Highly water-soluble arene-ruthenium(II) complexes: application to catalytic isomerization of allylic alcohols in aqueous medium†

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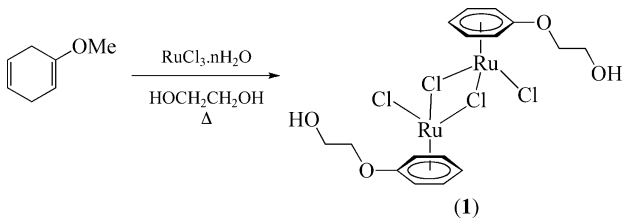
Arene-ruthenium(II) derivatives $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (L = $P(OMe)_3$ (**2a**), $P(OEt)_3$ (**2b**), $P(O^iPr)_3$ (**2c**), $P(OPh)_3$ (**2d**), PPh_3 (**2e**)) have been prepared from the dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\}_2]$ and the appropriate P-donor ligand. The hydroxyethoxy substituent on the arene induces water-solubility of the resulting complexes (up to 755 g L^{-1}); in particular derivative **2a** being one hundred times more soluble in water than its *p*-cymene congener $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{P(OMe)_3\}]$. Compounds **2a–e** are active catalysts for isomerization of allylic alcohols into the corresponding ketones in aqueous medium. The best performances are obtained with derivatives **2a–c** which have shown the highest activity reported to date for the isomerization of aromatic or disubstituted substrates in water.

Introduction

The main interest in using water as reaction solvent stems from its low cost, and its non-toxic and non-hazardous nature. Therefore, during the last two decades, the increasing awareness of environmental concerns has motivated the development of novel metal-promoted processes in aqueous media, disclosing a wide variety of highly efficient and selective synthetic approaches.[1] In this context, a large number of water-soluble organometallic complexes were synthesized and applied as catalysts.[1–3] The most common strategy to obtain such derivatives consists of introducing hydrophilic ligands in the coordination sphere of the metal, P-donor ligands being usually employed.[2–3] Thus, a huge number of arene-ruthenium(II) complexes containing water-soluble phosphine ligands have been prepared, finding applications associated to their biological properties,[4] as well as their catalytic activity in aqueous media.[3] Nevertheless, the modulation of steric and electronic features of hydrophilic P-donor ligands usually requires tedious synthetic work, therefore making difficult the optimization of the catalytic efficiency of these systems.

An alternative to synthesize water-soluble arene-ruthenium(II) complexes consists of using organometallic precursors of the type $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ bearing a hydrophilic functionalized arene ligand. Then, their reactions with conventional P-donor ligands, possessing different electronic and steric properties, would offer an easy access to a wide variety of water-soluble $[RuCl_2(\eta^6\text{-arene})(PR_3)]$ compounds. Surprisingly, despite the great number of functionalized-arene ruthenium(II) derivatives already known,[5] their behavior in water has been almost unexplored,[6] most of the reported studies being essentially focused on the formation of tethered derivatives.[5,7]

A particularly attractive functionalized precursor is $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\}_2]$ (**1**) which is readily prepared, through a one-pot process, from commercial reagents. Its synthesis, reported by White *et al.*, is based on the reaction of $RuCl_3{\cdot}nH_2O$ with 1-methoxy-1,4-cyclohexadiene and ethylene glycol at 80 °C (Scheme 1).[8] Despite the easy access to **1** in large scale, its coordination chemistry and applications in catalysis remain almost unexplored.[8–10] Moreover, its behavior in water has not been studied at all. Herein, we describe the synthesis of novel complexes derived from **1** and their application in the catalytic redox-type isomerization of allylic alcohols in aqueous media.



(**1**)

Scheme 1 Synthetic pathway reported for precursor **1**.

Results and discussion

Synthesis of complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (L = $P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$, $P(OPh)_3$, PPh_3)

Treatment of the dimeric precursor $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\}_2]$ (**1**)[8] with a slight excess of the appropriate phosphite or phosphine ligand in dichloromethane at room temperature affords the new mononuclear ruthenium(II)

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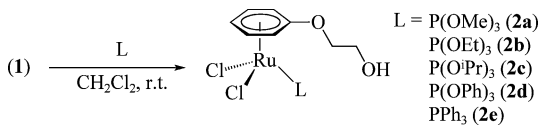
complexes [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)(L)$] (L = $P(OMe)_3$ (**2a**), $P(OEt)_3$ (**2b**), $P(O^iPr)_3$ (**2c**), $P(OPh)_3$ (**2d**), PPh_3 (**2e**)), which have been isolated as air-stable orange-red solids (Scheme 2).



Scheme 2 Synthesis of complexes **2a–e**.

Spectroscopic data and elemental analyses for compounds **2a–e** are in agreement with the proposed formulations. In particular, the $^{31}P\{^1H\}$ NMR spectra recorded in $CDCl_3$ show a unique singlet signal at δ = 110.1–121.0 (**2a–d**) and 31.1 (**2e**) ppm, *i.e.* in the expected range for phosphite- and phosphine-ruthenium complexes, respectively.[11] The C_v-symmetry of **2a–e** is evidenced, in ^1H as well as in $^{13}C\{^1H\}$ NMR spectra, by the equivalency of the two *meta*- and the two *ortho*-positions of the η^6-arene ligand.

In addition, the structure of **2b** was unambiguously confirmed by a single crystal X-ray diffraction study. Complex **2b** exhibits the expected pseudooctahedral three-legged piano-stool geometry around the ruthenium atom (Fig. 1). The most remarkable features are (i) the bond angle C(6)–O(1)–C(7) = 121.4(3)° and (ii) the torsion angle C(1)–C(6)–O(1)–C(7) = 2.1(5)°, both consistent with a sp^2-type hybridization for the oxygen atom adjacent to the arene ring. This is indicative of the participation of the oxygen nucleus to the delocalized π-system of the arene. Similar structural data have been already reported for other arene-ruthenium(II) complexes containing η^6-PhOR units.[8,9,12]

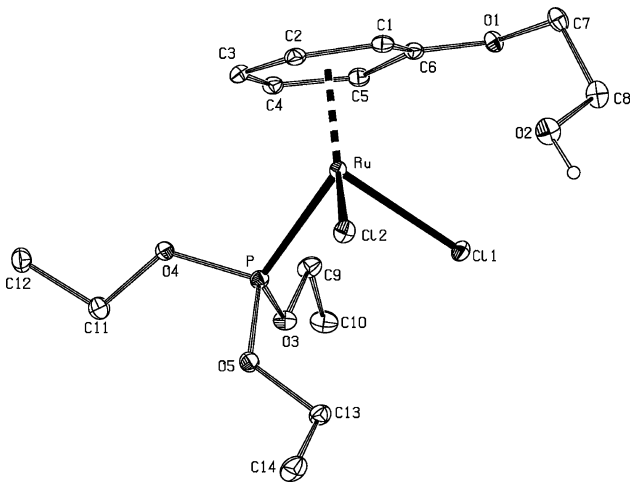


Fig. 1 ORTEP-type view of the structure of [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}$] (**2b**). Hydrogen atoms, except the OH one, are omitted for clarity. Thermal ellipsoids are drawn at 20% probability level. Selected bond lengths (Å) and angles (deg): Ru–Cl(1) = 2.4128(8), Ru–Cl(2) = 2.4061(8), Ru–P = 2.2786(9), C(6)–O(1) = 1.338(4), Cl(1)–Ru–Cl(2) = 87.34(3), Cl(1)–Ru–P = 87.79(3), Cl(2)–Ru–P = 90.44(3), C(6)–O(1)–C(7) = 121.4(3).

Table 1 Water-solubility of different arene-ruthenium(II) complexes[a]

Complexes	$S_{20°C}$ (g L^{-1})
[{RuCl(μ-Cl)(η^6-$C_6H_5OCH_2CH_2OH$)}$_2$], **1**	10.8
[$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OMe)_3\}$], **2a**	755
[$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}$], **2b**	27.2
[$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(O^iPr)_3\}$], **2c**	67.3
[$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OPh)_3\}$], **2d**	insoluble[b]
[$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)(PPh_3)$], **2e**	insoluble[b]
[$RuCl_2(\eta^6$-*p*-cymene)$\{P(OMe)_3\}$], **3a**	7.3
[$RuCl_2(\eta^6$-*p*-cymene)$\{P(OEt)_3\}$], **3b**	insoluble[b]
[$RuCl_2(\eta^6$-*p*-cymene)$\{P(O^iPr)_3\}$], **3c**	insoluble[b]
[$RuCl_2(\eta^6$-*p*-cymene)$\{P(OPh)_3\}$], **3d**	insoluble[b]
[$RuCl_2(\eta^6$-*p*-cymene)(PPh_3)], **3e**	insoluble[b]

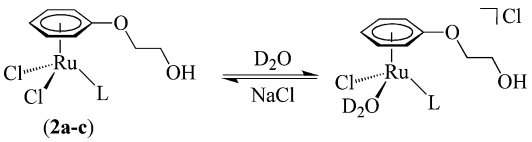
[a] At 20 °C. [b] Water-solubility values inferior to 0.5 g L^{-1}.

Behavior of complexes [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)(L)$] (2a–e) in water

Since the objective of this work is the use of compounds **2a–e** as catalysts in aqueous medium, their behavior in water has been explored. Firstly, the water-solubility of **2a–e** was measured at 20 °C (Table 1). Thus, we found that their solubility strongly depends on the nature of the P-donor ligand coordinated onto the metal. Complexes **2d** and **2e**, containing an aryl phosphite or phosphine, respectively, are almost insoluble in water, due to the repulsive interactions between the solvent and the aromatic fragments. In contrast, derivatives **2a–c** bearing an aliphatic ligand readily dissolve in water. Among them, the trimethylphosphite compound (**2a**) presents an extremely high solubility, it being possible to dissolve 755 mg of this complex in only 1 mL of water. As far as we known this is the highest water-solubility reported up to now for arene-ruthenium(II) complexes, the $S_{20°C}$ values of such derivatives usually ranging from 0 to 70 g L^{-1}.[13,14]

In order to determine to what extend the hydroxyethoxy-functionalized arene contributes to the water-solubility of complexes [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)(L)$] (**2a–e**), $S_{20°C}$ values of the analogous *p*-cymene derivatives [$RuCl_2(\eta^6$-*p*-cymene)(L)] (L = $P(OMe)_3$ (**3a**), $P(OEt)_3$ (**3b**), $P(O^iPr)_3$ (**3c**), $P(OPh)_3$ (**3d**), PPh_3 (**3e**))[15,16] were also measured (Table 1). As we can observe, replacement of $C_6H_5OCH_2CH_2OH$ by *p*-cymene gives rise to a dramatic decrease of the solubility in water. Thus, compound [$RuCl_2(\eta^6$-*p*-cymene)$\{P(OMe)_3\}$] (**3a**) is 100 time less soluble than its congener [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)\{P(OMe)_3\}$] (**2a**), and **3b–3e** are almost insoluble (Table 1).

The stability of complexes **2a–c** in water has been studied. $^{31}P\{^1H\}$ NMR spectra of **2a–c** recorded in D_2O show, along with the expected signals due to [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)(L)$], those corresponding to the aquo-species [$RuCl(D_2O)(\eta^6$-$C_6H_5OCH_2CH_2OH)(L)$][Cl], resulting from the dissociation of one chloride ligand and the coordination of a D_2O molecule to the metal (Scheme 3).[17] Spectroscopic data of these aquo-derivatives are consistent with the loss of the C_v-symmetry in the molecule (details are given in the ESI†).[18] Moreover, the molar conductivities of **2a–c** (Λ_M = 47–79 S cm^2 mol^{-1}) measured in water showed values in accordance with the presence of an equilibrium between a neutral compound and a 1 : 1 electrolyte species. As observed for other arene-ruthenium(II) complexes, the formation of these aquo-derivatives is completely suppressed



Scheme 3 Behavior of complexes **2a–c** in water.

when a tenfold excess of NaCl is added to the aqueous solutions (Scheme 3).[17] The reversible Ru–Cl bond cleavage is the unique process observed in water. In this sense, although free phosphites are readily hydrolyzed in aqueous media, the coordinated phosphites in **2a–c** remain unaltered even after 24 h in water.[19]

Electrochemical study of complexes [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)(L)$] (2a–e)

The redox behavior of complexes **2a–e** has been investigated using cyclovoltammetry (CV). For comparative purposes, the redox potentials of *p*-cymene and benzene analogues, **3a–e** and [$RuCl_2(\eta^6$-benzene)(L)] (L = $P(OMe)_3$ (**4a**), $P(OEt)_3$ (**4b**), $P(O^iPr)_3$ (**4c**), PPh_3 (**4e**)),[20] have been measured under the same conditions.[21] The CV of all the derivatives shows a quasi-reversible oxidation wave corresponding to the Ru(II)-Ru(III) redox system. Formal potentials ($E^{\circ\prime}$) values *versus* the ferrocinium–ferrocene redox couple are given in Fig. 2.[22] Regardless of the nature of the arene, the formal potential of complexes [$RuCl_2(\eta^6$-arene)(L)] decreases in the sequence L = $P(OPh)_3$ (**d**) > $P(OMe)_3$ (**a**) > $P(OEt)_3$ (**b**) > PPh_3 (**e**) > $P(O^iPr)_3$ (**c**), in accordance with the increasing donor capacity of the ligand (Fig. 2). On the other hand, the $C_6H_5OCH_2CH_2OH$-based compounds (**2a–e**) present higher potentials than their *p*-cymene analogues (**3a–e**) but lower than the benzene ones (**4a–c**, **4e**). Therefore, we can conclude that the electronic donor capacity of $C_6H_5OCH_2CH_2OH$ is intermediate between that of benzene and *p*-cymene.

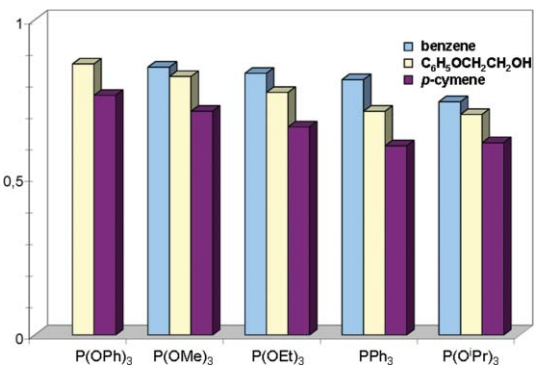
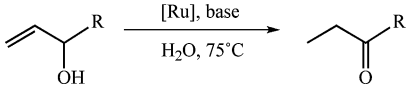


Fig. 2 Formal potential (in V) of complexes [$RuCl_2(\eta^6$-arene)(L)] (arene = $C_6H_5OCH_2CH_2OH$ (**2**), *p*-cymene (**3**), benzene (**4**); L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $P(O^iPr)_3$ (**c**), $P(OPh)_3$ (**d**), PPh_3 (**e**)). Numeric values indicated in ref. 23.

Catalytic isomerization of allylic alcohols into carbonyl compounds

The redox isomerization of allylic alcohols promoted by transition metal complexes represents a straightforward synthetic route to the corresponding saturated ketones (Scheme 4).[24] This process, extensively developed in organic medium, has been much less studied in water.[14,16,25,26] In particular, isomerizations of aromatic and/or sterically hindered substrates are still challenging in aqueous media.[14,26]

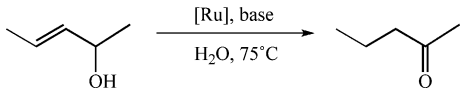


Scheme 4 Catalytic redox isomerization of allylic alcohols.

The catalytic activity of complexes **2a–e** has been checked in the isomerization of different allylic alcohols of the type CH_2=CHCH(OH)R (Table 2), which contain a terminal carbon–carbon double bond. In a typical experiment, 4 mmol of substrate, 1 mol% of catalyst, 5 mol% of KO^tBu and 20 mL of water were heated at 75 °C and the reaction was monitored by GC analyses of aliquots. Under these conditions, excellent performances have been achieved for all allylic alcohols tested, it being possible to transform them quantitatively in 5–45 minutes when catalysts **2a–c** were employed. Aliphatic and aromatic substrates give rise to similar results, and electron-withdrawing (entries 11–13 and 16–18) or electron-donor substituents (entries 21–23 and 26–28) on the benzene ring do not particularly affect the catalytic activity of **2a–c**.

For all substrates, the poorly water-soluble derivatives **2d–e**, and specially the triphenylphosphite one (**2d**), show lower activities than the highly soluble catalysts **2a–c**. Nevertheless, this behavior does not seem to be directly related to the water-solubility since the same tendency is observed in the catalytic isomerizations performed in THF solutions (see ESI†), in which all complexes are completely soluble. There is neither a clear correlation between the catalytic performances of **2a–e** and their steric and electronic features.[27] Thus, a possible explanation to the low activity presented by **2d–e** could be the easy deactivation of the catalytic species through orthometalation of one of the aromatic rings of PPh_3 or $P(OPh)_3$.[28]

Interestingly, complexes **2a–c** are also highly active in the isomerization of 3-penten-2-ol (Scheme 5 and Table 3), an allylic alcohol disubstituted on the C=C bond. It is well known that the transformation of such a substrate is problematic,[24,29] particularly in aqueous medium.[26a–c] Indeed, allylic alcohols of the type R^1HC=CHCH(OH)R^2 are difficult to isomerize, giving rise to low turnover frequencies (TOF values ranging from 0 to 10 h^{-1}).[26a–c]



Scheme 5 Isomerization of 3-penten-2-ol.

It is worthy of mention that catalyst **2a** is able to convert quantitatively 3-pent-2-ol into 2-pentanone within only 30 min (Table 3, entry 1). This result, which corresponds to a TOF value of 200 h^{-1}, is by far the best reported up to now for the isomerization of a disubstituted allylic alcohol in an aqueous medium.[26a–c] As observed in Table 3, compounds **2b–c** are also able to promoted the transformation of 3-penten-2-ol, although their catalytic activity is lower than that of **2a** (Table 3). For this substrate, it seems that the increasing steric hindrance when moving from **2a** to **2c** makes the coordination of the C=C bond

Table 2 Isomerization of allylic alcohols CH_2=CHCH(OH)R catalyzed by complexes [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)$(L)] (**2a–e**)[a]

Entry	R	Catalyst [L]	Time/min	Yield (%)[b]	TOF/h^{-1}[c]
1	^{n}Pent	**2a** [$P(OMe)_3$]	15	99	400
2		**2b** [$P(OEt)_3$]	15	99	400
3		**2c** [$P(O^iPr)_3$]	5	99	1200
4		**2d** [$P(OPh)_3$]	40	99	150
5		**2e** [PPh_3]	30	96	192
6	Ph	**2a** [$P(OMe)_3$]	10	99	600
7		**2b** [$P(OEt)_3$]	15	99	400
8		**2c** [$P(O^iPr)_3$]	10	99	600
9		**2d** [$P(OPh)_3$]	60	96	96
10		**2e** [PPh_3]	60	99	100
11	4-ClC_6H_4	**2a** [$P(OMe)_3$]	20	98	294
12		**2b** [$P(OEt)_3$]	30	97	194
13		**2c** [$P(O^iPr)_3$]	30	98	196
14		**2d** [$P(OPh)_3$]	22 h	78	4
15		**2e** [PPh_3]	45	90	120
16	4-BrC_6H_4	**2a** [$P(OMe)_3$]	15	97	388
17		**2b** [$P(OEt)_3$]	25	96	230
18		**2c** [$P(O^iPr)_3$]	45	99	132
19		**2d** [$P(OPh)_3$]	25 h	84	3
20		**2e** [PPh_3]	17 h	93	5
21	4-$Me_2NC_6H_4$	**2a** [$P(OMe)_3$]	15	99	400
22		**2b** [$P(OEt)_3$]	15	99	400
23		**2c** [$P(O^iPr)_3$]	30	99	200
24		**2d** [$P(OPh)_3$]	6 h	99	17
25		**2e** [PPh_3]	60	99	100
26	4-$MeOC_6H_4$	**2a** [$P(OMe)_3$]	10	97	582
27		**2b** [$P(OEt)_3$]	15	99	400
28		**2c** [$P(O^iPr)_3$]	15	99	400
29		**2d** [$P(OPh)_3$]	24 h	79	3
30		**2e** [PPh_3]	24 h	82	3

[a] Reactions carried out at 75 °C using 4 mmol of appropriate allylic alcohols, 1 mol% of Ru, 5 mol% of KO^tBu and 20 mL of water. [b] GC determined. [c] Turnover frequency ((mol product/mol Ru)/time).

Table 3 Isomerization of 3-penten-2-ol catalyzed by complexes [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)$(L)] (**2a–c**)[a]

Entry	Catalyst [L]	Time/min	Yield (%)[b]	TOF/h^{-1}[c]
1	**2a** [$P(OMe)_3$]	30	99	200
2	**2b** [$P(OEt)_3$]	30	92	184
3	**2c** [$P(O^iPr)_3$]	240	86	22

[a] Reactions carried out at 75 °C using 4 mmol of 3-penten-2-ol, 1 mol% of Ru, 5 mol% of KO^tBu and 20 mL of water. [b] GC determined. [c] Turnover frequency ((mol product/mol Ru)/time).

on the metal center more difficult,[30] resulting in a lower catalytic efficiency (TOF values from 200 to 22 h^{-1}).

Conclusions

In this work, an easy route to functionalized-arene ruthenium(II) complexes [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH)$(L)] (L = $P(OMe)_3$ (**2a**), $P(OEt)_3$ (**2b**), $P(O^iPr)_3$ (**2c**), $P(OPh)_3$ (**3d**), PPh_3 (**3e**)) has been described in a two-step process from commercially available precursors. We have evidenced that the presence of the hydroxyethoxy substituent on the arene could confer high water-solubility to the resulting organometallic derivatives. In particular, [$RuCl_2(\eta^6$-$C_6H_5OCH_2CH_2OH$){$P(OMe)_3$}] is 100 times more soluble in water than its *p*-cymene parent.

Complexes **2a–c**, containing aliphatic P-donor ligands, have proven to be highly efficient catalysts for redox isomerization of allylic alcohols in aqueous medium. They are particularly effective to transform challenging substrates, such as aromatic or disubstituted ones (*i.e.* allylic alcohols of the type CH_2=CHCH(OH)R or R^1HC=CHCH(OH)R^2). For these particular substrates, the catalytic performances reached are, by far, the highest reported to date for isomerization in an aqueous medium.

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-$C_6H_5OCH_2CH_2OH$)}$_2$] (**1**),[8] [$RuCl_2(\eta^6$-*p*-cymene)(L)] (L = $P(OMe)_3$ (**3a**), $P(OEt)_3$ (**3b**), $P(O^iPr)_3$ (**3c**), $P(OPh)_3$ (**3d**), PPh_3 (**3e**))[15] and [$RuCl_2(\eta^6$-$C_6H_6)$(L)] (L = $P(OMe)_3$ (**4a**), $P(OEt)_3$ (**4b**), $P(O^iPr)_3$ (**4c**), PPh_3 (**4e**))[20] which were prepared following the methods 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. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^{-3} water solutions, with a Jenway PCM3 conductimeter. Cyclovoltammetric measurements were performed at 20 °C with a "µAutolab type III" apparatus equipped with a three-electrode system. Platinum

disk electrode, spiral shaped platinum wire and silver wire were used as working-, counter- and reference-electrodes, respectively. CV experiments were carried out with CH_2Cl_2 solutions of the appropriate complex (0.5×10^{-3} M) and [N^nBu_4][PF_6] (0.1 M) as electrolyte. Formal CV potentials ($E^{\circ\prime}$) are referenced relative to potential of the [Cp_2Fe]–[Cp_2Fe]$^+$ couple (E° = 0.184 V) run under identical conditions ($E^{\circ\prime} = E^\circ$(complex$^+$/complex) – E°([Cp_2Fe]$^+$/[Cp_2Fe])).[21] Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C and H analyses were carried out with a Perkin-Elmer microanalyzer. GC and GC/MSD measurements were made on a Hewlett-Packard HP6890 equipment (Supelco Beta-Dex™ 120 column; 30 m; 250 μm) and an Agilent 6890 N equipment coupled to a 5973 mass detector (HP-1MS column; 30 m; 250 μm), respectively.

Preparation of [$RuCl_2$(η^6-$C_6H_5OCH_2CH_2OH$){$P(OMe)_3$}], 2a

A slurry of 0.300 g of [{Ru(μ-Cl)Cl(η^6-$C_6H_5OCH_2CH_2OH$)}$_2$] (**1**) (0.484 mmol) and 137 μL of $P(OMe)_3$ (1.161 mmol) in 150 mL of dichloromethane was stirred for 9 h at room temperature. The resulting solution was then filtered through Kieselguhr and evaporated to dryness. The purification by column chromatography over silica gel, using a mixture of CH_2Cl_2–acetone (1 : 2), afforded **2a** as a red solid. Yield: 0.207 g (49 %). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 121.0 (s). ^1H NMR, $CDCl_3$, δ: 5.89 (m, 2 H, H_{meta}), 5.37 (d, 2 H, $^3J_{HH}$ = 5.1, H_{ortho}), 4.94 (t, 1 H, $^3J_{HH}$ = 4.9, H_{para}), 4.40 (m, 2 H, OCH_2), 4.03 (m, 2 H, OCH_2), 3.81 (d, 9 H, $^3J_{PH}$ = 11.1, OMe), 3.5 (broad s, 1 H, OH). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 144.3 (d, $^2J_{PC}$ = 5.6, C_{ipso}), 92.9 (s, C_{meta}), 72.6 (s, C_{para}), 72.3 (s, CH_2O), 72.0 (d, $^2J_{PC}$ = 10.4, C_{ortho}), 60.6 (s, CH_2OH), 54.2 (d, $^2J_{PC}$ = 5.6, OMe). Anal. calcd for $C_{11}H_{19}Cl_2O_5PRu$: C, 30.43; H, 4.41. Found: C, 30.21; H, 4.14. IR (KBr), $\nu_{(OH)}$: 3446 cm^{-1}. Λ_M = 79 S cm^2 mol^{-1} (in water). $S_{20°C}(H_2O)$ = 755 mg.mL^{-1}.

Preparation of [$RuCl_2$(η^6-$C_6H_5OCH_2CH_2OH$){$P(OEt)_3$}], 2b

Following the same procedure, **2b** was prepared as an orange solid, using 0.300 g (0.484 mmol) of **1** and 0.2 mL (1.161 mmol) of $P(OEt)_3$. Yield: 0.181 g (39 %). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 116.9 (s). ^1H NMR, $CDCl_3$, δ: 5.81 (m, 2 H, H_{meta}), 5.33 (d, 2 H, $^3J_{HH}$ = 5.1, H_{ortho}), 4.88 (t, 1 H, $^3J_{HH}$ = 5.1, H_{para}), 4.37 (m, 2 H, OCH_2), 4.18 (dq, 6 H, $^3J_{HH} = {}^3J_{PH}$ = 7.0, CH_2Me), 4.02 (m, 2 H, CH_2OH), 3.58 (broad s, 1 H, OH), 1.29 (t, 9 H, $^3J_{HH}$ = 7.0, CH_2Me). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 144.0 (d, $^2J_{PC}$ = 5.6, C_{ipso}), 92.8 (s, C_{meta}), 72.7 (s, C_{para}), 72.2 (s, CH_2O), 71.8 (d, $^2J_{PC}$ = 10.4, C_{ortho}), 63.1 (d, $^2J_{PC}$ = 5.6, CH_2Me), 60.5 (s, CH_2OH), 16.2 (d, $^3J_{PC}$ = 6.4, CH_2Me). Anal. calcd for $C_{14}H_{25}Cl_2O_5PRu$: C, 35.30; H, 5.29. Found: C, 35.44; H, 5.38. IR (KBr), $\nu_{(OH)}$: 3441 cm^{-1}. Λ_M = 74 S cm^2 mol^{-1} (in water). $S_{20°C}(H_2O)$ = 27.2 mg.mL^{-1}.

Preparation of [$RuCl_2$(η^6-$C_6H_5OCH_2CH_2OH$){$P(O^iPr)_3$}], 2c

Following the same procedure, **2c** was prepared as a red solid, using 0.300 g (0.484 mmol) of **1** and 287 μL (1.164 mmol) of $P(O^iPr)_3$. Yield: 0.223 g (44 %). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 110.1 (s). ^1H NMR, $CDCl_3$, δ: 5.77 (m, 2 H, H_{meta}), 5.24 (d, 2 H, $^3J_{HH}$ = 6.3, H_{ortho}), 4.89 (m, 3 H, $CHMe_2$), 4.82 (t, 1 H, $^3J_{HH}$ = 5.1, H_{para}), 4.37 (m, 2 H, OCH_2), 4.02 (m, 2 H, OCH_2), 3.65 (broad s, 1 H, OH), 1.29 (d, 18 H, $^3J_{HH}$ = 6.3, $CHMe_2$). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 143.8 (d, $^2J_{PC}$ = 4.8, C_{ipso}), 93.0 (s, C_{meta}), 73.1 (s, C_{para}), 72.1 (s, CH_2O), 71.5 (d, $^2J_{PC}$ = 7.2, C_{ortho}), 71.3 (d, $^2J_{PC}$ = 10.4, $CHMe_2$), 60.5 (s, CH_2OH), 24.0 (d, $^3J_{PC}$ = 4.0, $CHMe_2$). Anal. calcd for $C_{17}H_{31}Cl_2O_5PRu$: C, 39.39; H, 6.03. Found: C, 39.51; H, 5.89. IR (KBr), $\nu_{(OH)}$: 3492 cm^{-1}. Λ_M = 47 S cm^2 mol^{-1} (in water). $S_{20°C}(H_2O)$ = 67.3 mg.mL^{-1}.

Preparation of [$RuCl_2$(η^6-$C_6H_5OCH_2CH_2OH$){$P(OPh)_3$}], 2d

Following the same procedure, **2d** was prepared as a red solid, using 0.300 g (0.484 mmol) of **1** and 304 μL (1.161 mmol) of $P(OPh)_3$. Chromatographic purification was carried out with a 1 : 1 mixture of CH_2Cl_2 and acetone. Yield: 0.304 g (51 %). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 113.8 (s). ^1H NMR, $CDCl_3$, δ: 7.45–7.19 (m, 15 H, OPh), 5.48 (m, 2 H, H_{meta}), 4.84 (d, 2 H, $^3J_{HH}$ = 6.3, H_{ortho}), 4.24 (m, 2 H, OCH_2), 3.98 (m, 2 H, OCH_2), 3.58 (t, 1 H, $^3J_{HH}$ = 5.3, H_{para}), 3.41 (broad s, 1 H, OH). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 151.1 (d, $^2J_{PC}$ = 8.8, C_{ipso} OPh), 145 (d, $^2J_{PC}$ = 4.0, C_{ipso}), 129.7, 125.3 and 121.8 (all s, $C_{aromatic}$ OPh), 93.2 (s, C_{meta}), 72.3 (d, $^2J_{PC}$ = 5.6, C_{ortho}), 71.7 (s, C_{para}), 71.6 (s, CH_2O), 60.7 (s, CH_2OH). Anal. calcd for $C_{26}H_{25}Cl_2O_5PRu$: C, 50.33; H, 4.06. Found: C, 50.20; H, 4.29. IR (KBr), $\nu_{(OH)}$: 3420 cm^{-1}. $S_{20°C}(H_2O)$ inferior to 0.5 mg mL^{-1}.

Preparation of [$RuCl_2$(η^6-$C_6H_5OCH_2CH_2OH$)(PPh_3)], 2e

Following the same procedure, **2e** was prepared as an orange solid, using 0.300 g (0.484 mmol) of **1** and 0.304 g (1.161 mmol) of PPh_3. Chromatographic purification was carried out with a 2 : 1 mixture of CH_2Cl_2 and acetone. Yield: 0.301 g (54 %). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 31.1 (s). ^1H NMR, $CDCl_3$, δ: 7.76–7.35 (m, 15 H, PPh_3), 5.41 (m, 2 H, H_{meta}), 5.26 (d, 2 H, $^3J_{HH}$ = 5.4, H_{ortho}), 4.39 (m, 2 H, OCH_2), 4.05 (m, 2 H, OCH_2), 4.00 (t, 1 H, $^3J_{HH}$ = 5.1, H_{para}), 3.66 (broad s, 1 H, OH). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 142.2 (s, C_{ipso}), 128.2–134.2 (m, $C_{aromatic}$), 91.8 (s, C_{meta}), 75.7 (s, C_{para}), 72.3 (s, CH_2O), 70.3 (d, $^2J_{PC}$ = 7.2, C_{ortho}), 60.7 (s, CH_2OH). Anal. calcd for $C_{26}H_{25}Cl_2O_2PRu$: C, 54.55; H, 4.40. Found: C, 54.34; H, 4.21. IR (KBr), $\nu_{(OH)}$: 3420 cm^{-1}. $S_{20°C}(H_2O)$ inferior to 0.5 mg mL^{-1}.

Typical procedure for catalytic isomerization of allylic alcohols into ketones

Under an nitrogen atmosphere, the ruthenium catalyst precursor (0.04 mmol, 1 mol%), 20 mL of deoxygenated water, potassium *tert*-butoxide (0.2 mmol, 5 mol%), and allylic alcohol (4 mmol) were introduced into a Schlenk tube fitted with a condenser. Then, the mixture was heated at 75 °C. The reaction was monitored by GC and GC/MSD analyses of aliquots, taken every 5 min during the first hour and then the interval time was increased progressively. Saturated ketones were the only products generated. The identity of the products was assessed by comparison of the ^1H and $^{13}C\{^1H\}$ NMR spectra with the spectroscopic data already reported for the corresponding ketones and the fragmentation observed in GC/MSD analyses.

Crystal structure determination

Crystallographic data for **2a** and **2b** have been deposited with the Cambridge Crystallographic Data Center as supplementary publications Nos. CCDC 728240 (**2a**) and 728241 (**2b**). Copies

of the data can be obtained free of charge in the ESI† or *via* www.ccdc.cam.ac.uk/data_request/cif.

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