6H_4)P(4-$BrC_6H_4)_2$] · $2CH_3CO_2H$.

The high regioselectivity observed in the metalation of P(4-$BrC_6H_4)_2(C_6H_5)$ prompted us to prepare bis orthometalated compounds with a mixed set of phosphines, $Rh_2(O_2CCH_3)_2$[[(4-BrC_6H_3)P(4-BrC_6H_4)(C_6H_5)]-[(C_6H_4)P($C_6H_5)_2$] · $2CH_3CO_2H$, **5**. When a solution of **4** and P($C_6H_5)_3$ (1:1.1 molar ratio) in a mixture of toluene and acetic acid (3:1 volume ratio) was irradiated for 24 h, two isomeric compounds, **5a** and **5b**, were formed (Fig. 1). By a combination of chromatography and crystallization techniques they were separated in 33% and 37% yield, respectively, and were structurally characterized by X-ray methods. A third possible isomer, $Rh(O_2CCH_3)_2$[(C_6H_4)P(4-$BrC_6H_4)_2$][(C_6H_4)P($C_6H_5)_2$] · $2CH_3CO_2H$, was detected in solution in minor amount but was eliminated during the purification process. The ^{31}P NMR data for **5a** and **5b** are very similar and show the presence of two different phosphorus environments centred at around 19.0 and 20.5 ppm.

As an alternative synthetic route for compounds **5a** and **5b**, we reacted $Rh_2(O_2CCH_3)_3$[(C_6H_4)P($C_6H_5)_2$] · $2CH_3CO_2H$ with equimolar amount of phosphine **2**. The same three compounds were formed but the reaction

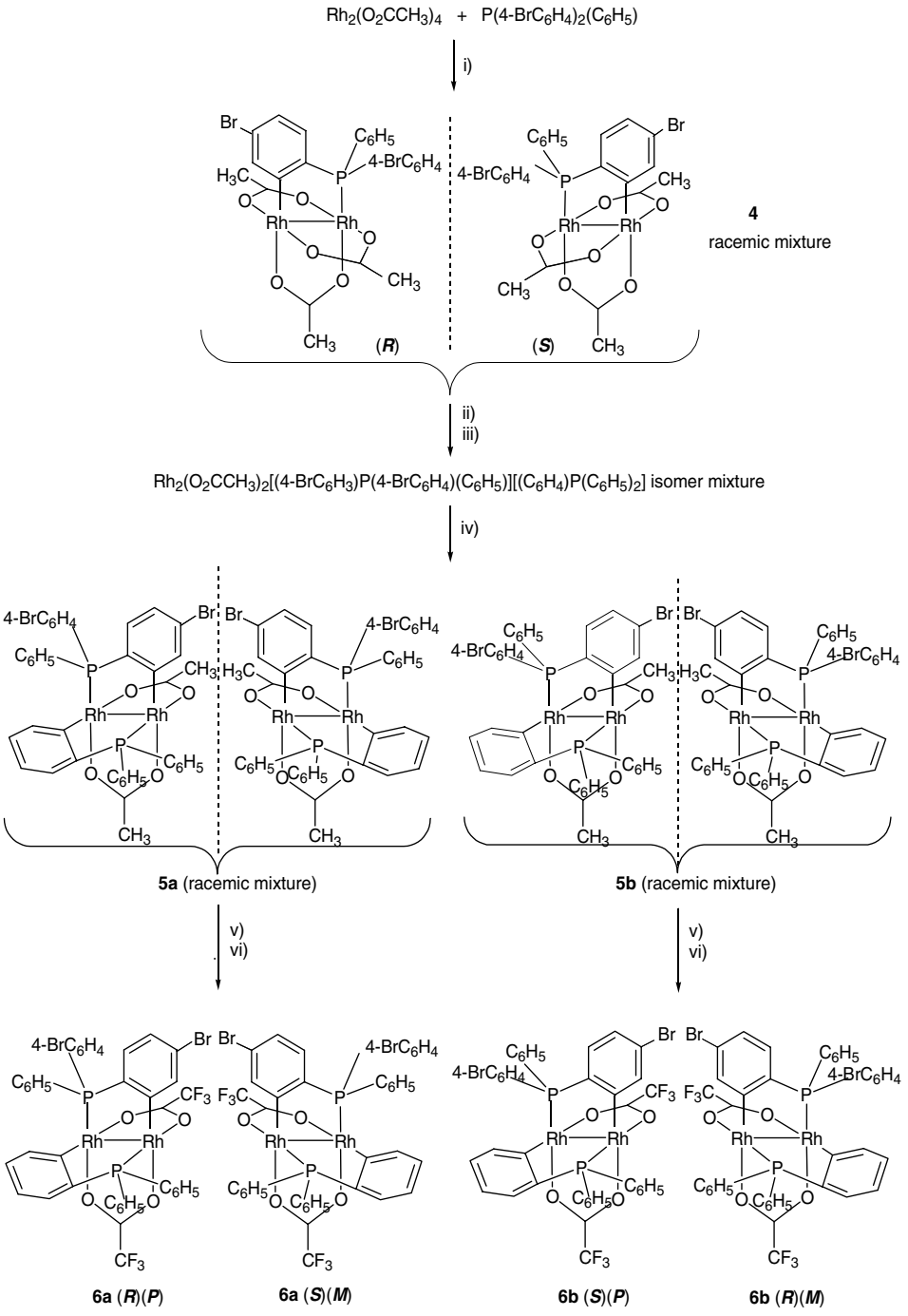


Fig. 1. Synthesis of pure enantiomeric bis cyclometalated compounds. (i) Reflux in toluene/acetic acid (3:1) for 4 h. (ii) PPh_3 (molar ratio 1:1.1). (iii) Irradiation for 24 h. (iv) Chromatography in SiO_2, elution with hexane/ethyl acetate/acetic acid (100:50:1). (v) ProtosH in a 1:10 molar ratio, reflux in toluene for 30′, chromatography in SiO_2, elution with CH_2Cl_2/diethyl ether (95:5 and 10 mg Hprotos/100 mL). (vi) CF_3CO_2H, chromatography in SiO_2, elution with CH_2Cl_2/ethyl acetate/trifluoroacetic acid (100:100:1). (*R*) and (*S*) are assigned to the configuration of the chiral P atom.

was not as clean as in the previous case. Consequently, the purification process was tedious and the final yields were lower (14% and 30%, respectively).

Compounds **5a** and **5b** with a mixed set of metalated phosphines are asymmetric molecules (Point Group C_1) and they present backbone chirality in the same way as the symmetric bis cyclometalated compounds $Rh_2(O_2CCH_3)_2[PC]_2 \cdot 2CH_3CO_2H$ (Point Group C_2). This backbone chirality produces enantiomers with ***M*** and ***P*** configuration [14]. These four enantiomers (Fig. 1), **6**, have been separated via ligand exchange with *N*-(4-methylphenylsulphonyl)-L-proline (protosH). Further chromatography allowed to separate the resulting diastereoisomers. The pure diastereoisomers were reacted

with trifluoroacetic acid to exchange the carboxylate ligands and obtain the pure enantiomers as trifluoroacetate derivatives. For both compounds, the enantiomer arising from the first eluted diastereoisomer was assigned to the ***M***-configuration [11].

Tris 4-tolylphosphine was also used replacing triphenylphosphine derivative in the above described reactions. Thus the readily available monometalated compound $Rh_2(O_2CCH_3)_3[(4\text{-}CH_3C_6H_3)P(4\text{-}CH_3C_6H_4)_2]\cdot 2CH_3CO_2H$ and an equimolar amount of the functionalized phosphine $P(4\text{-}BrC_6H_4)_2(C_6H_5)$ were irradiated in the experimental conditions already described. A mixture of the three possible isomers was obtained, two of formula $Rh(O_2CCH_3)_2\text{-}[(4\text{-}BrC_6H_3)P(4\text{-}BrC_6H_4)(C_6H_5)][(4\text{-}CH_3C_6H_3)P(4\text{-}CH_3\text{-}C_6H_4)_2]\cdot 2CH_3CO_2H$ and $Rh(O_2CCH_3)_2[(C_6H_4)P(4\text{-}BrC_6H_4)_2]\text{-}[(4\text{-}CH_3C_6H_3)P(4\text{-}CH_3C_6H_4)_2]\cdot 2CH_3CO_2H$ in a ratio 7:7:1. All the efforts to isolated pure compounds were unsuccessful.

3. Asymmetric catalysis

Compounds **6a**(*R*)(***P***), **6a**(*S*)(***M***), **6b**(*S*)(***P***) and **6b**(*R*)(***M***) were tested as catalysts in inter- and intramolecular cyclopropanation reactions.

3.1. Intermolecular cyclopropanation

The reaction of ethyl diazoacetate with styrene was used as model reaction to study the catalytic effectiveness, as well as the stereo- and enantioselectivity induced by the catalysts in the intermolecular cyclopropanation.

The results obtained in the cyclopropanation of styrene with ethyl diazoacetate using compounds **6a** and **6b** deserve a comparison with those reported for related dirhodium (II) catalysts containing triphenylphosphine and other *p*-substituted arylphosphines of formula $Rh(O_2CCF_3)_2[(4\text{-}XC_6H_3)P(4\text{-}XC_6H_4)_2]_2$ [8], (X = H, CH_3, F). The observed yields 60–70% (Table 1), are among the highest reported for these cyclometalated dirhodium (II) compound. Only the bulkier catalyst $Rh(O_2C(C_6H_5)_3)_2[(C_6H_4)P(C_6H_5)_2]_2$ [9] showed better yield (94%) but the enantioselectivity of this catalyst was very low (39 and 6% for **8** and **9**, respectively). The enantioselectivities observed for **6a** and **6b** are among the highest. All these compounds exhibit low diastereoselectivity.

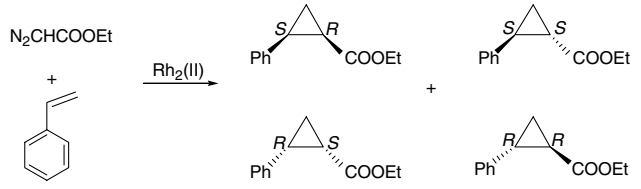
3.2. Intramolecular cyclopropanation

For the intramolecular processes, 1-diazo-5-hexen-2-one, **10** [19] was used as model substrate.

The cyclization of the diazo compound **10** in refluxing *n*-pentane was used to compare the catalytic behavior of **6a** and **6b** with other previously studied dirhodium (II) catalyst with orthometalated phosphines. Both catalysts afforded ketone **11** in high yield (92–95%) (Table 2). The activity of these catalysts is quite high as they work efficiently using a substrate:catalyst ratio of 1000, without any decrease in the enantioselectivities. Both the yields and the enantioselectivities compared well with the values reported for similar rhodium catalysts [9].

Catalyst **6a**(*S*)(***M***) and **6b**(*R*)(***M***) show very similar asymmetric induction and produce the same ketone with identical configuration, (1*R*, 5*S*), as it was the case for the reported rhodium catalysts with ***M*** configuration. This confirms that, as expected, the backbone configuration plays a dominant role in the catalytic induction because of the location of the bromo-substituent in the phenyl ring, far away from the catalytic centre.

Table 1
Asymmetric cyclopropanation of styrene



7 **8** **9**

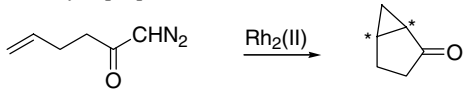
Catalyst	*T* (°C)	Yield[a]	**8/9**	% ee[b]		Configuration[c]
				8	**9**	**8/9**
6a(*S*)(***M***)	36	60	45/55	87	86	(1*S*, 2*R*/1*S*, 2*S*)
6b(*R*)(***M***)	36	70	50/50	85	83	(1*S*, 2*R*/1*S*, 2*S*)

[a] Cyclopropanation yield based on diazo ester.
[b] ee values calculated in this paper were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-β-CDX column.
[c] Configuration assignment was based on the GC retention times.

3.3. Structures of *5a* and *5b*

Crystals suitable for X-ray structure determination have been obtained for **5a** and **5b** (racemic mixture).

Table 2
Intramolecular cyclopropanation reaction



10 **11**

Catalyst	Ratio (**10**/cat)	**11**		
		Yield[a]	% ee[b]	Configuration[c]
6a(*S*)(***M***)	1000	93	56	1*R*, 5*S*
6a(*R*)(***P***)	150	93	45	1*S*, 5*R*
6b(*R*)(***M***)	1000	92	51	1*R*, 5*S*
6b(*S*)(***P***)	150	95	55	1*S*, 5*R*

[a] Cyclopropanation yield based on diazo ketone.
[b] ee values calculated in this paper were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-β-CDX column.
[c] Configuration assignment was based on the GC retention times.

Views of ***M*** configuration of both structures are shown in Figs. 2 and 3, respectively, together with important bond distances and angles. In both structures, the two rhodium atoms are bridged by four ligands: two acetate groups and two cisoid cyclometalated phosphines, $(C_6H_4)P(C_6H_5)_2$ and $(p\text{-}BrC_6H_3)P(p\text{-}BrC_6H_4)(C_6H_5)$ in a head-to-tail arrangement. Two oxygens of two acetic acid molecules, occupying the axial positions, complete the slightly distorted octahedral coordination. As observed in all the related compounds, each of these acetic molecules undergoes an O···H–O interaction with one oxygen atom of each bridging acetate group. The values of the Rh–Rh bond distances (2.51 Å in both cases) fall within the range reported for dirhodium compounds of comparable structures.

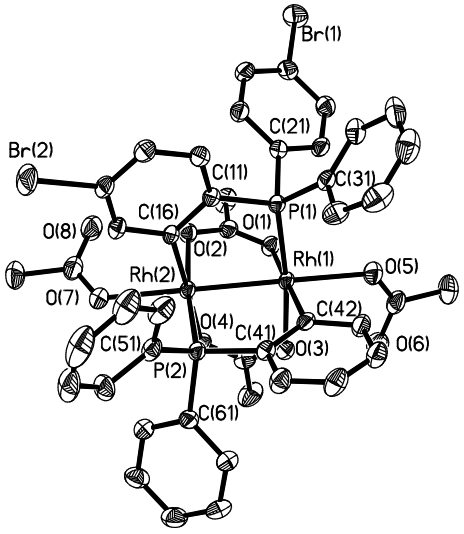


Fig. 2. Ortep diagram for Compound **5a**. Thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å) are: Rh(1)–Rh(2) = 2.5170(6), Rh(1)–P(1) = 2.2202(2), Rh(1)–C(42) = 1.984(7), Rh(2)–P(2) = 2.2156(2), Rh(2)–C(16) = 1.974(6), Rh(2)–Br(1) = 7.37. Selected angles (°) are: P(2)–Rh(1)–Rh(2) = 87.53(4), C(16)–Rh(2)–Rh(1) = 98.01(2), P(1)–Rh(1)–Rh(2) = 86.97(4). Hydrogen atoms are omitted for clarity.

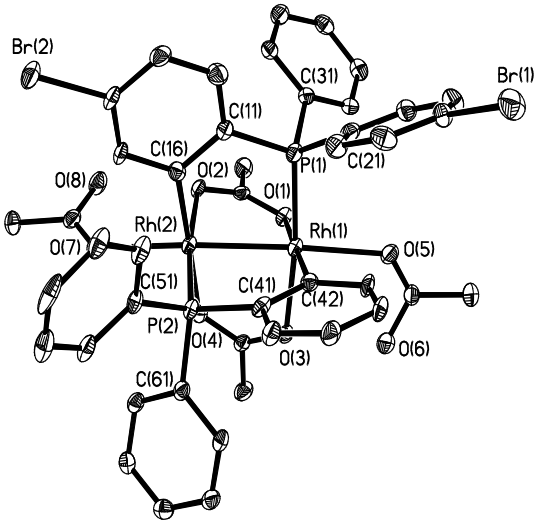


Fig. 3. Ortep diagram for Compound **5b**. Thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å) are: Rh(1)–Rh(2) = 2.5135 (9), Rh(1)–P(1) = 2.195(2), Rh(1)–C(42) = 1.983(8), Rh(2)–P(2) = 2.214(2), Rh(2)–C(16) = 1.987(9), Rh(2)–Br(1) = 8.13. Selected angles (°) are: P(2)–Rh(1)–Rh(2) = 86.83(6), C(16)–Rh(2)–Rh(1) = 97.9(2), P(1)–Rh(1)–Rh(2) = 87.60(6). Hydrogen atoms are omitted for clarity.

4. Conclusion

Two new orthometalated dirhodium (II) catalysts with backbone chirality and a center of chirality at one phosphorus atom have been synthesized and their catalytic behaviour in asymmetric inter- and intramolecular cyclopropanation reactions has been studied. The yields and the enantioselectivities observed in the cyclopropanation of styrene with ethyldiazoacetate are among the highest values observed for related dirhodium (II) catalysts. In the cyclization reaction of 1-diazo-5-hexen-2-one, the catalysts gave high yields and the enantioselectivities compared well with the values reported for similar dirhodium (II) catalysts.

In both reactions, the ***M*** and ***P*** configurations of each dirhodium compound induced identical enantiocontrol but with opposite ee values, that supports the generally accepted idea that the catalytic reaction occurs via a rhodium-carbenoid species. The chirality at the P atom has no influence on the catalytic results as the 4-Br-substituents in the phenyl rings are far away from the catalytic centre.

5. Experimental section

Commercially available $Rh_2(O_2CCH_3)_4 \cdot (CH_3OH)_2$ was purchased from Pressure Chemical Co. $P(C_6H_5)_3$, CF_3CO_2H, styrene and ethyldiazoacetate were used as purchased. All solvents were of analytical grade. *N*-*p*-tolylsulfonyl-L-proline (ProtosH) [20], 1-diazo-5-hexen-2-one [21], $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2] \cdot 2CH_3CO_2H$ [17], $Rh_2(O_2CCH_3)_3[4\text{-}CH_3C_6H_3)P(4\text{-}CH_3C_6H_4)_2] \cdot 2CH_3CO_2H$ [22], $P(4\text{-}BrC_6H_4)(C_6H_5)_2$ and $P(4\text{-}BrC_6H_4)_2(C_6H_5)$ [23] were synthesized according to the method described in the literature. All the irradiations were made with an OSRAM (60 w, 230 V) lamp. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz and a Bruker 400 MHz spectrometers as solutions in $CDCl_3$. Chemical shifts are reported in ppm. The coupling constants (*J*) are in Hertz (Hz). Analysis were provided by Centro de Microanálisis Elemental, Universidad Complutense de Madrid. Column chromatography was performed on silica gel

(35–70 mesh). Solvent mixtures are volume/volume mixtures, unless specified otherwise. All reactions were carried out in oven-dried glassware under argon atmosphere, although the isolated solids are air-stable. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at the Na–D line in 10 cm quartz cuvettes. The ee values were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-β-CDX column.

5.1. Synthesis of $Rh_2(O_2CCH_3)_2[(4\text{-}BrC_6H_3)P(C_6H_5)_2]$-$[(4\text{-}CH_3C_6H_3)P(4\text{-}CH_3C_6H_4)_2] \cdot 2CH_3CO_2H$ (**3**)

5.1.1. Method A

$Rh_2(O_2CCH_3)_3[(4\text{-}CH_3C_6H_3)P(4\text{-}CH_3C_6H_4)_2] \cdot 2CH_3CO_2H$ (100 mg, 0.124 mmol, 1.0 equiv.) and $P(C_6H_5)_2(4\text{-}BrC_6H_4)$ (48 mg, 0.141 mmol, 1.1 equiv.) were dissolved in a mixture of toluene and acetic acid (3:1, 100 mL) to give a red solution. It was stirred and irradiated under an argon atmosphere for 14 h and the color turned purple. After evaporation to dryness the crude product was purified by column chromatography (silica gel–hexane, 2×30 cm). Elution with hexane/CH_2Cl_2/acetic acid (100:100:1) afforded one purple band which was collected and evaporated to dryness. The ^{31}P NMR spectrum showed that the product was a mixture of different orthometalated compounds. The chromatography was repeated (silica gel–hexane, 2×50 cm) using hexane/ethyl acetate/acetic acid (100:100:1) as eluent. A large band was collected in two equal fractions, the first one contained the main product. The solvent was eliminated under vacuum, the residue was solved in CH_2Cl_2 and precipitation with hexane gave pure compound **3** as a purple powder (35 mg, yield 26%).

5.1.2. Method B

$Rh_2(O_2CCH_3)_3[(4\text{-}CH_3C_6H_3)P(4\text{-}CH_3C_6H_4)_2] \cdot 2CH_3CO_2H$ (50 mg, 0.062 mmol, 1.0 equiv.) and $P(C_6H_5)_2(4\text{-}BrC_6H_4)$ (23 mg, 0.067 mmol, 1.1 equiv.) were dissolved in a mixture of toluene and acetic acid (3:1, 40 mL) to give a red solution. The solution was refluxed for 3 h and the colour changed to purple. After evaporation to dryness the crude product was purified by column chromatography (silica gel–hexane, 1.5×30 cm) following the same procedure described in method A, gave pure compound **3** (12 mg, yield 18%).

^1H NMR: δ 1.25 (s, 6H), 1.87 (s, 3H), 2.21 (s, 6H), 2.34 (s, 3H) 2.36 (s, 3H), 6.40 (t, $J = 8.6$ Hz, 1H), 6.58–6.60 (m, 2H), 6.71 (bs, 1H), 6.78–6.82 (m, 4H), 6.88 (d, $J = 8.3$ Hz, 1H), 6.92–6.98 (m, 3H), 7.02–7.08 (m, 2H), 7.16–7.20 (m, 2H), 7.25 (m, 1H), 7.35–7.44 (s, 3H), 7.56–7.60 (m, 2H), 7.64–7.70 (m, 2H). $^{13}C\{^1H\}$ NMR: δ 21.3, 21.4, 22.0, 22.4, 22.7, 123.2–145.8 (aromatic signals), 165.3 (m, metalated), 170.4 (m, metalated), 180.5, 182.6, 182.8. $^{31}P\{^1H\}$ NMR: δ 17.5 (dd; $^1J_{P-Rh} = 167$ Hz, $^2J_{P-Rh} = 7$ Hz), 21.2 (dd, $^1J_{P-Rh} = 173$ Hz, $^2J_{P-Rh} = 7$ Hz). Anal. Calcd. for $C_{47}H_{47}BrO_8P_2Rh_2$: C, 51.90; H, 4.35. Found: C, 51.35; H, 4.32%.

5.2. Synthesis of $Rh_2(O_2CCH_3)_3[(4\text{-}BrC_6H_3)P(4\text{-}BrC_6H_4)(C_6H_5)] \cdot 2CH_3CO_2H$ (**4**)

$Rh_2(O_2CCH_3)_4 \cdot 2\ CH_3OH$ (250 mg, 0.494 mmol) was dissolved under reflux in a mixture of toluene and acetic acid (3:1, 120 mL) and $P(4\text{-}BrC_6H_4)_2(C_6H_5)$ (226, 0.538 mmol, 1.1 equiv.) dissolved in toluene (15 mL), was slowly added to the green solution. The solution changed from green to red and after 1/2 h of stirring without further heating, became deep blue. After refluxing for 4 h the solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel–hexane, 3×30 cm). Elution with hexane/ethyl acetate/acetic acid (100:50:1) separated a deep blue band. Removal of the solvent gave a crude oil which was recrystallized from CH_2Cl_2/hexane yielding a deep blue solid (378 mg, yield 83%). The ^{31}P NMR showed that the solid contained a mixture of monometalated products in a 12:1 ratio. The major product was identified as the monometalated $Rh_2(O_2CCH_3)_3[(4\text{-}BrC_6H_3)P(4\text{-}BrC_6H_4)(C_6H_5)] \cdot 2CH_3CO_2H$, **4**. ^1H NMR: δ 1.28 (s, 3H), 1.40 (s, 3H), 2.24 (s, 6H), 2.34 (s, 3H), 6.68 (t, $J = 8.9$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.30–7.47 (m, 9H), 8.78 (s, 1H). $^{13}C\{^1H\}$ NMR: δ 21.9, 23.5, 23.7, 24.0, 123.3–143.0 (aromatic signals), 166.2 (dd, $J = 34.0$ Hz, $J = 24.6$ Hz, metalated), 180.8, 184.0, 191.3. $^{31}P\{^1H\}$ NMR: δ 18.8 (dd; $^1J_{P-Rh} = 150$ Hz, $^2J_{P-Rh} = 6$ Hz). Anal. Calcd. for $C_{28}H_{29}Br_2O_{10}PRh_2$: C, 36.44; H, 3.15. Found: C, 36.98; H, 3.23%.

5.3. Synthesis of $Rh_2(O_2CCH_3)_2[(4\text{-}BrC_6H_3)P(4\text{-}BrC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2] \cdot 2CH_3CO_2H$, **5a** and **5b**

$Rh_2(O_2CCH_3)_3[(4\text{-}BrC_6H_3)P(4\text{-}BrC_6H_4)(C_6H_5)] \cdot 2CH_3CO_2H$, **4**, (100 mg, 0.108 mmol, 1.0 equiv.) and $P(C_6H_5)_3$ (31.3 mg, 0.119 mmol, 1.1 equiv.) were dissolved in a mixture of toluene and acetic acid (3:1, 100 mL) to give a red solution. The solution was stirred under an argon atmosphere and irradiated for 20 h during which it turned purple. The solvent was removed at reduced pressure. The residual red oil was dissolved in 5 mL of CH_2Cl_2/hexane (1:1) and chromatographed on a column (silica gel–hexane, 1.5×50 cm). Elution with hexane/ethyl acetate/acetic acid (100:50:1) separated two red bands in equal amounts which were collected. Both solutions were evaporated to dryness and the crude oils were recrystallized from CH_2Cl_2/hexane yielding red solids, **5a** and **5b**.

5a. Yield (45 mg, 37%). ^{1}H NMR: δ 1.25 (s, 6H), 2.18 (s, 6H), 6.38 (t, J = 7.8 Hz, 1H), 6.60–6.66 (m, 3H), 6.80–6.88 (m, 5H), 7.02–7.06 (m, 2H), 7.14–7.20 (m, 4H), 7.32–7.44 (m, 7H), 7.56–7.62 (m, 4H). ^{13}C{^{1}H} NMR: δ 22.3 (s, axial CH_3COOH), 22.5 (s, bridge CH_3COO^-), 22.8 (s, bridge CH_3COO^-), 122–146 (m, aromatic), 164.8 (m, metalated), 169.2 (m, metalated), 179.8 (s, axial CH_3COOH), 181.7 (d, J_{P-C} = 2 Hz, bridge CH_3COO^-), 181.9 (d, J_{P-C} = 3 Hz, bridge CH_3COO^-). ^{31}P{^{1}H} NMR: δ 19.4 (dd, $^1J_{P-Rh}$ = 168 Hz, $^2J_{P-Rh}$ = 8 Hz), 20.9 (dd, $^1J_{P-Rh}$ = 173 Hz, $^2J_{P-Rh}$ = 7 Hz). Anal. Calcd for $C_{44}H_{40}Br_2O_8P_2Rh_2$: C, 46.98; H, 3.58. Found: C, 46.00; H, 3.54%.

5b. Yield (41 mg, 33%). ^{1}H NMR: δ 1.23 (s, 6H), 2.18 (s, 6H), 6.34 (t, J = 8.7 Hz, 1H), 6.65 (m, 3H), 6.76 (m, 1H), 6.88 (m, 4H), 7.06 (m, 2H), 7.16 (m, 4H), 7.38 (m, 7H), 7.63 (m, 4H). ^{13}C{^{1}H} NMR: δ 22.2 (s, axial CH_3COOH), 22.6 (s, bridge CH_3COO^-), 121.3–140.4 (aromatic signals), 164.9 (m, metalated), 169.0 (m, metalated), 179.5 (s, axial CH_3COOH), 181.7 (s, bridge CH_3COO^-), 181.9 (d, bridge CH_3COO^-). ^{31}P{^{1}H} NMR: δ 19.0 (dd, $^1J_{P-Rh}$ = 168 Hz, $^2J_{P-Rh}$ = 7 Hz), 20.5 (dd, $^1J_{P-Rh}$ = 173 Hz, $^2J_{P-Rh}$ = 7 Hz). Anal. Calcd for $C_{44}H_{40}Br_2O_8P_2Rh_2$: C, 46.98; H, 3.58. Found: C, 47.38; H, 3.63%.

5.4. General procedure for the synthesis of enantiomerically pure Rh(II) complexes with orthometalated arylphosphines

Rh(II) diastereoisomers were prepared by a modified method first published by our group [13]. To a solution of the bis orthometalated dirhodium (II) compound (157 mg, 0.140 mmol, 1.0 equiv.) in toluene (20 mL) was added *N*-(4-methylphenylsulphonyl)-L-proline (protosH) (376 mg, 1.40 mmol, 10 equiv.) in a 1:10 molar ratio. The mixture was heated under reflux for 30 min. The solvent was evaporated under reduced pressure and the crude product was dried under vacuum. This procedure was repeated four times with new addition of 20 mL of toluene each time. The resulting red solid was dissolved in CH_2Cl_2/hexane (1:1, 5 mL) and the solution was transferred to a column of chromatography (silica gel–hexane, 2 × 50 cm). Elution with CH_2Cl_2/diethyl ether (95:5 and 10 mg Hprotos/100 mL) separated both diastereoisomers. The solutions were evaporated under reduced pressure. Each diastereoisomer was dissolved in 10 mL of CH_2Cl_2 and five drops of trifluoroacetic acid were added; the mixture was stirred for half an hour. The solution was concentrated, transferred to a column (silica gel–hexane, 1.5 × 50 cm) and eluted with CH_2Cl_2/ethyl acetate/trifluoroacetic acid (100:100:1). The resulting solution was evaporated and the residue was crystallized from CH_2Cl_2/hexane.

5.5. $Rh_2(O_2CCF_3)_2[(4\text{-}BrC_6H_3)P(4\text{-}BrC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2]\cdot 2H_2O$ [**6a**(*S*)(***M***)] and [**6a**(*R*)(***P***)]

Spectroscopic data: ^{1}H NMR: δ 6.45 (m, 1H), 6.60–6.80 (m, 6H), 6.84–6.98 (m, 4H), 7.04–7.12 (m, 2H), 7.14–7.22 (m, 2H), 7.32–7.46 (m, 7H), 7.50–7.62 (m, 4H). ^{13}C{^{1}H} NMR: δ 114.9 (q, CF_3, J_{C-F} = 287 Hz) 122–146 (m, aromatic), 160.6 (m, metalated) 164.8 (m, metalated), 166.5 (q, CF_3COO, J_{C-F} = 38 Hz). ^{31}P{^{1}H} NMR: δ 16.5 (bd, $^1J_{P-Rh}$ = 165 Hz), 18.2 (bd, $^1J_{P-Rh}$ = 172 Hz).

6a(*S*)(***M***): Yield 47%. $[\alpha]_D^{20} = -160$ (c = 0.020, $CHCl_3$). Anal. Calcd. for $C_{40}H_{30}Br_2F_6O_6P_2Rh_2$: C, 41.82; H, 2.61. Found: C, 41.46; H, 2.83%.

6a(*R*)(***P***): Yield 73%. $[\alpha]_D^{20} = +157$ (c = 0.021, $CHCl_3$). Anal. Calcd. for $C_{40}H_{30}Br_2F_6O_6P_2Rh_2$: C, 41.82; H, 2.61. Found: C, 41.27; H, 2.75%.

5.6. $Rh_2(O_2CCF_3)_2[(4\text{-}BrC_6H_3)P(4\text{-}BrC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2]\cdot 2H_2O$ [**6b**(*R*)(***M***)] and **6b**(*S*)(***P***)

Spectroscopic data: ^{1}H NMR: δ 6.42 (m, 1H), 6.60–6.76 (m, 6H), 6.84–7.00 (m, 4H), 7.14–7.22 (m, 4H), 7.32–7.46 (m, 7H), 7.50–7.60 (m, 4H). ^{13}C{^{1}H} NMR: δ 114.8 (q, CF_3, J_{C-F} = 287 Hz) 122–146 (m, aromatic), 160.9 (m, metalated) 164.9 (m, metalated), 166.4 (q, CF_3COO, J_{C-F} = 39 Hz). ^{31}P{^{1}H} NMR: δ 16.9(bd, $^1J_{P-Rh}$ = 166 Hz), 18.4 (bd, $^1J_{P-Rh}$ = 172 Hz).

6b(*R*)(***M***): Yield 61%. $[\alpha]_D^{20} = -115$ (c = 0.020, $CHCl_3$). Anal. Calcd. for $C_{40}H_{28}Br_2F_6O_6P_2Rh_2$: C, 41.82; H, 2.61. Found: C, 41.15; H, 2.81%.

6b(*S*)(***P***): Yield 60%. $[\alpha]_D^{20} = +119$ (c = 0.021, $CHCl_3$). Anal. Calcd. for $C_{40}H_{28}Br_2F_6O_6P_2Rh_2$: C, 41.82; H, 2.61. Found: C, 41.46; H, 2.86%.

5.7. Catalytic intermolecular cyclopropanation

The reactions of ethyl diazoacetate with styrene were performed by slow addition (1.5 mL/h) of the solution of the diazo compound (81 μL, 0.8 mmol) in pentane (5 mL) to a refluxing solution (20 mL) containing the rhodium (II) complex (1 mol%) and the styrene (230 μL, 2.0 mmol) in the same solvent. After complete addition, the reaction mixture was stirred at reflux for 2 h and cooled to room temperature. The resulting solution was filtered through a short plug of silica to remove the catalyst and the solvent was evaporated under reduced pressure. The yield of the reaction was calculated by ^{1}H and ^{13}C NMR spectroscopy and the enantiopurities of the products were calculated by chiral gas chromatography (oven temperature 100 °C for 5 min, then 2 °C/min to 200 °C). t_R: *cis*-(1*S*,2*R*), 22.22 min; *cis*-(1*R*,2*S*), 22.56 min; *trans*-(1*R*,2*R*), 24.76 min; *trans*-1*S*,2*S*, 24.98 min.

5.8. Intramolecular cyclopropanation

Diazo compound **10** was prepared from the corresponding carboxylic acid by reaction with methyl chloroformate, followed by treatment with freshly prepared diazomethane. Catalytic reactions were performed by addition of a solution of **10** (50 mg) in pentane (5 mL) to a refluxing solution (10 mL) containing the rhodium (II) complex (molar ratio of **10** to Rh(II) see Table 2) in the same solvent; the mixture was heated at reflux for 1 h. The work-up procedure of the reaction mixture was similar to that mentioned above for the intermolecular processes. The yield of the reaction was calculated by ^{1}H and ^{13}C NMR spectroscopy. The cyclization product was purified by HPLC and the enantiomeric excesses were calculated by chiral gas chromatography (oven temperature 70 °C for 1 min, then 6 °C/min to 200 °C). t_R: (1*R*,5*S*), 7.42 min; (1*S*,5*R*), 8.02 min.

6. X-ray crystallographic study

Well formed crystals of complexes **5a** and **5b** were used for X-ray structures determination in a Kappa CCD diffractometer (Mo Kα radiation, λ = 0.71067 Å). Unit-cell dimensions were determined by a least squares fit of 50 reflections. Systematic absences in both cases were consistent with the space group $P\bar{1}$. The structures were solved by direct methods using the SHELXTL [24] software package. The correct positions for the rhodium atoms were deduced from an E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were placed in geometrically generated positions and refined riding on the carbon atom to which they are attached except in the water molecule of crystallization in compound **5a**. Details of the data collection, cell dimensions and structure refinement are given in Table 3.

Table 3
Crystallographic data

	5a · H_2O	**5b**
Empirical formula	$C_{44}H_{38}Br_2O_9P_2Rh_2$	$C_{44}H_{38}Br_2O_8P_2Rh_2$
Molecular mass	1138.32	1122.32
Wavelength	0.71067	0.71067
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.6790(2)	11.4130(3)
b (Å)	12.1130(2)	11.9410(3)
C (Å)	18.6680(3)	18.5390(6)
α (°)	74.6090(6)	72.5160(19)
β (°)	86.3810(7)	79.2410(13)
γ (°)	64.1040(7)	63.1710(13)
V (Å^3)	2286.29(7)	2146.55(10)
Z	2	2
Density (calculated)	1.654	1.736
Absorption coefficient	2.591	2.757
Reflections collected	38715	37811
Goodness-of-fit on F^2	1.087	1.102
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0650, wR_2 = 0.0982	R_1 = 0.0690, wR_2 = 0.1428

CCDC-238509 (**5a**), and -238510 (**5b**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retriving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ; Fax: (internat) +44-1223/336-033; E-mail: deposit@ccdc.cam.uk].

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