#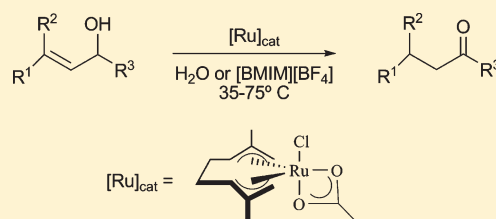 Redox Isomerization of Allylic Alcohols into Carbonyl Compounds Catalyzed by the Ruthenium(IV) Complex [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl($\kappa^2 O$, O-CH$_3$CO$_2$)] in Water and Ionic Liquids: Highly Efficient Transformations and Catalyst Recycling

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ABSTRACT: Isomerization reactions of allylic alcohols into carbonyl compounds can be efficiently performed in both water and in ionic liquids using [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl($\kappa^2 O,O$-CH$_3$CO$_2$)] as catalyst. In both cases, the catalytic system could be recycled up to five times.

Isomerization reactions are processes which proceed with atom economy, as no byproducts are generated.[1] Metal-catalyzed redox isomerizations of readily accessible allylic alcohols are typical examples, and they constitute a useful and straightforward synthetic route to carbonyl compounds which are very valuable raw materials in organic chemistry (see Scheme 1). Although this synthetic methodology, mostly using organic solvents, has been extensively studied,[2a,b] there has been an increasing interest to search for new catalytic approaches in water,[2c] as a genuinely environmentally friendly reaction medium.[3] However, in contrast to the growing number of new efficient catalytic methodologies in aqueous medium competitive with those reported for organic solvents[4,5] (most of them requiring the presence of a cocatalyst), to the best of our knowledge only a few catalytic isomerization of allylic alcohols using ionic liquids[6,7] as alternative green reaction media have been reported.[8]

We have recently been engaged in studying these types of catalytic isomerizations in aqueous medium, and we have reported that the bis(allyl)ruthenium(IV) complexes [Ru(η^3:η^2:η^3-C$_{12}$H$_{18}$)Cl$_2$] (**1**; C$_{12}$H$_{18}$ = dodeca-2,6,10-triene-1,12-diyl) and [{Ru(η^3:η^3-C$_{10}$H$_{16}$)(μ-Cl)(Cl)}$_2$] (**2**; C$_{10}$H$_{16}$ = 2,7-dimethyl-octa-2,6-diene-1,8-diyl) are among the most active catalysts reported to date.[9] Despite this fact, the reactions proceed in a heterogeneous manner due to the very low solubility of the catalysts in water. We envisioned that an improved catalytic activity might be achieved by using a soluble alternative catalyst, also allowing the design of a synthetic methodology involving the catalyst recycling. Herein we report the catalytic activity of the acetate ruthenium(IV) complex [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl($\kappa^2 O,O$-CH$_3$CO$_2$)][10] (**3**) (see Figure 1), which is soluble in both water and ionic liquids. Remarkably, (i) this catalyst shows a high efficiency for the isomerization of allylic alcohols in both water and ionic liquids, (ii) it is active under mild reaction conditions (35 °C)
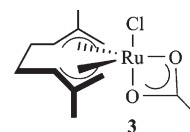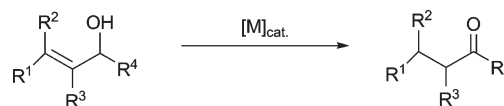

Figure 1. Structure of [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl($\kappa^2 O,O$-CH$_3$CO$_2$)] (**3**).

**Scheme 1. Catalytic Isomerization of Allylic Alcohols**

and in the absence of base, (iii) it is a phosphine-free metal catalyst (in contrast to most of the known active ruthenium catalysts), and (iv) it is readily recoverable and remains active up to five runs.

First, we checked the activity of complex **3** in the isomerization of 1-octen-3-ol as a model reaction (see Table 1). Thus, when a solution of 1-octen-3-ol in water was heated at 75 °C with a catalyst loading of 0.2 mol %, octan-3-one was formed in 99% yield after only 5 min (Table 1, entry 1) (TOF = 6000 h^{-1}) a value which is, to the best of our knowledge, the highest reported in the literature using water as pure solvent in the absence of any cocatalyst.[11] Catalyst **3** is also very efficient in the isomerization of a variety of allylic alcohols,[12] proving the wide scope of this catalytic transformation (results are summarized in Table 1). For most of the substrates tested, a quantitative formation of the saturated carbonyl compound is achieved in less than 15 min.

Table 1. Isomerization of Various Allylic Alcohols Catalyzed by $[\mathrm{Ru}(\eta^3{:}\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\kappa^2 O,O\text{-}\mathrm{CH}_3\mathrm{CO}_2)]$ (3) in $\mathrm{H}_2\mathrm{O}$ and $[\mathrm{BMIM}][\mathrm{BF}_4]$[a]
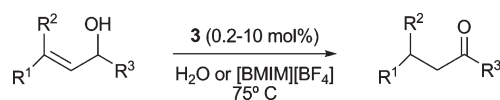
entry	Substrate	Product	H$_2$O Catalyst loading	H$_2$O Yield %[b] (time) TOF/h^{-1c}	[BMIM][BF$_4$] Catalyst loading	[BMIM][BF$_4$] Yield % (time) TOF/h h^{-1c}
1[d]			0.2 mol%	>99 (5 min) 6000	1 mol%	>99 (5 min) 1200
2			0.2 mol%	98 (15 min) 1960	1 mol%	>99 (5 min) 1200
3			0.2 mol%	98 (15 min) 1960	1 mol%	>99 (5 min) 1200
4			0.2 mol%	93 (15 min) 1860	1 mol%	>99 (5 min) 1200
5			0.2 mol%	89 (15 min) 1780	1 mol%	97 (5 min) 1164
6			0.2 mol%	71 (30 min) 710	1 mol%	>93 (5 min) 1116
7			1 mol%	>99 (5 min) 1200	1 mol%	>99 (1 h) 100
8			10 mol%	71 (1 h.) 7	10 mol%	88 (1 h.) 9
9			5 mol%	93 (1 h.) 18	5 mol%	65 (1 h.) 17
10			5 mol%	74 (2 h.) 7	5 mol%	70 (2 h.) 7
11			10 mol%	78 (20 h.) < 1	10 mol%	76 (22 h.) < 1
12			10 mol%	18 (3 h.) < 1	10 mol%	0

[a] General conditions: reactions performed under N_2 atmosphere at 75 °C using 1 mmol of the allylic alcohol in 5 mL of water or in 1 g of $[\mathrm{BMIM}][\mathrm{BF}_4]$ ($[\mathrm{BMIM}][\mathrm{BF}_4]$ = 1-butyl-3-methylimidazolium tetrafluoroborate). [b] Yields determined by GC. [c] Turnover frequencies ((mol of product)/(mol of Ru))/time were calculated at the time indicated in each case. [d] The reaction performed at 35 °C using 1 mmol of the allylic alcohol and 1 mol % of complex 3 in 5 mL of water leads to a quantitative yield in 30 min.

As far as the allylic alcohols are concerned, there is a strong dependence upon the substitution of the carbon–carbon double bond, as previously observed with the Ru(IV) catalysts **1** and **2**.[13] Thus, the monosubstituted alcohols (entries 1–5) are readily isomerized with TOF values of 710–6000 h^{-1}. For the transformation of the allylic alcohol into propanal (entry 6), a longer reaction time (30 min) and only moderate yield (71%) are observed. Also, when 1,1- and 1,2-disubstituted allylic alcohols are used (entries 8–11),

longer reaction times and higher catalyst loadings (5–10 mol %) are required. In the case of trisubstituted allylic alcohols such as 3-methyl-2-buten-1-ol (entry 12), complex **3** only could achieve an 18% yield of the 3-methylbutyraldehyde after 3 h of reaction. Remarkably, complex **3** (1 mol %) is also able to isomerize 1-octen-3-ol into octan-3-one quantitatively under very mild conditions (35 °C, see entry 1 and footnote *d* in Table 1) after only 30 min, proving the outstanding catalyst efficiency in water.[14]

Table 2. Isomerization of 1-Octen-3-ol Catalyzed by Complex 3 in Water and [BMIM][BF$_4$]: Catalyst Recycling
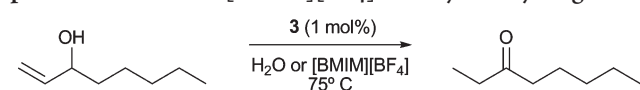
	H$_2$O		[BMIM][BF$_4$]	
cycle	time	yield, %[b] (TON)[c]	time	yield, %[b] (TON)[c]
1	5 min	99 (99)	5 min	99 (99)
2	10 min	99 (198)	20 min	99 (198)
3	10 min	99 (297)	30 min	95 (293)
4	20 min	96 (396)	1 h	97 (390)
5	1.5 h	99 (495)	2 h	96 (487)

[a] General conditions: reactions performed at 75 °C under N$_2$ atmosphere using 4 mmol of 1-octen-3-ol in 20 mL of H$_2$O or 2 mmol of 1-octen-3-ol in 2 g of [BMIM][BF$_4$]. [b] Determined by GC. [c] Cumulative TON values (turnover number = (mol of product)/(mol of Ru)).

Complex **3** also shows a high catalytic efficiency using ionic liquids as alternative environmentally friendly solvents. Thus, in a model reaction, to our satisfaction, the isomerization of 1-octen-3-ol was catalyzed by **3** (1 mol %) at 75 °C in [BMIM][BF$_4$][15] ([BMIM][BF$_4$] = 1-butyl-3-methylimidazolium tetrafluoroborate), affording quantitatively and chemoselectively 3-octanone in only 5 min (entry 1, Table 1).[16] As for the isomerization in water, the catalytic reaction in the ionic liquid also tolerates a diverse array of allylic alcohols. Thus, the monosubstituted alcohols are readily isomerized (entries 1–7, TOF values 100–1200 h^{-1}), while disubstituted allylic alcohols (entries 8–11) required longer reaction times and higher Ru loadings (5–10 mol %), as previously observed in water.[17] Nevertheless, complex **3** is totally inactive in the isomerization of trisubstituted allylic alcohols such as 3-methyl-2-buten-1-ol in [BMIM][BF$_4$] (entry 12).

The lifetime of a catalytic system and its level of reusability are very important factors.[18] In this regard, the good solubility of complex **3** in both water (4.7 mg/mL) and [BMIM][BF$_4$] (4.8 mg/mL) allows it to be recycled easily after simple extraction of the final product with immiscible hexane (3 × 5 mL). Comparative results in water and [BMIM][BF$_4$] using the isomerization of 1-octen-3-ol into 3-octanone as a model reaction are shown in Table 2. Thus, we have found that while no appreciable loss of activity occurs in water during the first four consecutive runs (5–20 min, 99% GC yields), the efficiency of the ionic liquid solution decreases considerably after the first four recycling cycles, 1 h of heating being required in the fourth cycle to obtain a quantitative conversion. It is important to note that both catalytic systems could be recycled in five consecutive times in 1.5 or 2 h (entry 5), leading to cumulative TON values of 495 and 487. The aqueous solution could be recycled for one more consecutive cycle, needing for this case 18 h of heating to achieve a quantitative conversion.

In summary, we have demonstrated that the complex [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl(κ^2O,O-CH$_3$CO$_2$)] (**3**), which is soluble in both water and ionic liquids, is a highly efficient and recoverable catalyst for the isomerization of allylic alcohols into their corresponding saturated carbonyl derivatives. It is important to note that this catalyst not only is among the most efficient ones reported in the literature in water but also is active under very mild reaction conditions (35 °C). Since, in addition, this catalyst does not

involve the presence of phosphines and no base as cocatalyst is required, this synthetic methodology can be considered as a genuine example of a catalytic application of an organometallic compound in a *green* chemical process. Mechanistic studies and further efforts to develop new catalytic systems active and recoverable in ionic liquids are presently underway.

■ **EXPERIMENTAL SECTION**

Typical Procedure for the Catalytic Reactions. The corresponding allylic alcohol (1–4 mmol) and the appropriate solvent (water 5–20 mL; 1–2 g of [BMIM][BF$_4$]) were introduced into a sealed tube under a nitrogen atmosphere. Complex **3** (0.2–10 mol % of Ru) was then introduced at room temperature, and the resulting solution was heated at 75 °C for the indicated time (the course of the reaction was monitored by regular sampling and analysis by GC). After completion of the reaction, the organic product was extracted with hexane (3 × 5 mL).

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(11) For the isomerization of 1-octen-3-ol under these reaction conditions, catalyst **3** is much more active than the monomer **1** (TOF = 600 h^{-1}) or dimer **2** (TOF = 750 h^{-1}).[9] Other rhodium phosphine-free catalysts[4f] displayed lower turnover frequencies than did complex **3**.

(12) Longer reaction times are requiered for the isomerization of 1-octen-3-ol with the series of mononuclear derivatives [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$(L)] (L = PR$_3$, P(OR)$_3$, RCN) and [Ru(η^3:η^3-C$_{10}$H$_{16}$)-Cl(CH$_3$CN)$_2$)].[9b]

(13) It is well-known that the isomerization of allylic alcohols becomes more difficult as the number of substituents increase on the C=C double bond.[2]

(14) At this point, is important to note that catalyst **3** is, to the best of our knowledge, the first ruthenium catalyst active in the redox isomerization of allylic alcohols under mild conditions (35 °C) using water as pure solvent. As far as we are aware, only one further rhodium(I) complex is also active in the catalytic isomerization of allylic alcohols at ambient temperature.[4f]

(15) The observed rate of the reaction was not dependent on the nature of the counterion of the ionic liquid; for example, the efficiency of the reaction was maintained when [BMIM][PF$_6$] (98%, 5 min) was used as solvent.

(16) The use of a lower catalyst loading (0.2 mol %) slowed down the reaction; 92% conversion of 1-octen-3-ol in octan-3-one was achieved after 2 h.

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