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Catalytic Isomerization of Allylic Alcohols by (η^6-*p*-Cymene)-Ruthenium(II) Complexes in Organic and Aqueous Media: New Recyclable and Highly Efficient Catalysts in Water Containing Ammonium-Functionalized Ligands

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Dedicated to our friend Antonio Abad on the occasion of his retirement.

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: The water-soluble complexes [$RuCl_2(\eta^6$-*p*-cymene){κ-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_3)_n$}][$SbF_6]_n$ [n = 1 (**4a**), 2 (**4b**) or 3 (**4c**)] have been prepared from the neutral precursors [$RuCl_2(\eta^6$-*p*-cymene){κ-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_2)_n$}] [n = 1 (**2a**), 2 (**2b**) or 3 (**2c**)] and MeI *via* quaternization of the nitrogen atom of the terminal aminoalkyl groups, and subsequent counteranion exchange by the treatment with $AgSbF_6$. Complexes **2a**–**c** and **4a**–**c** have proven to be highly active catalysts for isomerization of allylic alcohols in THF and aqueous media, respectively. Moreover, the water-soluble catalysts **4a**–**c** can be reused after a simple extraction process at the end of the reaction. In particular, **4c** presents a remarkable capability to be recycled, being active during 10 successive runs.

Keywords: allylic alcohol; ammonium ligands; isomerization, recycling; ruthenium; water-soluble

Introduction

Catalytic organic reactions in water are among the most appealing challenges of modern organic chemistry.[1] The use of water as an environmental friendly solvent for organic reactions has been triggered by the interest both in academic laboratories and industries to accomplish the principles of green chemistry.[2] In particular, catalytic transformations in water with atom economy are specially attractive and significant achievements have recently been disclosed.[1,2]

In the context of our interest to develop catalytic synthetic methodologies in water, we have recently reported the isomerization of allylic alcohols into carbonyl compounds catalyzed by bis-allylruthenium(IV) complexes [$RuCl_2(\eta^3{:}\eta^2{:}\eta^3$-$C_{12}H_{18})$] (**A**) ($C_{12}H_{18}$ = dodeca-2,6,10-triene-1,12-diyl) and [{$RuCl(\mu$-$Cl)(\eta^3{:}\eta^3$-$C_{10}H_{16})$}$_2$][3] (**B**) ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) and by arene-ruthenium(II) derivatives [$RuCl_2(\eta^6$-arene){$P(CH_2OH)_3$}] (**C**) and [$RuCl(\eta^6$-arene){$P(CH_2OH)_3$}$_2$][Cl] (**D**).[4] Although catalysts **A** and **B** have proven to be highly efficient with TOF values up to *ca.* 62,000 h^{-1}, they can be recycled only when volatile products are formed.[3] In contrast, some complexes of type **C** have been reused up to seven times, albeit they present only moderate activity.[4] With these precedents in mind we believe that there is a need to develop new efficient and easily recyclable catalytic systems in water for this atom economy process.

Transition metal complexes containing water-soluble phosphines as ligands are among the most common and efficient catalysts in aqueous media.[5] In particular, a series of metal catalysts of palladium,[6] rhodium,[7] and ruthenium[7i,7k,8] containing cationic phosphine ligands bearing ammonium functions in the backbone have been reported. Only some of them can be recycled while retaining the catalytic activity throughout several cycles.

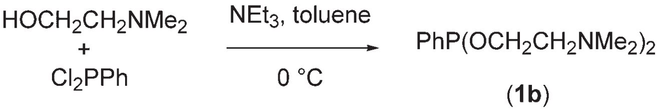
Here we describe the synthesis of the novel water-soluble arene-ruthenium(II) complexes [$RuCl_2(\eta^6$-*p*-cymene){κ-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_3)_n$}][$SbF_6]_n$ (n = 1, 2 or 3) and their neutral precursors [$RuCl_2(\eta^6$-*p*-cymene){κ-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_2)_n$}] as well as their catalytic activity in the isomerization of allylic alcohols in water and THF, respectively. Both types of complexes are highly efficient catalysts and the hydro-soluble derivatives show a remarkable capability to be recycled (up to 10 cycles).

Results and Discussion

In order to compare the catalytic activity in organic and aqueous reaction media the arene-ruthenium(II) complexes [$RuCl_2(\eta^6$-*p*-cymene){*κ*-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_2)_n$}] [n = 1 (**2a**), 2 (**2b**), 3 (**2c**)] and [$RuCl_2(\eta^6$-*p*-cymene){*κ*-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_3)_n$}][X]$_n$ [X = I, n = 1 (**3a**), 2 (**3b**), 3 (**3c**); X = SbF_6, n = 1 (**4a**), 2 (**4b**), 3 (**4c**)], containing neutral and cationic phosphorus-donor ligands, respectively, have been synthesized. The latter are formed by the quaternization of the nitrogen atom in the terminal aminoalkyl groups of the neutral complexes.

Synthesis of the Precursor Complexes [$RuCl_2(\eta^6$-*p*-cymene){*κ*-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_2)_n$}] [n = 1 (2a); 2 (2b); 3 (2c)]

Following a similar methodology to that previously used to prepare the related phosphinite $PPh_2(OCH_2CH_2NMe_2)$[9] (**1a**) and phosphite $P(OCH_2CH_2NMe_2)_3$[10] (**1c**) ligands, the new phosphonite ligand $PPh(OCH_2CH_2NMe_2)_2$ (**1b**) was synthesized in good yield by condensation of dichlorophenylphosphine with two equivalents of dimethylaminoethanol in the presence of NEt_3 (Scheme 1).

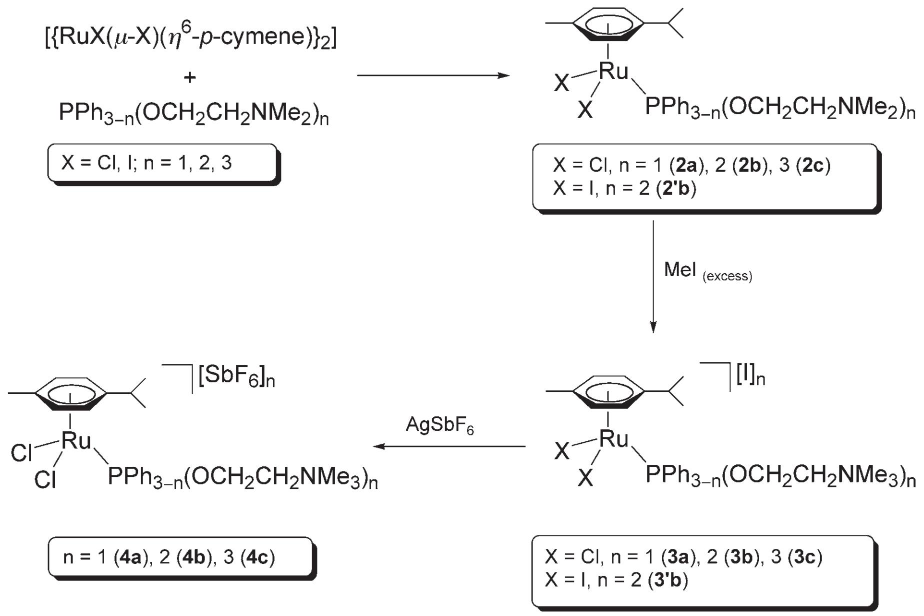


Scheme 1. Synthesis of the phosphonite ligand **1b**.

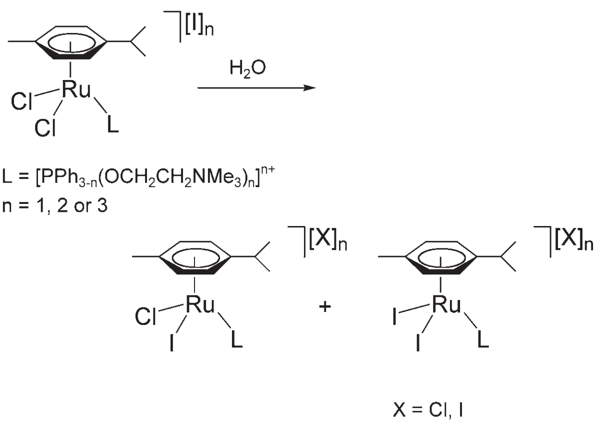
The reaction of the dimer [{$RuCl(\mu$-$Cl)(\eta^6$-*p*-cymene)}$_2$][11] with a slight excess of ligand $PPh_{3-n}(OCH_2CH_2NMe_2)_n$ [n = 1 (**1a**); 2 (**1b**); 3 (**1c**)], in dichloromethane at room temperature leads to the formation of the corresponding complexes [$RuCl_2(\eta^6$-*p*-cymene){*κ*-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_2)_n$}] [n = 1 (**2a**); 2 (**2b**); 3 (**2c**)] (Scheme 2). Spectroscopic and analytical data confirm the proposed formulation (see Supporting Information). In particular, the $^{31}P\{^1H\}$ NMR spectra show a unique signal at $\delta = 113.1$ (**2a**), 138.0 (**2b**) and 113.8 (**2c**) ppm, in the expected range for phosphinite, phosphonite and phosphite complexes, respectively.[12] The iodide phosphonite derivative [$RuI_2(\eta^6$-*p*-cymene){*κ*-(*P*)-$PPh(OCH_2CH_2NMe_2)_2$}] (**2′b**) is similarly prepared starting from the iodide dimer [{$RuI(\mu$-$I)(\eta^6$-*p*-cymene)}$_2$][13] and ligand **1b**.

Synthesis of the Cationic Complexes [$RuCl_2(\eta^6$-*p*-cymene){*κ*-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_3)_n$}][X]$_n$ [X = I, n = 1 (3a); 2 (3b); 3 (3c); X = SbF_6, n = 1 (4a); 2 (4b); 3 (4c)]

The treatment of the amino-complexes **2a–c** and **2′b** with an excess of methyl iodide affords the related quaternary ammonium derivatives [$RuCl_2(\eta^6$-*p*-cymene){*κ*-(*P*)-$PPh_{3-n}(OCH_2CH_2NMe_3)_n$}][I]$_n$ [n = 1 (**3a**); 2 (**3b**); 3 (**3c**)] and [$RuI_2(\eta^6$-*p*-cymene){*κ*-(*P*)-$PPh(OCH_2CH_2NMe_3)_2$}][I]$_2$ (**3′b**), respectively (72–88%;



Scheme 2. Synthesis of arene-ruthenium(II) complexes.



Scheme 3. Evolution of complexes **3a–c** in water.

Scheme 2). As expected due to their ionic composition, these compounds are water-soluble, the solubility increasing with the number of ammonium groups in the molecule. Nevertheless, the solutions of the cationic chloride complexes **3a–c** in water evolve into a mixture of compounds after a period of 2–24 hours. The spectroscopic data which are very similar to those of the related starting complexes suggest the formation of mixtures containing diiodide and chloride-iodide derivatives, as the result of complete or partial metathesis between chloride ligands and iodide counteranions, respectively (Scheme 3). This is confirmed by the stability of the all-iodide complex $[RuI_2(\eta^6\text{-}p\text{-cymene})\{\kappa\text{-}(P)\text{-}PPh(OCH_2CH_2NMe_3)_2\}][I]_2$ (**3′b**) in water.

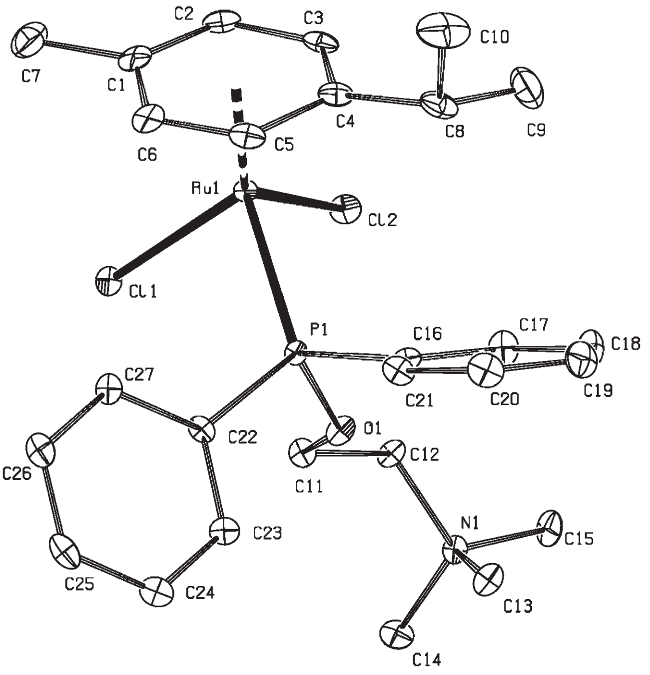


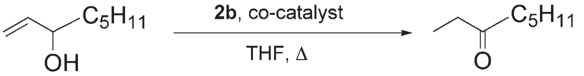
Figure 1. ORTEP-type view of the structure of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{PPh_2(OCH_2CH_2NMe_3)\}][SbF_6]$ (**4a**) showing the crystallographic labelling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Ru–C* = 1.7246(2); Ru–Cl(1) = 2.4072(7); Ru–Cl(2) = 2.4123(7); Ru–P = 2.3149 (7); O–P = 1.612(2); C*–Ru–Cl(1) = 126.265(18); C*–Ru–Cl(2) = 123.85(2); C*–Ru–P = 132.01(2); Cl(1)–Ru–Cl(2) = 88.86(2); Cl(1)–Ru–P = 83.30(2); Cl(2)–Ru–P = 88.76(2); O–P–C(16) = 95.09(12); O–P–C(22) = 103.27(12); C(16)–P–C(22) = 103.42(14). C* = centroid of the *p*-cymene ring [C(1), C(2), C(3), C(4), C(5), C(6)].

In order to avoid this metathical process, the iodide counteranions in **3a–c** were replaced by non-coordinating $[SbF_6]^-$ anions. The reaction of complexes **3a**, **3b** and **3c** with one, two and three equivalents of $AgSbF_6$, respectively, in dichloromethane or a mixture of dichloromethane and methanol, affords the hexafluoroantimonate salts $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa\text{-}(P)\text{-}PPh_{3-n}(OCH_2CH_2NMe_3)_n\}][SbF_6]_n$ [n = 1 (**4a**); 2 (**4b**); 3 (**4c**)] (Scheme 2). The reactions proceed through the selective exchange of the iodide counteranions, keeping the chloride ligands unchanged. The completion of this substitution process has been checked by ICP-MAS analyses of iodine, which indicate in all cases a value lower than 0.2%.

The structure of **4a** has been unequivocally confirmed by a single-crystal X-ray diffraction study. Although the crystal contains two symmetrically independent molecules, only one is described here since they show similar features. An ORTEP view is shown in Figure 1; selected bond distances and angles are listed in the caption. The molecule shows a pseudooctahedral three-legged piano-stool coordination around the ruthenium atom, which is bonded to the *p*-cymene acting as a η^6 ligand, the phosphorus atom of the phosphinite ligand and the two chloride ligands.

Catalytic Isomerization of Allylic Alcohols in Organic Medium

In order to compare the efficiency of our catalysts in both organic and aqueous media, we have explored first the catalytic activity of the neutral complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{PPh_{3-n}(OCH_2CH_2NMe_2)_n\}]$ (**2a–c**), in THF. Since it is well known that the efficiency of the catalysts in the isomerization of allylic alcohols strongly depends on the addition of base or chloride abstractor,[3,14,15] we have checked the catalytic performances in the presence of different co-catalysts. In a typical experiment, the ruthenium precursor $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa\text{-}(P)\text{-}PPh(OCH_2CH_2NMe_2)_2\}]$ (**2b**) (1 mol % Ru) and the



Scheme 4. Isomerization of 1-octen-3-ol into octan-3-one.

Table 1. Isomerization of 1-octen-3-ol into octan-3-one in THF catalyzed by **2b** in presence of different co-catalysts.[a]

Entry	Co-catalyst		Time [min]	Yield [%]	TOF [h^{-1}][b]
1	–	–	240	0	0
2	$AgSbF_6$	(2 mol %)	165	6	2
3	Li_2CO_3	(2 mol %)	290	0	0
4	Na_2CO_3	(2 mol %)	290	8	2
5	K_2CO_3	(2 mol %)	215	98	27
6	Cs_2CO_3	(2 mol %)	195	98	30
7	LiOH[c]	(2 mol %)	295	22	5
8	CsOH[c]	(2 mol %)	135	98	44
9	KO-*t*-Bu	(2 mol %)	60	99	99
10	KO-*t*-Bu	(1 mol %)	155	98	38
11	KO-*t*-Bu	(5 mol %)	5	99	1188
12	KO-*t*-Bu[d]	(5 mol %)	60	99	4950
13	KO-*t*-Bu[e]	(5 mol %)	60	0	0

[a] Reactions carried out at 75 °C using 4 mmol of 1-octen-3-ol and 1 mol % of **2b** in 20 mL of THF.
[b] Turnover frequency [(mol product/mol Ru)/time].
[c] Monohydrated.
[d] With 0.02 mol % of **2b**.
[e] In the absence of ruthenium catalyst.

co-catalyst (2 mol %) were added to a 0.2 M solution of 1-octen-3-ol (4 mmol) in THF and heated at 75 °C (Scheme 4), the reaction being monitored by gas chromatography. Results are summarized in Table 1.

The key role of the co-catalyst is clearly evidenced when the reaction is carried out in the presence of only the precursor **2b** since no conversion is observed after 4 hours (entry 1). Although the catalyst **2b** becomes active in the presence of 2 mol % of alkaline carbonate and hydroxide (entries 4–8) and $AgSbF_6$ (entry 2), the best result is obtained in the presence of KO-*t*-Bu (entry 9). Performing experiments with different Ru/KO-*t*-Bu molar ratios it is found that a considerable improvement of the catalytic activity is observed by increasing the molar ratio from 1 to 5 (entries 9–11), the isomerization being completed within only 5 minutes for the latter molar ratio (entry 11). In a blank experiment, we have also checked that co-catalyst KO-*t*-Bu is not able to promote the transformation in the absence of the ruthenium complex (entry 13). Remarkably, the activity of **2b** is retained at lower catalyst loadings. As an example, using 0.02 mol % of ruthenium, 1-octen-3-ol (0.2 M in THF, substrate/Ru/KO-*t*-Bu = 5000/1/250)[16] is quantitatively transformed within 1 hour (entry 12; TOF = 4950 h^{-1}).

Under the optimal catalytic conditions found for the model reaction (substrate/Ru/KO-*t*-Bu ratio = 100/1/5), the catalytic activities of complexes **2a** and **2c** have also been investigated (Table 2) and we found that the transformation is likewise completed in only 5 min (entries 1–3). When the reaction temperature is lowered (35 °C) the efficiency of catalysts **2a–c** still remains very high affording quantitative conversion into 3-octanone within 15–30 min (entries 4–6). For comparative purposes the catalytic activity of other arene-ruthenium(II) complexes, namely [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$], [$RuCl_2$(η^6-*p*-cymene)(PPh_3)] and [$RuCl_2$(η^6-*p*-cymene){$P(OEt)_3$}] (**5**), have been also checked (entries 7–9 in Table 2). In contrast to the dimer [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] for which the transformation requires a significantly longer reaction time, the mononuclear derivatives present similar activity to that of complexes **2a–c**. Noteworthy, the novel compound [$RuCl_2$(η^6-*p*-cymene){$P(OEt)_3$}] (**5**) (see preparation in Supporting Information) leads to quantitative yield in only 10 min (entry 9).

Complex **2a**, the most active amino-derivative catalyst, is also highly efficient in the isomerization of other allylic alcohols such as 1-hepten-3-ol, 1-hexen-3-ol, 1-penten-3-ol, 3-penten-2-ol and 1-phenyl-prop-2-en-1-ol which are quantitatively transformed within 15 minutes (entries 1–5, Table 3). Furthermore, homoallylic substrates, such as 4-penten-2-ol, can be also isomerized into the corresponding carbonyl compound although a longer reaction time is required (entry 6).

Catalytic Isomerization of Allylic Alcohols in Water

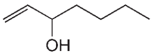
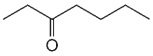
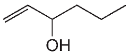
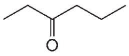
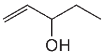
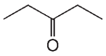
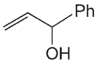
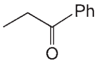
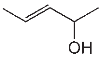
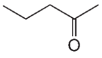
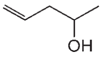
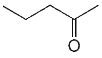
The catalytic isomerization of 1-octen-3-ol and 1-penten-3-ol in water using the hydro-soluble catalysts **4a–c** has been studied. The reactions were performed using 1 mol % of ruthenium pre-catalyst, 5 mol % of KO-*t*-Bu, and 4 mmol of the corresponding allylic alcohol in 20 mL of water at 75 °C. The results are summarized in Table 4. Although all of them are active, catalysts **4a** and **4b** are able to convert quantitatively both substrates very rapidly within 15 min (entries 1, 3, 4 and 6). The following features deserve to be mentioned: a) Complexes

Table 2. Comparison of different catalysts in the isomerization of 1-octen-3-ol into octan-3-one in THF.[a]

Entry	Catalyst	T [°C]	Time [min]	Yield [%][b]	TOF [h^{-1}][c]
1	**2a**	75	5	99	1188
2	**2b**	75	5	99	1188
3	**2c**	75	5	99	1188
4	**2a**	35	15	99 [30]	396
5	**2b**	35	15	99 [20]	396
6	**2c**	35	30	99 [3]	198
7	[{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$]	35	105	97	55
8	[Ru(η^6-*p*-cymene)Cl_2(PPh_3)]	35	30	99	198
9	[Ru(η^6-*p*-cymene)Cl_2{P(OEt)$_3$}] (**5**)	35	10	98	588

[a] Reactions carried out using 4 mmol of 1-octen-3-ol, 1 mol % of catalyst and 5 mol % of KO-*t*-Bu, in 20 mL of THF.
[b] Yields after 5 min in brackets.
[c] Turnover frequency [(mol product/mol Ru)/time].

Table 3. Isomerization of various unsaturated alcohols catalyzed by complex **2a**[a]

Entry	Substrate	Product	T [°C]	Time	Yield [%]	TOF [h^{-1}][b]
1			35	15 min	99	396
2			35	15 min	99	396
3			35	15 min	99	396
4			75	15 min	99	396
5[c]			75	5 min	95[d]	228
6			75	5h25	85[e]	16

[a] Reactions carried out using 4 mmol of substrate, 1 mol % of **2a** and 5 mol % of KO-*t*-Bu in 20 mL of THF.
[b] Turnover frequency [(mol product/mol Ru)/time].
[c] Substrate/Ru/KO-*t*-Bu = 100/5/25.
[d] Along with 5% of penten-2-ol and 3-penten-2-one.
[e] Along with 14% of penten-2-ol and 3-penten-2-one.

4a–c remain efficient even in the absence of base (entries 2, 5 and 8), although the reaction proceeds at a lower rate. This behavior contrasts with that of catalysts **2a–c** in THF, which are totally inactive without base. Probably, the higher polarity of water *vs.* THF favors the dissociation of the chloride ligands in the catalysts[17] and the deprotonation of the allylic alcohol. b) In contrast to the catalyst **4c** containing hexafluoroantimonate as counteranion, the related iodide compound [$RuCl_2$(η^6-*p*-cymene){κ-(*P*)-P($OCH_2CH_2NMe_3$)$_3$}][I]$_3$ (**3c**) only leads to very low conversion (entry 11) indicating that the presence of a non-coordinative counteranion is crucial. As we have commented before, the complex **3c** undergoes a chloride-iodide exchange process in water, giving rise to a mixture containing iodide complexes which are less prone to dissociate the halide ligands, as required to create a vacancy at the metal center. This problem can be circumvented by addition of KO-*t*-Bu, which acts both as base and as halide abstractor (entries 10 and 12, Table 4), affording the transformation of 1-octen-3-ol and 1-penten-3-ol in 10 and 5 min, respectively.

Since KO-*t*-Bu readily undergoes hydrolysis in water leading to the formation of KOH and *tert*-butanol, we also performed the isomerization of 1-octen-3-ol using KOH as co-catalyst. In all the cases, the catalytic activities are identical or slightly lower than that obtained with KO-*t*-Bu,[18] and they still remain inferior when a mixture of KOH and *tert*-butanol is used. These small differences in activity can be ascribed to the higher propensity of KOH to be carbonated and hydrated.

Since the great solubility of complexes **4a–c** in water allows the easy separation of the organic product from the catalyst by simple liquid-liquid extraction at the end of the reaction (see details in the Experimental Section), we have examined the catalyst recycling. Remark-

Table 4. Isomerization of allylic alcohols in water catalyzed by complexes **3c**, **4a–c**.[a]

Entry	Substrate	Catalyst	Time [min]	Yield [%]	TOF [h^{-1}][b]
1	1-octen-3-ol	**4a**	10	99	594
2	1-octen-3-ol	**4a**[c]	150	88	35
3	1-penten-3-ol	**4a**	15	97	388
4	1-octen-3-ol	**4b**	15	99	396
5	1-octen-3-ol	**4b**[c]	45	99	132
6	1-penten-3-ol	**4b**	5	99	1188
7	1-octen-3-ol	**4c**	35	99	170
8	1-octen-3-ol	**4c**[c]	115	99	52
9	1-penten-3-ol	**4c**	400	99	15
10	1-octen-3-ol	**3c**	10	97	582
11	1-octen-3-ol	**3c**[c]	160	15	6
12	1-penten-3-ol	**3c**	5	99	1188

[a] Reactions carried out at 75 °C using 4 mmol of substrate, 1 mol % of catalyst and 5 mol % of KO-*t*-Bu, in 20 mL of water.
[b] Turnover frequency [(mol product/mol Ru)/time].
[c] Without KO-*t*-Bu.

ably, catalysts **4a**, **4b** and **4c** can be recycled 3, 7 and 9 times, respectively, after the isomerization of 1-octen-3-ol into octan-3-one (Table 5). It seems that the higher the water-solubility of the catalyst precursor is, the better is the recycling process. Indeed, the tricationic complex **4c**, which is the most water-soluble catalyst, presents the higher capacity to be recycled (at least 10 runs). In contrast, **4a** can be only recycled 3 times, probably due to the leaching of the catalyst during the extraction process with the organic solvents in which it is somewhat soluble.

Table 5. Recycling of catalysts **4a–c** in the isomerization of 1-octen-3-ol into octan-3-one.[a]

Entry	Catalyst	Cycle	Time [min]	Yield [%]	TON[b]
1	**4a**	1	10	99	99
2		2	25	99	198
3		3	40	99	297
4		4	120	99	396
5		5	200	0	
6	**4b**	1	15	99	99
7		2	40	99	198
8		3	150	99	297
9		4	105	99	396
10		5	120	99	495
11		6	115	99	594
12		7	200	99	693
13		8	310	99	792
14	**4c**	1	35	99	99
15		2	65	99	198
16		3	65	99	297
17		4	70	99	396
18		5	70	99	495
19		6	70	99	594
20		7	80	99	693
21		8	115	99	792
22		9	80	99	891
23		10	215	99	990

[a] Reactions carried out at 75 °C using 4 mmol of 1-octen-3-ol, 1 mol % of catalyst, 5 mol % of KO-*t*-Bu, in 20 mL of water.
[b] TON = Turnover number (mol product/mol Ru). Cumulative TON values.

As far as we know, the performance of the pre-catalyst **4c** in terms of recycling capacity is at present the best reported.[3,4,19] Previous attempts to reuse the catalysts are limited to the ruthenium(IV) complexes [$RuCl_2(\eta^3{:}\eta^2{:}\eta^3\text{-}C_{12}H_{18})$] ($C_{12}H_{18}$ = dodeca-2,6,10-triene-1,12-diyl) and [{$RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$}$_2$] ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-dien-1,8-diyl),[3] the arene-ruthenium derivatives [$RuCl_2(\eta^6\text{-arene})\{P(CH_2OH)_3\}$] and [$RuCl(\eta^6\text{-arene})\{P(CH_2OH)_3\}_2$][Cl][4] and some rhodium complexes containing aryl-phosphonated and -sulfonated phosphines.[19] It is worthy of mention that 1-octen-3-ol represents one of the most challenging substrates for isomerization of allylic alcohols in water due to its steric requirement and its low water-solubility. It has been reported that its transformation is slow compared with other allylic alcohols[4,19a] and dramatic deactivation of the catalytic system is observed in the second cycle, requiring at least 24 h to complete the reaction.[4] In this context, both the high activities of **4a–c** and the excellent capability of recycling of **4c** represent a great advancement.

Conclusions

The isomerization of allylic alcohols into the corresponding saturated carbonyl compounds catalyzed by transition metal complexes represents a straightforward synthetic process which otherwise requires a two-steps sequence of oxidation and reduction reactions.[20,21] Furthermore, the total atom economy of this transformation makes it particularly attractive from an environmental point of view.[2] Despite these facts, the number of catalysts which are able to promote efficiently the isomerization of allylic alcohols in water remains very limited.[22,23]

In this work, a synthetic methodology to prepare new water-soluble complexes of the type $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa\text{-}(P)\text{-}PPh_{3-n}(OCH_2CH_2NMe_3)_n\}][SbF_6]_n$ (n = 1, 2 or 3) has been developed from the neutral derivatives $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa\text{-}(P)\text{-}PPh_{3-n}(OCH_2CH_2NMe_2)_n\}]$ *via* quaternization of the nitrogen atom of the terminal aminoalkyl groups and subsequent anion exchange. Both the water-soluble ionic complexes and their neutral precursors have proven to be highly active catalysts for the isomerization of allylic alcohols in aqueous and organic media, respectively. They are among the more efficient catalysts already reported. Moreover, the hydro-soluble complexes present a remarkable capacity to be recycled (up to 10 runs) which has no precedent in the literature.

We have also found that complexes **4a–c** remain active in the presence of isoprene.[24] It should be mentioned that almost all known catalysts able to perform allylic alcohol isomerization fail in presence of conjugated dienes.[22] Since allylic alcohols can be obtained by hydration of dienes, these complexes can be envisaged as potential catalysts for direct *one-pot* transformation of dienes into saturated ketones.[23c]

Experimental Section

General Remarks

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried and distilled under nitrogen before use. Allylic alcohols were obtained from commercial suppliers. GC measurements were made on a Hewlett-Packard HP6890 equipment using a Supelco Beta-Dex™ 120 (30 m, 250 μm) column.

General Procedure for Catalytic Isomerization of Allylic Alcohols

Under an inert atmosphere, the ruthenium catalyst precursor (0.04 mmol, 1 mol %), potassium *tert*-butoxide (0.2 mmol, 5 mol %), the allylic alcohol (4 mmol) and 20 mL of THF or deoxygenated water were introduced into a Schlenk tube fitted with a condenser. Then, the mixture was heated at the indicated temperature. The reaction was monitored by gas chromatography. The identity of the ketones was assessed by comparison with commercially available (Aldrich Chemical Co. or Acros Organics) pure samples.

Recycling Procedure

After cooling the reaction mixture, the product was extracted twice with 20 mL of hexane and twice with 15 mL of diethyl ether. Then traces of organic solvent were eliminated at reduced pressure. Substrate (4 mmol) was added and the mixture was heated again at the indicated temperature.

Crystal Structure Determination

Crystallographic data for **4a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC278297. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available

Preparation and characterization of **1b**, **2a–c**, **2′b**, **3a–c**, **3′b**, **4a–c** and **5**. Details of X-ray diffraction analysis.

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