Chiral phosphonite, phosphite and phosphoramidite η⁶-arene-ruthenium(II) complexes: application to the kinetic resolution of allylic alcohols†‡

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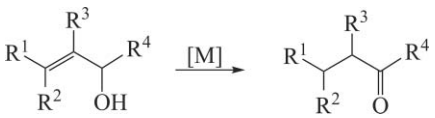
Received 15th March 2010, Accepted 1st June 2010
First published as an Advance Article on the web 21st July 2010
DOI: 10.1039/c0dt00140f

The synthesis and characterization of chiral arene-ruthenium complexes [$RuCl_2$(η⁶-arene){(*R*)-PR-(binaphthoxy)}] (arene = benzene (**1**), *p*-cymene (**2**), mesitylene (**3**); R = Ph (**a**), OPh (**b**), piperidyl (**c**)) are described. Derivatives **1–3** have been employed to promote the kinetic resolution of allylic alcohols through a redox-isomerization process. As a general trend, the best selectivities are attained with the more sterically hindered catalysts *i.e.* those containing *p*-cymene or mesitylene ligands.

Introduction

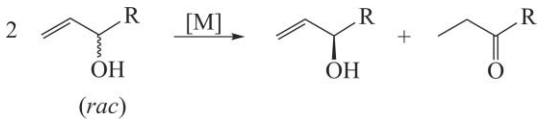
The catalytic redox-isomerization of allylic alcohols represents a useful synthetic process to generate aldehydes or ketones (Scheme 1).[1] The best performances for this transformation, in terms of both activity and selectivity, have been obtained with catalytic systems based on iron, ruthenium, rhodium and iridium complexes.[1–2] However, despite the extensive studies reported on this reaction, its asymmetric version, a potential route to optically active carbonyl compounds with a stereogenic center in α- ($R^3 \neq CHR^1R^2$) or β-position ($R^1 \neq R^2$), still remains almost unexplored.[3]



Scheme 1 Redox-isomerization of allylic alcohols.

Another asymmetric process, also based on this particular transformation and even less investigated, is the kinetic resolution of allylic alcohols.[4,5] In this case, the chiral catalyst employed preferably converts one enantiomer of the allylic alcohol into a ketone, affording enantio-enriched solutions of the other isomer (Scheme 2).

As far as we are aware, only two studies on this kinetic resolution reaction have been reported to date. The first one, involving *in situ* generated [RhCl{(−)-DIOP}] catalyst, allowed the generation of (*S*)-enantio-enriched 3-buten-2-ol with extremely low enantiomeric excess (1.09%).[4a] An improved selectivity was reached in the kinetic resolution of 4-hydroxy-2-cyclopentenone using the chiral complex [Rh{(*R*)-BINAP}$(MeOH)_2$][ClO_4] (e.e. = 91%).[4b] Nevertheless, this procedure presents a series of major drawbacks: (*i*) a very long reaction time is required (14 days), (*ii*) a low temperature (0 °C) must be maintained throughout the process, and (*iii*) a low yield in the *enantio*-enriched allylic alcohol is obtained (27%). Hence, the development of a selective metal-catalyzed resolution of allylic alcohols, easy to carry out, remains a challenge.



Scheme 2 Kinetic resolution of allylic alcohols.

During the last years, our research group has explored the catalytic activity of different arene-ruthenium(II) complexes in the redox-isomerization of allylic alcohols,[6] finding that phosphite, phosphinite and phosphonite derivatives of the type [$RuCl_2$(η⁶-*p*-cymene)(PR_3)] are particularly efficient to promote this transformation under extremely smooth reaction conditions.[6b,c] With these precedents in mind, we decided to investigate the catalytic behaviour of similar chiral complexes in the kinetic resolution of allylic alcohols. In particular, we focused our interest on arene-ruthenium(II) derivatives containing monodentate phosphonite-, phosphite- or phosphoramidite-ligands derived from binaphthol.

We must note that, during the last two decades, this type of ligands has been successfully employed in a huge number of highly selective asymmetric catalytic processes.[7] Thus, in the present work, we describe the synthesis of new chiral arene-ruthenium(II) complexes with P-donor ligands **a–c** (Fig. 1)[8] and a evaluation of their capacity to promote the kinetic resolution of allylic alcohols.

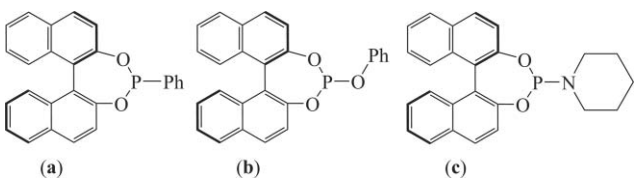


Fig. 1 Structure of (*R*)-enantiomer of the ligands **a–c**.

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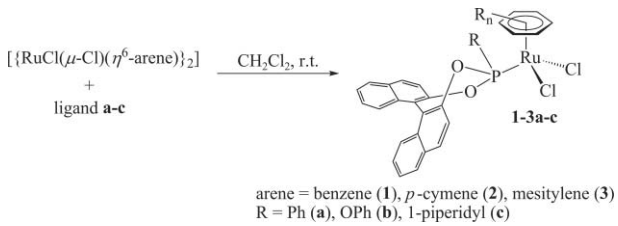
† Dedicated to the memory of José Manuel Concellón Gracia.

‡ Electronic supplementary information (ESI) available: X-Ray diffraction data and details on catalytic experiments. CCDC reference numbers 769455 (**1a**), 769456 (**1b**), 769457 (**3b**) and 769458 (**3c**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00140f

Results and discussion

Synthesis and characterization of the phosphonite-, phosphite- and phosphoramidite-complexes 1–3

Treatment of the benzene dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-benzene})\}_2]$[9] with a slight excess of ligands **a–c** in dichloromethane at room temperature gives rise to the selective formation of the corresponding mononuclear derivatives $[RuCl_2(\eta^6\text{-benzene})(L)]$ (L = **a** (**1a**), **b** (**1b**), **c** (**1c**)), which were isolated in good yields (Scheme 3). Similarly, the *p*-cymene and mesitylene analogues, $[RuCl_2(\eta^6\text{-}p\text{-cymene})(L)]$ (L = **a** (**2a**), **b** (**2b**), **c** (**2c**)) and $[RuCl_2(\eta^6\text{-mesitylene})(L)]$ (L = **a** (**3a**), **b** (**3b**), **c** (**3c**)), respectively, have been prepared starting from the dimeric precursors $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$[10] and $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-mesitylene})\}_2]$[11] (Scheme 3). All these arene-ruthenium(II) derivatives have been synthesized both in racemic ((*rac*)-**1–3**) and optically pure forms ((*R*)-**1–3**) using ligands **a–c** as a racemic mixture ((*rac*)-**a–c**) or as their (*R*)-enantiomer ((*R*)-**a–c**), respectively.



Scheme 3 Synthesis of complexes **1–3**.

Compounds **1–3**, isolated as air-stable orange–brown solids, have been characterized by means of standard spectroscopic techniques ($^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR) as well as elemental analysis, with all data fully consistent with the proposed formulations. In particular, the $^{31}P\{^1H\}$ NMR spectra for **1–3** show a unique singlet signal at δ 177.8–181.7 (**a**), 129.8–135.3 (**b**) and 139.9–147.8 ppm (**c**), the chemical shift observed falling within the expected range for a coordinated phosphonite, phosphite and phosphoramidite, respectively.[12]

The molecular structures of **1a**,[13] **1b**, **3b** and **3c** have been unambiguously confirmed by means of X-ray diffraction.[14] ORTEP plots are shown in Fig. 2, 3, 4 and 5, respectively, and selected bonding parameters appear in the captions. For all the derivatives, the geometry around the ruthenium atom can be described as a distorted octahedron, with the arene ligand occupying three coordination sites. The values of the interligand angles Cl(1)–Ru–Cl(2), Cl(1)–Ru–P(1) and Cl(2)–Ru–P(1), and those between the centroid (C*) of the η^6-arene ring and the legs lie in the expected range for pseudo-octahedral three-legged piano-stool ruthenium complexes.[15] As a general trend, the C*–Ru–P(1) angle is slightly larger than the C*–Ru–Cl(1) and C*–Ru–Cl(2) ones, probably to minimize the steric hindrance between the large phosphine and arene ligands.

The most relevant structural features of these complexes concern the position of the binaphthoxy unit. Thus, in **1a** and **1b**, which contain the less sterically hindered arene ligand (*i.e.* benzene), the binaphthoxy moiety points towards the arene. In contrast, probably due to steric grounds, in the mesitylene compounds, **3b** and **3c**, the binaphthoxy unit is oriented towards the opposite direction, the chiral fragment (*i.e.* the binaphthoxy unit) being now located near the chlorine atoms. During the catalytic experiments (see below), these chloride ligands are removed to allow the substrate coordination and the proximity of the chiral unit may enhance the selectivity of the process.

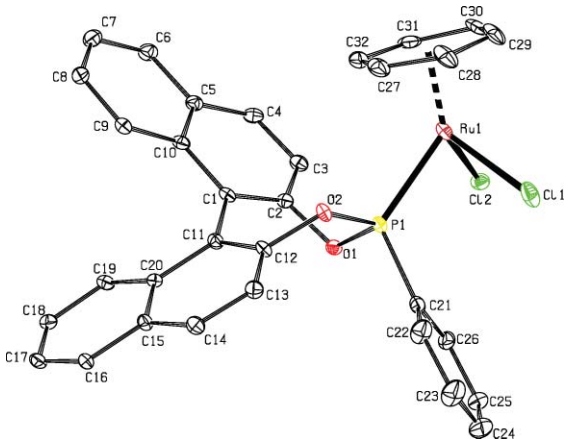


Fig. 2 ORTEP-type view of the structure of $[RuCl_2(\eta^6\text{-}C_6H_6)(\mathbf{a})]$ ($\mathbf{1a}\cdot\frac{1}{4}CH_2Cl_2$). Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms and CH_2Cl_2 molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C* 1.7110(4), Ru–Cl(1) 2.3904(14), Ru–Cl(2) 2.3980(11), Ru–P 2.2659(11); C*–Ru–Cl(1) 125.43(4), C*–Ru–Cl(2) 126.38(3), C*–Ru–P 131.86(3), Cl(1)–Ru–Cl(2) 88.38(5), Cl(1)–Ru–P 86.00(4), Cl(2)–Ru–P 84.37(4). C* denotes the centroid of the arene ring C(27)–C(32).

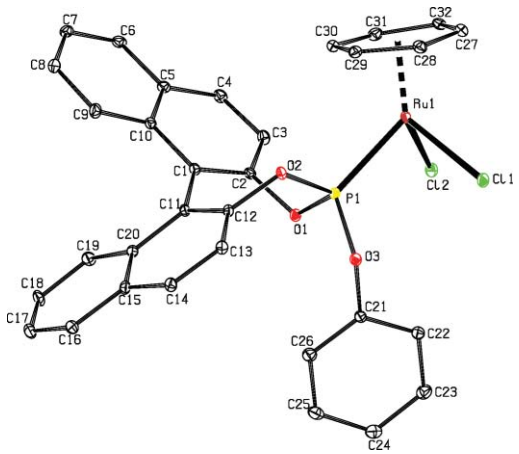


Fig. 3 ORTEP-type view of the structure of $[RuCl_2(\eta^6\text{-}C_6H_6)(\mathbf{b})]$ ($\mathbf{1b}\cdot\frac{1}{2}CH_2Cl_2$). Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms and CH_2Cl_2 molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C* 1.7038, Ru–Cl(1) 2.3975(13), Ru–Cl(2) 2.3968(13), Ru–P 2.2540(13); C*–Ru–Cl(1) 124.49(4), C*–Ru–Cl(2) 127.53(4), C*–Ru–P 128.92(4), Cl(1)–Ru–Cl(2) 87.34(5), Cl(1)–Ru–P 90.17(5), Cl(2)–Ru–P 85.10(5). C* denotes the centroid of the arene ring C(27)–C(32).

Kinetic resolution of allylic alcohols promoted by complexes 1–3

In a first step, we compared the activities and selectivities of all the chiral complexes (*R*)-**1–3** in the kinetic resolution of 1-phenyl-2-propen-1-ol (Table 1). The catalytic reactions were performed at 45 °C using 4 mmol of substrate, 1 mol% of ruthenium catalyst, 2 mol% of KO*t*Bu[16,17] and 20 mL of THF, and both conversions and enantiomeric excesses of the remaining alcohol were monitored by

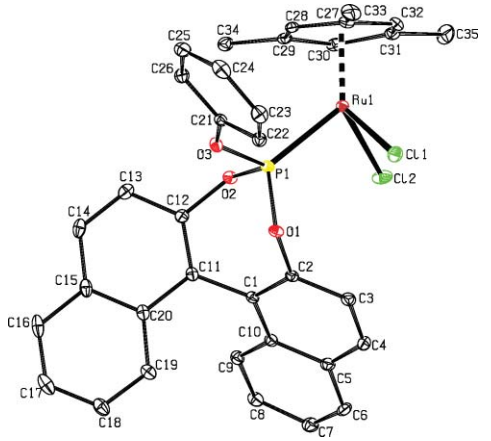


Fig. 4 ORTEP-type view of the structure of [$RuCl_2(\eta^6$-1,3,5-$C_6H_3Me_3$)(**b**)] (**3b**). Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C* 1.740(12), Ru–Cl(1) 2.4106(18), Ru–Cl(2) 2.3894(18), Ru–P 2.2372(16); C*–Ru–Cl(1) 125.9(9), C*–Ru–Cl(2) 125.0(6), C*–Ru–P 128.5(3), Cl(1)–Ru–Cl(2) 87.20(8), Cl(1)–Ru–P 89.62(6), Cl(2)–Ru–P 87.97(7). C* denotes the centroid of the arene ring C(27)–C(32).

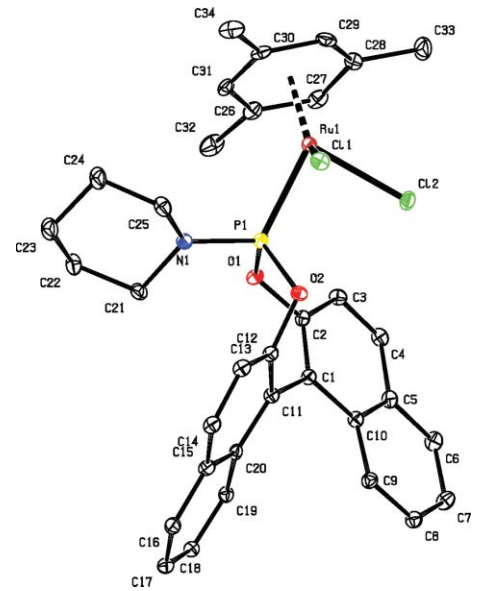
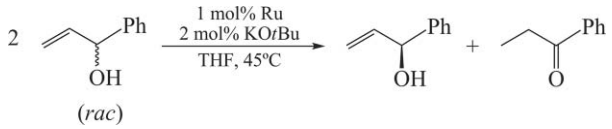


Fig. 5 ORTEP-type view of the structure of [$RuCl_2(\eta^6$-1,3,5-$C_6H_3Me_3$)(**c**)] (**3c**). Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C* 1.73(2), Ru–Cl(1) 2.4165(16), Ru–Cl(2) 2.3917(16), Ru–P 2.2618(11); C*–Ru–Cl(1) 127.7(4), C*–Ru–Cl(2) 124.7(3), C*–Ru–P 130.5(6), Cl(1)–Ru–Cl(2) 87.82(7), Cl(1)–Ru–P 84.94(6), Cl(2)–Ru–P 87.03(6). C* denotes the centroid of the arene ring C(26)–C(31).

GC analyses of aliquots. Under these conditions, all the catalysts are able to promote the redox-isomerization of 1-phenyl-2-propen-1-ol into 1-phenylpropan-1-one, reacting preferably with the *R* enantiomer. By this way, enantio-enriched solutions of the *S* isomer, albeit with low e.e. values (Table 1), are generated.[18] As a general trend, the best enantioselectivities are attained with catalysts containing the more sterically demanding arene ligands, *i.e. p*-cymene and mesitylene.[19] This behavior is probably related with the orientation of the chiral fragment in these derivatives (see above). As the P-donor ligands are concerned, those complexes containing the phosphite **b** are the most selective.

The metal-promoted resolution processes have been extended to other allylic alcohols with different aromatic substituents on the C(1) carbon, using catalysts **2b** and **3b** (Table 2). However, these substrates were revealed to be less reactive than 1-phenyl-2-propen-1-ol and required increasing the temperature reaction to 75 °C. Once again, phosphite-complexes **2b** and **3b** convert preferably the *R* enantiomers, furnishing the remaining *S* allylic alcohol albeit with low e.e. values.

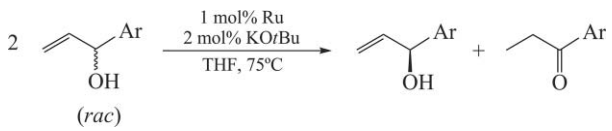
Table 1 Kinetic resolution of 1-phenyl-2-propen-1-ol promoted by complexes (*R*)-**1–3**[a]



Catalyst [arene]	*t*/h	Alcohol[b,c] (%)	e.e.[c] (%)
Phosphonite catalysts			
1a [benzene]	2.6	44	0
2a [*p*-cymene]	3	48	13(*S*)
3a [mesitylene]	0.33	45	15(*S*)
Phosphite catalysts			
1b [benzene]	2.9	48	15(*S*)
2b [*p*-cymene]	0.25	45	17(*S*)
3b [mesitylene]	4.9	50	16(*S*)
Phosphoramidite catalysts			
1c [benzene]	3.9	46	4(*S*)
2c [*p*-cymene]	7	47	6(*S*)
3c [mesitylene]	20	90	0

[a] Reactions carried out at 45 °C using 4 mmol of 1-phenyl-2-propen-1-ol, 1 mol% of the indicated catalyst, 2 mol% of KO*t*Bu and 20 mL of THF. [b] Allylic alcohol remaining. [c] Determined by GC, absolute configuration of the major enantiomer indicated in parentheses.

Table 2 Kinetic resolution of other allylic alcohols promoted by complexes (*R*)-**2b** and (*R*)-**3b**[a]



Ar	Catalyst	*t*/h	Alcohol[b,c] (%)	e.e.[c] (%)
4-ClC_6H_4	**2b**	2.5	50	8(*S*)
	3b	8	48	10(*S*)
4-BrC_6H_4	**2b**	1.5	49	12(*S*)
	3b	5	48	8(*S*)
4-$MeOC_6H_4$	**2b**	3.5	55	11(*S*)
	3b	7	49	10(*S*)
1-Naphthyl	**2b**	2.5	56	11(*S*)
	3b	2.5	50	16(*S*)

[a] Reactions carried out at 75 °C using 4 mmol of indicated allylic alcohol, 1 mol% of **2b** or **3b**, 2 mol% of KO*t*Bu and 20 mL of THF. [b] Allylic alcohol remaining. [c] Determined by GC, absolute configuration of the major enantiomer indicated in parentheses.

Conclusions

In summary, the synthesis and structural characterization of new chiral phosphonite, phosphite and phosphoramidite arene-ruthenium(II) complexes have been presented. These species belong to the scarce examples of catalytic systems able to promote the kinetic resolution of allylic alcohols through an isomerization reaction,[4] nevertheless the enantioselectivities obtained were by far lower that those reached through other kinetic resolution processes.[20] The relative orientation of the chiral binapthoxy unit respectively to the arene ligand seems to govern the selectivity of the catalysts. Studies focused on the synthesis and catalytic behavior of more structurally rigid tethered arene-ruthenium complexes, containing a chiral phosphite pendant, are currently under way in our laboratory.

Experimental

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers with the exception of compounds [{RuCl(μ-Cl)(η^6-arene)}$_2$],[9–11] ligands **a–c**,[8] 1-(4-chlorophenyl)prop-2-en-1-ol,[21] 1-(4-bromophenyl)prop-2-en-1-ol,[22] 1-(4-methoxyphenyl)prop-2-en-1-ol[21] and 1-(naphthalen-1-yl)prop-2-en-1-ol,[22] which were prepared following the method reported in the literature. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported in this paper. Optical rotations (α_D) were measured on a Perkin–Elmer 343 polarimeter at the wavelength of the yellow sodium D line (589 nm). The C, H and N analyses were carried out with a Perkin–Elmer microanalyzer. GC and GC/MSD measurements were made on a Hewlett–Packard HP6890 apparatus (Supelco Beta-Dex™ 120 column, 30 m, 250 μm or Gamma-Dex™ 225 column, 30 m, 250 μm) and an Agilent 6890 N apparatus coupled to a 5973 mass detector (HP-1MS column, 30 m, 250 μm), respectively.

Preparation of [RuCl$_2$(η^6-C$_6$H$_6$){(*rac*)-a}] ((*rac*)-1a)

A slurry of 0.288 g of [{RuCl(μ-Cl)(η^6-C$_6$H$_6$)}$_2$] (0.576 mmol) and 0.502 g of ligand (*rac*)-**a** (1.28 mmol) in 40 mL of dichloromethane was stirred for 24 h at room temperature. The resulting red solution was then filtered through Kieselguhr and evaporated to dryness. The brown solid was washed three times with a 1 : 3 mixture of diethyl ether–hexane and vacuum-dried. Yield: 0.666 g (90%). ^{31}P{^{1}H} NMR, CD_2Cl_2, δ 181.0 (s). ^{1}H NMR, CD_2Cl_2, δ 8.18–7.21 (m, 17 H, ArH), 5.40 (s, 6 H, C_6H_6). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ 149.8 (d, $^2J_{PC}$ = 13.2, C–O), 148.1 (d, $^2J_{PC}$ = 7.8, C–O), 132.7–118.2 (m, $C_{aromatic}$), 90.5 (d, $^2J_{PC}$ = 3.6, C_6H_6). Anal. Calc. for $C_{32}H_{23}Cl_2O_2PRu$: C, 59.82; H, 3.61. Found: C, 60.05; H, 3.76%.

Preparation of [RuCl$_2$(η^6-C$_6$H$_6$){(*R*)-a}] ((*R*)-1a)

Prepared through the same procedure using optically pure ligand (*R*)-**a**. Yield: 88%. $\alpha_D = -91°$ (c = 0.222 in CH_2Cl_2, at 20 °C).

Preparation of [RuCl$_2$(η^6-C$_6$H$_6$){(*rac*)-b}] ((*rac*)-1b)

Following the same procedure (*rac*)-**1b** was prepared as a brown solid, using 0.136 g (0.271 mmol) of [{RuCl(μ-Cl)(η^6-C$_6$H$_6$)}$_2$] and 0.246 g of ligand (*rac*)-**b** (0.602 mmol). Yield: 0.276 g (78%). ^{31}P{^{1}H} NMR, CD_2Cl_2, δ 129.8 (s). ^{1}H NMR, CD_2Cl_2, δ 8.07–6.92 (m, 17 H, ArH), 5.56 (s, 6 H, C_6H_6). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ 151.7 (d, $^2J_{PC}$ = 13.6, C–O), 148.8 (d, $^2J_{PC}$ = 12.8, C–O), 147.0 (d, $^2J_{PC}$ = 7.2, C–O), 132.4–121.0 (m, $C_{aromatic}$), 91.0 (d, $^2J_{PC}$ = 5.6, C_6H_6). Anal. Calc. for $C_{32}H_{23}Cl_2O_3PRu$: C, 58.37; H, 3.52. Found: C, 58.59; H, 3.67%.

Preparation of [RuCl$_2$(η^6-C$_6$H$_6$){(*R*)-b}] ((*R*)-1b)

Prepared through the same procedure using optically pure ligand (*R*)-**b**. Yield: 81%. $\alpha_D = -94°$ (c = 0.245 in CH_2Cl_2, at 20 °C).

Preparation of [RuCl$_2$(η^6-C$_6$H$_6$){(*rac*)-c}] ((*rac*)-1c)

Following the same procedure (*rac*)-**1c** was prepared as a brown solid, using 0.110 g (0.220 mmol) of [{RuCl(μ-Cl)(η^6-C$_6$H$_6$)}$_2$] and 0.195 g of ligand (*rac*)-**c** (0.488 mmol). Yield: 0.249 g (87%). ^{31}P{^{1}H} NMR, $CDCl_3$, δ 144.7 (s). ^{1}H NMR, $CDCl_3$, δ 8.04–7.23 (m, 12 H, ArH), 5.41 (s, 6 H, C_6H_6), 3.31–3.28 (m, 4 H, NCH_2), 1.61–1.21 (m, 6 H, CH_2). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ 149.6 (d, $^2J_{PC}$ = 13.6, C–O), 148.2 (d, $^2J_{PC}$ = 6.4, C–O), 132.7–121.2 (m, $C_{aromatic}$), 90.3 (d, $^2J_{PC}$ = 4.8, C_6H_6), 46.8 (d, $^2J_{PC}$ = 3.2, NCH_2), 26.3 (d, $^3J_{PC}$ = 4.8, NCH_2CH_2), 24.4 (s, CH_2). Anal. Calc. for $C_{31}H_{28}Cl_2NO_2PRu$: C, 57.33; H, 4.35; N, 2.16. Found: C, 57.49; H, 4.42; N, 2.07%.

Preparation of [RuCl$_2$(η^6-C$_6$H$_6$){(*R*)-c}] ((*R*)-1c)

Prepared through the same procedure using optically pure ligand (*R*)-**c**. Yield: 84%. $\alpha_D = -144°$ (c = 0.200 in CH_2Cl_2, at 20 °C).

Preparation of [RuCl$_2$(η^6-*p*-cymene){(*rac*)-a}] ((*rac*)-2a)

Following the same procedure (*rac*)-**2a** was prepared as a orange solid, using 0.317 g (0.518 mmol) of [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] and 0.451 g of ligand (*rac*)-**a** (1.15 mmol). Reaction time: 1 h. Yield: 0.654 g (91%). ^{31}P{^{1}H} NMR, $CDCl_3$, δ 181.7 (s). ^{1}H NMR, $CDCl_3$, δ 8.00–7.15 (m, 17 H, ArH), 5.50 and 5.37 (both d, 1 H each, $^3J_{HH}$ = 6.4, cymene), 5.15 and 4.58 (both d, 1 H each, $^3J_{HH}$ = 5.8, cymene), 2.82 (m, 1 H, C*H*Me$_2$), 2.09 (s, 3 H, Me), 1.23 (d, 3 H, $^3J_{HH}$ = 6.9, CH*Me*), 1.18 (d, 3 H, $^3J_{HH}$ = 6.8, CH*Me*). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ 149.7 (d, $^2J_{PC}$ = 12.8, C–O), 148.1 (d, $^2J_{PC}$ = 7.2, C–O), 133.8–118.1 (m, $C_{aromatic}$), 108.8 (d, $^2J_{PC}$ = 1.6, C cymene), 106.2 (d, $^2J_{PC}$ = 2.4, C cymene), 94.0 (d, $^2J_{PC}$ = 4.0, CH cymene), 92.7 (d, $^2J_{PC}$ = 10.3, CH cymene), 86.4 (d, $^2J_{PC}$ = 3.2, CH cymene), 83.6 (s, CH cymene), 30.6 (s, *C*HMe$_2$), 22.4 and 21.7 (both s, CH*Me*$_2$), 18.2 (s, Me). Anal. Calc. for $C_{36}H_{31}Cl_2O_2PRu$: C, 61.89; H, 4.47. Found: C, 62.03; H, 4.40%.

Preparation of [RuCl$_2$(η^6-*p*-cymene){(*R*)-a}] ((*R*)-2a)

Prepared through the same procedure using optically pure ligand (*R*)-**a**. Yield: 88%. $\alpha_D = -84°$ (c = 0.248 in CH_2Cl_2, at 20 °C).

Preparation of [$RuCl_2$(η⁶-*p*-cymene){(*rac*)-b}] ((*rac*)-2b)

Following the same procedure (*rac*)-**2b** was prepared as a orange solid, using 0.208 g (0.339 mmol) of [{RuCl(μ-Cl)(η⁶-*p*-cymene)}$_2$] and 0.308 g of ligand (*rac*)-**b** (0.753 mmol). Reaction time: 1 h. Yield: 0.363 g (75%). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ 130.7 (s). ^1H NMR, CD_2Cl_2, δ 8.10–6.95 (m, 17 H, ArH), 5.68 and 5.31 (both d, 1 H each, $^3J_{HH}$ = 6.2, cymene), 5.41 and 5.00 (both d, 1 H each, $^3J_{HH}$ = 5.9, cymene), 2.86 (m, 1 H, C*H*Me_2), 2.08 (s, 3 H, Me), 1.26 and 1.20 (both d, 3 H each, $^3J_{HH}$ = 6.9, CH*Me_2*). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ 151.8 (d, $^2J_{PC}$ = 12.6, C–O), 148.7 (d, $^2J_{PC}$ = 13.2, C–O), 148.2 (d, $^2J_{PC}$ = 7.2, C–O), 132.6–115.5 (m, $C_{aromatic}$), 110.6 (d, $^2J_{PC}$ = 3.0, C cymene), 104.0 (d, $^2J_{PC}$ = 2.4, C cymene), 92.7 (d, $^2J_{PC}$ = 6.6, CH cymene), 91.6 (d, $^2J_{PC}$ = 9.0, CH cymene), 88.1 (d, $^2J_{PC}$ = 4.8, CH cymene), 87.0 (d, $^2J_{PC}$ = 4.2, CH cymene), 30.7 (s, *C*HMe_2), 22.2 and 21.7 (both s, CH*Me_2*), 18.4 (s, Me). Anal. Calc. for $C_{36}H_{31}Cl_2O_3PRu$: C, 60.51; H, 4.37. Found: C, 60.70; H, 4.48%.

Preparation of [$RuCl_2$(η⁶-*p*-cymene){(*R*)-b}] ((*R*)-2b)

Prepared through the same procedure using optically pure ligand (*R*)-**b**. Yield: 79%. $\alpha_D = -65°$ (c = 0.215 in CH_2Cl_2, at 20 °C).

Preparation of [$RuCl_2$(η⁶-*p*-cymene){(*rac*)-c}] ((*rac*)-2c)

Following the same procedure (*rac*)-**2c** was prepared as a orange solid, using 0.183 g (0.299 mmol) of [{RuCl(μ-Cl)(η⁶-*p*-cymene)}$_2$] and 0.266 g of ligand (*rac*)-**c** (0.664 mmol). Reaction time: 1 h. Yield: 0.258 g (61%). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ 147.8 (s). ^1H NMR, $CDCl_3$, δ 8.08–7.31 (m, 12 H, ArH), 5.50 and 5.44 (both d, 1 H each, $^3J_{HH}$ = 5.9, cymene), 5.32 and 4.69 (both d, 1 H each, $^3J_{HH}$ = 5.6, cymene), 3.26 (broad s, 4 H, NCH_2), 2.88 (m, 1 H, C*H*Me_2), 2.12 (s, 3 H, Me), 1.37–0.90 (m, 6 H, CH_2), 1.20 (d, 3 H, $^3J_{HH}$ = 6.8, CHMe), 1.11 (d, 3 H, $^3J_{HH}$ = 6.9, CH*Me*). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ 149.8 (d, $^2J_{PC}$ = 12.6, C–O), 148.5 (d, $^2J_{PC}$ = 6.0, C–O), 132.8–121.3 (m, $C_{aromatic}$), 108.9 (d, $^2J_{PC}$ = 2.4, C cymene), 103.7 (d, $^2J_{PC}$ = 2.4, C cymene), 92.3 (d, $^2J_{PC}$ = 4.8, CH cymene), 90.6 (d, $^2J_{PC}$ = 9.6, CH cymene), 89.1 (d, $^2J_{PC}$ = 5.4, CH cymene), 85.7 (d, $^2J_{PC}$ = 3.0, CH cymene), 44.7 (d, $^2J_{PC}$ = 2.4, NCH_2), 30.5 (s, *C*HMe_2), 26.4 (d, $^3J_{PC}$ = 5.4, NCH_2CH_2), 24.6 (d, $^4J_{PC}$ = 1.2, CH_2), 22.2 and 21.2 (both s, CH*Me_2*), 18.3 (s, Me). Anal. Calc. for $C_{35}H_{36}Cl_2NO_2PRu$: C, 59.58; H, 5.14; N, 1.99. Found: C, 59.43; H, 5.25; N, 2.04%.

Preparation of [$RuCl_2$(η⁶-*p*-cymene){(*R*)-c}] ((*R*)-2c)

Prepared through the same procedure using optically pure ligand (*R*)-**c**. Yield: 62%. $\alpha_D = -122°$ (c = 0.200 in CH_2Cl_2, at 20 °C).

Preparation of [$RuCl_2$(η⁶-mesitylene){(*rac*)-a}] ((*rac*)-3a)

Following the same procedure (*rac*)-**3a** was prepared as a orange solid, using 0.257 g (0.440 mmol) of [{RuCl(μ-Cl)(η⁶-mesitylene)}$_2$] and 0.384 g of ligand (*rac*)-**a** (0.978 mmol). Reaction time: 4 h. Yield: 0.572 g (95%). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ 177.8 (s). ^1H NMR, $CDCl_3$, δ 8.08–6.91 (m, 17 H, ArH), 4.90 (s, 3 H, $C_6H_3Me_3$), 2.11 (s, 9 H, $C_6H_3Me_3$). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ 148.7 (d, $^2J_{PC}$ = 14.7, C–O), 148.2 (d, $^2J_{PC}$ = 6.7, C–O), 134.8–121.2 (m, $C_{aromatic}$), 108.5 (d, $^2J_{PC}$ = 2.7, C mesitylene), 84.9 (d, $^2J_{PC}$ = 5.3, CH mesitylene), 18.1 (s, Me). Anal. Calc. for $C_{35}H_{29}Cl_2O_2PRu$: C, 61.41; H, 4.27. Found: C, 61.33; H, 4.13%.

Preparation of [$RuCl_2$(η⁶-mesitylene){(*R*)-a}] ((*R*)-3a)

Prepared through the same procedure using optically pure ligand (*R*)-**a**. Yield: 93%. $\alpha_D = -26°$ (c = 0.253 in CH_2Cl_2, at 20 °C).

Preparation of [$RuCl_2$(η⁶-mesitylene){(*rac*)-b}] ((*rac*)-3b)

Following the same procedure (*rac*)-**3b** was prepared as a orange solid, using 0.095 g (0.163 mmol) of [{RuCl(μ-Cl)(η⁶-mesitylene)}$_2$] and 0.148 g of ligand (*rac*)-**b** (0.362 mmol). Reaction time: 4 h. Yield: 0.159 g (70%). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ 135.3 (s). ^1H NMR, $CDCl_3$, δ 8.05–7.05 (m, 17 H, ArH), 4.94 (s, 3 H, $C_6H_3Me_3$), 2.17 (s, 9 H, $C_6H_3Me_3$). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ 151.6 (d, $^2J_{PC}$ = 6.9, C–O), 149.3 (d, $^2J_{PC}$ = 8.0, C–O), 148.4 (d, $^2J_{PC}$ = 12.3, C–O), 132.7–120.3 (m, $C_{aromatic}$), 108.4 (d, $^2J_{PC}$ = 3.2, C mesitylene), 86.2 (d, $^2J_{PC}$ = 6.4, CH mesitylene), 18.6 (s, Me). Anal. Calc. for $C_{35}H_{29}Cl_2O_3PRu$: C, 60.01; H, 4.17. Found: C, 60.23; H, 4.09%.

Preparation of [$RuCl_2$(η⁶-mesitylene){(*R*)-b}] ((*R*)-3b)

Prepared through the same procedure using optically pure ligand (*R*)-**b**. Yield: 74%. $\alpha_D = -18°$ (c = 0.255 in CH_2Cl_2, at 20 °C).

Preparation of [$RuCl_2$(η⁶-mesitylene){(*rac*)-c}] ((*rac*)-3c)

Following the same procedure (*rac*)-**3c** was prepared as a orange solid, using 0.179 g (0.306 mmol) of [{RuCl(μ-Cl)(η⁶-mesitylene)}$_2$] and 0.300 g of ligand (*rac*)-**c** (0.751 mmol). Reaction time: 4 h. Yield: 0.297 g (70%). $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ 139.9 (s). ^1H NMR, CD_2Cl_2, δ 8.04–7.17 (m, 12 H, ArH), 5.09 (s, 3 H, $C_6H_3Me_3$), 3.34–2.75 (broad s, 4 H, NCH_2), 2.27 (s, 9 H, $C_6H_3Me_3$), 1.51–1.31 (m, 6 H, CH_2). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ 149.5 (d, $^2J_{PC}$ = 4.8, C–O), 149.4 (d, $^2J_{PC}$ = 12.0, C–O), 134.8–121.5 (m, $C_{aromatic}$), 108.3 (s, C mesitylene), 85.0 (d, $^2J_{PC}$ = 5.6, CH mesitylene), 46.7 (d, $^2J_{PC}$ = NCH_2), 26.4 (d, $^3J_{PC}$ = 6.4, NCH_2CH_2), 24.6 (s, CH_2), 18.6 (s, Me). Anal. Calc. for $C_{34}H_{34}Cl_2NO_2PRu$: C, 59.05; H, 4.96; N, 2.03. Found: C, 59.25; H, 4.08; N, 2.09%.

Preparation of [$RuCl_2$(η⁶-mesitylene){(*R*)-c}] ((*R*)-3c)

Prepared through the same procedure using optically pure ligand (*R*)-**c**. Yield: 67%. $\alpha_D = -21°$ (c = 0.200 in CH_2Cl_2, at 20 °C). H, 4.40.

General procedure for the catalytic kinetic resolution of allylic alcohols

Under and inert atmosphere, the allylic alcohol (4 mmol), the catalyst precursor (1 mol%), potassium *tert*-butoxide (2 mol%), and 20 mL of THF were introduced into a Schlenk tube fitted with a condenser. Then, the mixture was heated at 45 °C. The conversion and the enantiomeric excess of the remaining alcohol were monitored by GC analyses of aliquots. In the case of 1-phenyl-2-propen-1-ol, the absolute configuration of the major enantiomer has been determined by comparison of GC analyses of commercially available (*R*)-1-phenyl-2-propen-1-ol. For the other

substrates, the assignment of absolute configuration is based on the sign of optical rotation of the isolated alcohol.[22,23]

Acknowledgements

This work was supported by Spanish "Ministerio de Educación y Ciencia" (Projects CTQ2006-084885/BQU and CSD2007-00006 (Consolider Ingenio 2010 program)) and FICYT of Asturias (Project IB08-036). M. A. F.-Z. and B. L.-B. thank the MEC (FPU program) and the FICYT (PCTI-Severo Ochoa program), respectively, for the award of a Ph.D grant and M. S. (from the University of Hamburg, Germany) thanks the Erasmus Program.

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