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ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 468–474
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Redox isomerisation of allylic alcohols catalysed by water-soluble ruthenium complexes in aqueous systems

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Received 3 August 2007; received in revised form 5 November 2007; accepted 7 November 2007
Available online 13 November 2007

Abstract

The process of catalytic isomerisation of various allylic alcohols (alk-1-en-3-ols) into saturated ketones under mild conditions is reported. The water-soluble $Na_4[\{RuCl_2(m\text{tppms})_2\}_2]$ complex, previously reported by us as a precursor to very active hydrogenation catalysts was also found an active catalyst of the redox isomerisation of allylic alcohols in aqueous media. The new Na[Ru(CO)Cp($m$tppms)$_2$] as well as $Na_4[\{RuCl(\mu\text{-}Cl)(C{=}C{=}CPh_2)(m\text{tppms})_2\}_2]$ and $Na_2[RuClCp(m\text{tppms})_2]$ also showed good to excellent catalytic activities for redox isomerisations in aqueous systems at 50–80 °C under inert atmosphere.

Keywords: Allylic alcohols; Redox isomerisation; Catalysis; Water-soluble complexes; *m*tppms; Ruthenium

1. Introduction

Catalytic isomerisation of allylic alcohols (e.g. Scheme 1) is an attractive strategy for the synthesis of saturated carbonyl compounds [1–4]. Such internal redox reactions (transpositions) show 100% atom economy and therefore much effort has been spent on the study of these processes following the seminal works of Blum [5] and Trost [6]. Redox isomerisation of an allylic alcohol can be regarded as an internal oxidation followed by reduction (or the reverse sequence). However, sensitive substrates may not survive the conditions of oxidation and/or reduction therefore catalytic redox isomerisations are especially useful in syntheses requiring mild reaction conditions.

In most previous investigation, isomerisation processes have been studied in organic solvents, such as THF [7,8] and alkanes [9]. Very efficient catalyst systems were developed based on ruthenium complexes [10–12]. For example, the bis(allyl)-ruthenium(IV) dimer, $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) catalysed the isomerisation of oct-1-en-3-ol in THF at 75 °C with a turnover frequency (TOF) as high as 62 500 h^{-1} [TOF = (mol converted substrate)(mol catalyst)$^{-1}$ h^{-1}] [12]. A specific application is the reduction of allylic alcohols in propan-2-ol when the isomerisation and consequent transfer hydrogenation is catalyzed by the same complex, $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)\}_2]$ [13]. Isomerisation of allylic alcohols was also studied with Rh(I)-catalysts in phase-transfer assisted aqueous-organic biphasic systems [14] in which, however, the catalytically active Rh(I) complex resided in the organic phase.

Water as an environment-friendly solvent for organic reactions attracts more and more interest both from industrial and academic viewpoints [15–18]. The most common

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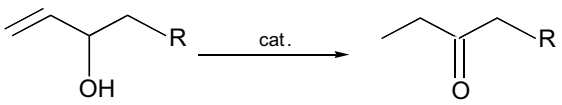
doi:10.1016/j.jorganchem.2007.11.011



Scheme 1. Isomerisation of 1-alkene-3-ols.

and efficient catalysts in aqueous media are transition metal complexes containing water-soluble phosphines, such as the monosulfonated and trisulfonated triphenylphosphines, usually as their sodium salts (*m*tppms-Na [19,20] and *m*tppts-Na_3 [21,22], respectively). A wide range of homogeneous catalysts containing rhodium, ruthenium, palladium, iridium, and other metals coordinated by water soluble phosphine ligands have been reported [15–18,23].

Water-soluble ruthenium(II) complexes of *m*tppms (such as $Na_4[\{RuCl_2(mtppms)_2\}_2]$ (**1**)) have been shown to act as selective catalysts for the hydrogenation of α,β-unsaturated aldehydes [24,25] as well as of the stereoselective hydrogenation of disubstituted alkynes [26]. The pH of the aqueous phase decisively influenced the selectivity what was attributed to the pH-dependent formation of the mono- and dihydride species, $Na_3[RuHCl(mtppms)_3]$ and $Na_3[RuH_2(mtppms)_3]$, respectively [27,28]. These findings call attention to a thorough investigation of the pH-effects in aqueous organometallic catalytic processes.

The catalytic isomerisation of allylic alcohols in aqueous systems has already been investigated. McGrath and Grubbs used $[Ru(H_2O)_6](tos)_2$ (tos = *p*-toluenesulfonate) for their mechanistic studies on allyl alcohol isomerisation in water [29]. Other ruthenium-based catalysts for aqueous processes included $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ [12], $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa\text{-}(P)\text{-}PPh_{3-n}(OCH_2CH_2NMe_3)_n\}][SbF_6]_n$ ($n = 1$, 2 or 3) [30], $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa\text{-}(P)\text{-}PPh_{3-n}(OCH_2CH_2NMe_2)_n\}]$ ($n = 1,2$ or 3) [30], $[RuCl_2(\eta^6\text{-arene})\{P(CH_2OH)_3\}]$ [31] and $[RuCl_2(\eta^6\text{-arene})$ (THPA)] (THPA = 2,4,10-trimethyl-1,2,4,5,7,10-hexaaza-3-phosphatricyclo-[3.3.1.$1^{3,7}$]decane) [32].

Several water-soluble rhodium(I) complexes were also applied as catalyst in such reactions [33–35]. The turnover frequencies determined under optimum conditions were generally less than 500 h^{-1}, with the notable exception of the catalyst prepared in situ from $Rh_2(SO_4)_3$ and *m*tppts-Na_3 (TOF = 2520 h^{-1} in the reaction of oct-1-en-3-ol in THF at 80 °C [34]). It should be noted that in the above studies no attempts were made to control the pH of the aqueous solutions (phases), e.g. by using appropriate buffers.

Table 1
Isomerisation of oct-1-en-3-ol catalyzed by **2** as a function of the pH

pH	Conversion (%)
2.2	51
4.0	97
5.0	100
7.0	16

Conditions: 15.5 mg **2** (0.013 mmol Ru), 0.15 mL oct-1-en-3-ol (1.0 mmol), 80 °C, 3 mL 0.1 M phosphate buffer, 1 h reaction time.

In addition to tertiary phosphine-containing catalysts, a few complexes with N-heterocyclic carbene ligands were also used as catalysts of redox isomerisation of allylic alcohols in aqueous media showing a maximum turnover frequency of 65 h^{-1} [36,37].

For long, we have been interested in the syntheses and catalytic properties of water-soluble organometallic complexes of ruthenium(II) [38] and in the effects of the aqueous phase on reactions catalyzed by such complexes [39–41]. Here, we describe the catalytic activity of $Na_4[\{RuCl_2(mtppms)_2\}_2]$ (**1**), $Na_4[\{RuCl(\mu\text{-}Cl)(C{=}C{=}CPh_2)(mtppms)_2\}_2]$ (**2**), [42] and $Na_2[RuClCp(mtppms)_2]$ (**3**), [43] in the isomerisation of allylic alcohols in water. In addition, the synthesis and some catalytic properties of the novel water-soluble complex $Na[Ru(CO)Cp(mtppms)_2]$ (**4**), are also reported. (See Scheme 2.)

2. Results and discussion

2.1. Catalytic isomerisation of oct-1-en-3-ol in water

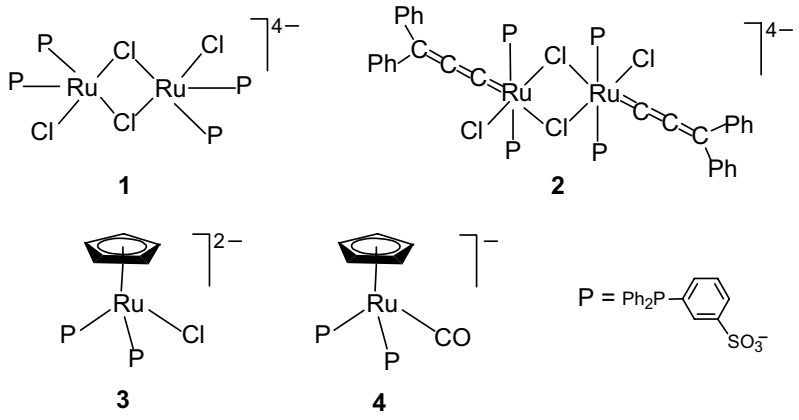
The catalytic isomerisation by water soluble ruthenium complexes **1**–**4** of terminal allylic alcohols has been studied. Reactions were performed in 3 mL of water using 0.5 mol% of ruthenium catalyst and 1 mmol of the corresponding allylic alcohol. Progress of the reactions was monitored by gas chromatography or ^1H NMR spectroscopy. The effects of various reaction parameters on the isomerisation of oct-1-en-3-ol catalysed by the water-soluble ruthenium complex $Na_4[\{RuCl_2(mtppms)_2\}_2]$ (**1**) are shown in Figs. 1–4.

As shown in Fig. 1, water-soluble complex **1** was active in catalysis of the isomerisation of oct-1-en-3-ol to give selectively 3-octanone. No products other than 3-octanone were detected. After a slight induction period the reaction proceeds steadily with a turnover frequency (TOF) of 79 (mol substrate)(mol Ru)$^{-1}$ h^{-1}. (Turnover frequencies calculated for the middle part of the *S*-curve and for the sake of comparison of catalysts TOF-s are given for 1 mol of Ru rather than for 1 mol of the complexes of which **1** and **2** are dimeric in contrast to the monomeric **3** and **4**.)

The yield of the transformation was observed to be dependent of the pH of the aqueous phase (Fig. 2). After 1 h at 50 °C the highest isomerisation yield was obtained at pH 5.0 (45%). In more acidic solutions the catalytic activity of **1** dropped sharply. Therefore in further studies the pH of the reaction was adjusted to the range of 5–7.

A study of the reaction rate as a function of temperature was undertaken in the range from 20 to 60 °C. It is seen in Fig. 3 that there was hardly any reaction below 40 °C, however, above this temperature the reaction rate increased exponentially with increasing temperatures. It is important to point out that at 60 °C a conversion of 97% is obtained in a reaction time of 1 h, corresponding to a TOF of 101 h^{-1}.

Catalysis of the isomerisation reaction by **1** was also studied in the presence of free *m*tppms; the results are



Scheme 2. Structures of complexes **1**–**4**.

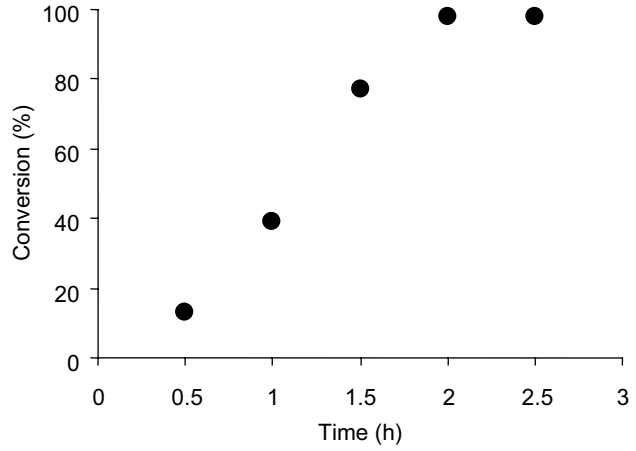


Fig. 1. Isomerisation of oct-1-en-3-ol catalysed by **1** as a function of time. *Conditions:* 10.0 mg **1** (0.01 mmol Ru), 0.16 mL oct-1-en-3-ol (1.04 mmol), 50 °C, 3 mL 0.1 M phosphate buffer, pH 7.0.

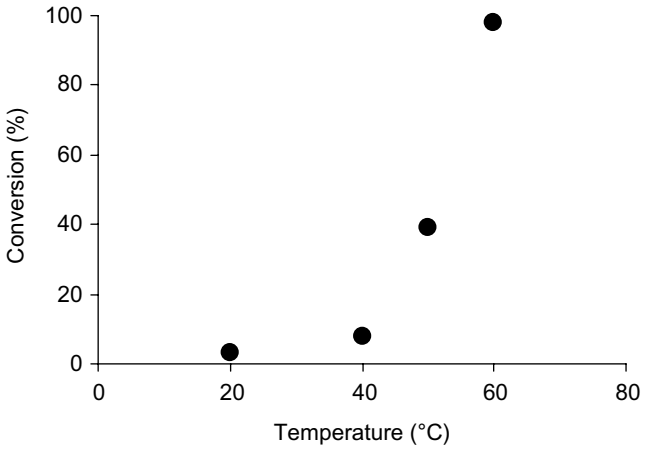


Fig. 3. Isomerisation of oct-1-en-3-ol catalysed by **1** as a function of temperature. *Conditions:* 10.0 mg **1** (0.01 mmol Ru), 0.16 mL oct-1-en-3-ol (1.04 mmol), 3 mL 0.1 M phosphate buffer, pH 7.0, 1 h reaction time.

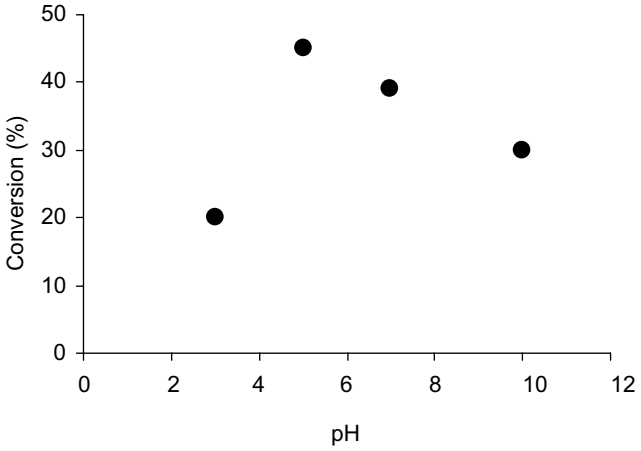


Fig. 2. Isomerisation of oct-1-en-3-ol catalysed by **1** as a function of the pH of the aqueous phase. *Conditions:* 10.0 mg **1** (0.01 mmol Ru), 0.16 mL oct-1-en-3-ol (1.04 mmol), 50 °C, 3 mL 0.1 M phosphate buffer, 1 h reaction time.

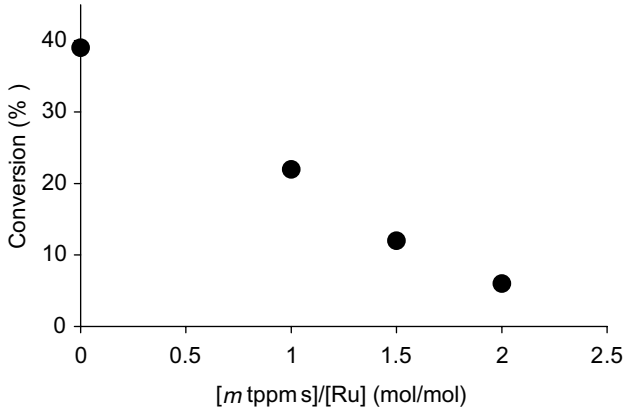


Fig. 4. Effect of free *m*tppms on the isomerisation of oct-1-en-3-ol catalysed by **1**. *Conditions:* 10.0 mg **1** (0.01 mmol Ru), 0.16 mL oct-1-en-3-ol (1.04 mmol), 50 °C, 3 mL 0.1 M phosphate buffer, pH 7.0, 1 h reaction time.

depicted in Fig. 4. The results show a strong inhibition of the reaction by the ligand excess, therefore the best catalytic activity was observed in the absence of excess *m*tppms.

In summary, these experiments showed that oct-1-en-3-ol could be rapidly and quantitatively isomerized to 3-octanone (97%) by **1** in water under very mild conditions (60 °C, pH 7) with a TOF as high as 101 h^{-1}.

This promising result led us to investigate the catalytic activity of other water-soluble ruthenium complexes containing *m*tppms. The allenylidene ruthenium complex $Na_4[\{RuCl(\mu\text{-}Cl)(C{=}C{=}CPh_2)(mtppms)_2\}_2]$ (**2**) [42] was studied in the isomerisation of oct-1-en-3-ol into 3-octanone under similar reaction conditions to those with **1** as catalyst. Allenylidene and vinylidene ruthenium complexes are among the most efficient catalysts in catalysed alkene isomerisation [44,45] but of that kind of complexes **2** is the only example known in literature which shows good solubility in water.

Although complex **2** is an active catalyst of the isomerisation process, its activity at 50 °C was lower than that observed for **1**. Nevertheless at 80 °C and pH 5.0 the complex mediated the quantitative isomerisation of oct-1-en-3-ol into the corresponding ketone (Table 1). It is important to point out that this reaction is very sensitive to the pH of the reaction mixture as the conversion yield dropped down from 100% to 16% when the pH was modified from 5 to 7.

These results evidenced two important points: (a) coordination of an allenylidene ligand to the central metal ion may lead to a reduction of the isomerisation yield, and (b) a precise control of the reaction pH is mandatory in case of these kind of catalysts. Nevertheless, at the optimum pH the activity of **2** (TOF = 77 h^{-1} at pH 5.0) was comparable to that of **1**.

$Na_2[RuClCp(mtppms)_2]$ (**3**) [43] is a water-soluble half-sandwich complex of ruthenium. This compound showed excellent catalytic activity in the isomerisation of oct-1-en-3-ol at 80 °C. With 1 mol% catalyst 100% conversions were achieved in the pH range 2.2–7.0 and the effect of the pH on the reaction rate could be observed only with a high substrate/catalyst loading, i.e. [S]/[C]=1100 (Fig. 5). Under the conditions of Fig. 5 the highest activity (100% conversion) corresponds to TOF = 2226 h^{-1}.

The rate of the isomerisation of oct-1-en-3-ol increased sharply with the temperature (Fig. 6). It is noteworthy that this catalyst remains active even at room temperature. This compares favourably to the case of **1**, where hardly any activity could be observed below 40 °C (vide supra).

$Na_2[RuClCp(mtppms)_2]$ (**3**) showed pronounced stability in water. The $^{31}P\{^1H\}$ NMR spectrum of the complex in aqueous solution did not change appreciably during 24 h at 40 °C, and only after 4 days was its decomposition to unidentified products observed. The stability of **3** in water suggests no extensive ligand dissociation from the complex. This is in line with the finding that even at high chloride excess the catalytic activity of **3** is decreased only by 15% (Table 2). However, it cannot be excluded that reaction of **3** with allylic alcohols generates a chloride-free Ru(II)-hydride complex with loosely bound *m*tppms ligands, which in turn is capable of fast catalysis of the redox isomerisation.

In order to clarify the role of ligand elimination from **3** in the catalytic isomerisation of the oct-1-en-3-ol in water, we synthesized the carbonyl complex $Na[Ru(CO)Cp(mtppms)_2]$ (**4**) in which the Cl^- ligand in **3** was substituted by CO. The reaction of CO with **3** did not proceed at 40 °C in 24 h, however, on the addition of AgOTf $Na[Ru(CO)Cp(mtppms)_2]$ (**4**) was readily obtained. This complex is water-soluble and stable in the temperature range used for catalytic evaluations. At pH 7.0, **4** catalyzed the redox isomerisation of oct-1-en-3-ol to octan-3-one with a TOF as low as 10 h^{-1}. This result shows that

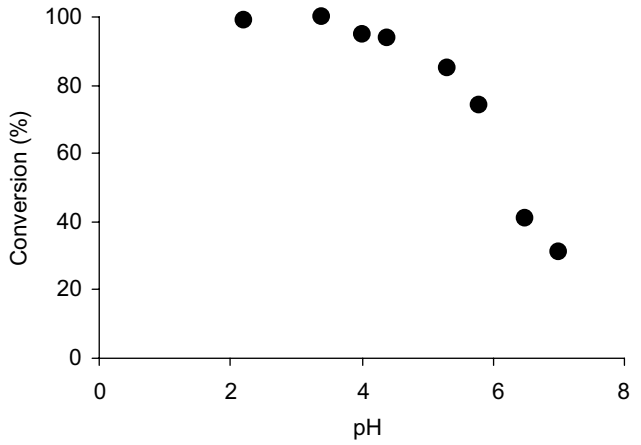


Fig. 5. Isomerisation of oct-1-en-3-ol catalyzed by **3** as a function of pH. *Conditions:* 4.5 mg **3** (0.0045 mmol Ru), 0.75 mL oct-1-en-3-ol (5.0 mmol), 80 °C, 3 mL of 0.1 M phosphate buffer, 0.5 h reaction time.

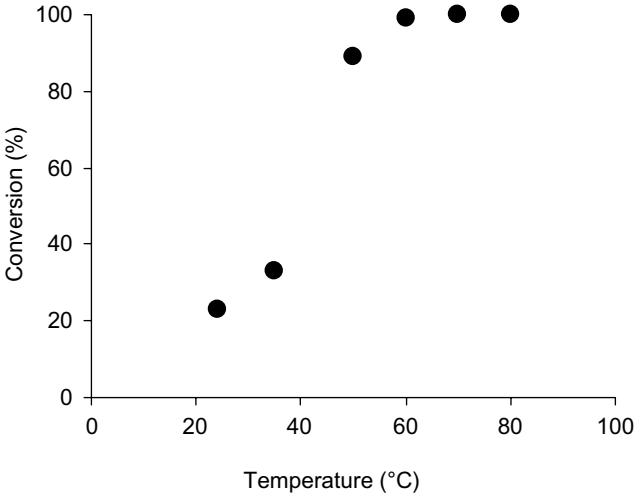


Fig. 6. Isomerisation of oct-1-en-3-ol catalyzed by **3** as a function of temperature. *Conditions:* 9 mg **3** (0.009 mmol), 0.15 mL oct-1-en-3-ol (1.0 mmol), 3 mL of 0.1 M phosphate buffer, pH 4.0, 0.5 h reaction time.

Table 2
Isomerisation of oct-1-en-3-ol catalyzed by **3** as a function of chloride concentration of the aqueous phase

$[Cl^-]$ (M)	$[Cl^-]$/[Ru]	Conversion (%)	TOF (h^{-1})
0.1	67	100	222
0.2	133	92	204
0.4	267	85	189

Conditions: 4.5 mg **3** (0.0045 mmol Ru), 0.15 mL oct-1-en-3-ol (1.0 mmol), 80 °C, 3 mL of 0.1 M phosphate buffer, 0.5 h reaction time.

replacement of chloride by a tightly bound CO blocks catalysis to a large extent. The remaining activity may be due to phosphine dissociation under catalysis conditions.

2.2. Isomerisation of allylic alcohols catalysed by complexes 1–4

The catalytic properties of complexes **1**–**4** were compared in the redox isomerisation of several alk-1-en-3-ols. Although there is a difference in the temperature in case of **1** (50 °C) and **2** and **3** (80 °C), the data of Table 3 show unambiguously that all the three complexes displayed high catalytic activities in the redox isomerisation of this set of substrates. With the exception of prop-2-en-1-ol (allyl alcohol) the yields of corresponding carbonyl compounds obtained by using **2** and **3** are uniformly high. In contrast, **4** was again found less suitable for this type of catalysis, and for meaningful conversions at 50 °C, pH 7.0 reaction times as long as 2.5 h were needed (oct-1-en-3-ol: 25%; hept-1-en-3-ol: 38%; hex-1-en-3-ol; 20%, pent-1-en-3-ol 20%). The case of allyl alcohol deserves special mention since the conversions obtained with catalysts **1** and **2** were strikingly low compared to the results with the other substrates in Table 3. The isomerisation of this compound gives rise to the formation of propanal, while with all the other substrates the corresponding methyl ketones are obtained. Aldehydes may undergo CO-abstraction leading to the formation of less active catalysts. In order to check this possibility, following the reaction of allyl alcohol with **1** as catalyst we have pumped the reaction mixture dry and recorded the IR spectrum of the residue (in KBr) – a medium strong absorption band was observed at 1923 cm^{-1}. Although this frequency does not correspond to the ν(CO) values of the known *cis*-$Na_2[RuCl_2(CO)_2(m\text{tppms})_2]$ (2000 and 2060 cm^{-1}) [46], or to that of $Na_2[RuCl_2(CO)(m\text{tppms})_2]$ (1971 cm^{-1}) [47], it supports the assumption of the formation of Ru-carbonyls. Nevertheless, the exact nature of the transformations of **1** during the isomerisation of allylic alcohol needs further elucidation.

2.3. General discussion

The results described in this communication show that $Na_4[\{RuCl_2(m\text{tppms})_2\}_2]$ (**1**), $Na_4[\{RuCl(\mu\text{-}Cl)(C{=}C{=}CPh_2)(m\text{tppms})_2\}_2]$ (**2**), $Na_2[RuClCp(m\text{tppms})_2]$ (**3**), and to a lesser extent $Na[Ru(CO)Cp(m\text{tppms})_2]$ (**4**) are active catalysts of redox isomerisation of allylic alcohols in water and in aqueous-organic biphasic systems. (In general, such transpositions are catalyzed by Ru-hydride species, so complexes **1**–**4** are better described as catalyst precursors.) Of the four complexes **3** turned out to be the most active with turnover frequencies as high as 2226 h^{-1}, nevertheless **1** and **2** also showed TOFs in the range of 70–100 h^{-1} which corresponds to good catalytic performance in comparison with the catalyst reported earlier in the literature.

Table 3
Isomerisation of allylic alcohols catalyzed by complexes **1**–**3**

Substrate	Conversion (%)		
	1	**2**	**3**
Oct-1-en-3-ol	39	100	100
Hept-1-en-3-ol	36	99	97
Hex-1-en-3-ol	96	99	99
Pent-1-en-3-ol	90	93	98
But-1-en-3-ol	100	88	98
Prop-2-en-1-ol	10	55	100

Conditions: 0.01 mmol catalyst, 1 h reaction time, 3 mL 0.1 M phosphate buffer. (**1**) Substrate 1.04 mmol, 50 °C, pH 7.0; (**2**) substrate 1.00 mmol, 80 °C, pH 5.0; (**3**) substrate 1.00 mmol, 80 °C, pH 4.0.

Although it is not possible to make detailed statements on the mechanistic features of these reactions (furthermore not all four catalysts may work according to the same mechanism), a common feature of the isomerisation of allylic alcohols in water with **1**–**3** is the strong influence of pH. It is worth recalling, that the catalysis of allylic alcohol isomerisations in organic solvents is strongly accelerated by bases, the most widely used base being KO^{t}Bu [7–13]. In some cases it was explicitly shown that the base is needed for the formation of the catalytically active Ru(II)-hydride species [9] (however, we did not investigate the formation of such hydrides in the reactions of **1**–**4** and allylic alcohols). Furthermore, one of the accepted mechanisms of the redox isomerisation of allylic alcohols includes the formation of alkoxo-intermediates [29] or an η^3-oxo-allyl coordination of the substrate [5,12]. Such coordinations may be also facilitated by the presence of appropriate bases, therefore an increase of the basicity of the aqueous phase may lead to the increase of the catalytic activity. Conversely, the sharp decrease of the catalytic activities of **1** and **3** above pH 5 suggests that in alkaline solutions the strong coordination of hydroxide prevents the coordination of allylic alcohols and stops catalysis.

3. Experimental

3.1. General remarks

All reactions and manipulations were routinely performed under an atmosphere of dry nitrogen or argon using standard vacuum-line and Schlenk techniques. Solvents were dried and deoxygenated under nitrogen/vacuum before use. Reagents were obtained from Sigma–Aldrich-Fluka and Lancaster and used without purification. Doubly distilled water was used throughout. Gas chromatographic measurements were made on a Hewlett-Packard HP 5890 Series II equipment using a 2 m Carbowax 20 M on 80/100 Chromosorb 3.5% KOH column and FID. ^{1}H NMR spectra were recorded in D_2O or $CDCl_3$ solutions on a Bruker AM300 or on a Bruker AVANCE DRX300 spectrometer operating at ca. 300 MHz (^{1}H) and ca. 75.4 MHz (^{13}C), respectively. Peak positions are reported relative to tetramethylsilane calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). $^{31}P\{^1H\}$ NMR spectra were recorded

on the same instrument operating at ca. 121 MHz. Chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive.

3.2. Synthesis of complexes

3.2.1. Known compounds

The water-soluble phosphine ligand, *m*tppms-Na (*m*tppms-Na=$Ph_2P(C_6H_4$-*3*-$SO_3Na)$) and the complexes $Na_4[\{RuCl_2(mtppms)_2\}_2]$ (**1**) [20], $Na_4[\{RuCl(\mu\text{-}Cl)(C{=}C{=}CPh_2)(mtppms)_2\}_2]$ (**2**) [42], and $Na_2[RuClCp(mtppms)_2]$ (**3**) [43] were prepared according to the literature.

3.2.2. Synthesis of Na[Ru(CO)Cp(mtppms)$_2$] (4)

A Schlenk vessel containing $Na_2[RuClCp(mtppms)_2]$ (**3**; 0.1 g, 0.107 mmol) dissolved in 10 mL of ethanol was cooled at 0 °C and then CO was bubbled through the solution for 20 min. Into the resulting pale yellow solution 0.030 g (0.12 mmol) of AgOTf was added and the solution was stirred for further 1 h at room temperature, then filtered and the solvent evaporated. The resulting pale yellow solid was dissolved in ethanol (5 mL) and precipitated by diethyl ether (4 mL). The pale yellow precipitate was recovered by filtration, washed with diethyl ether (2 × 2 mL) and air dried. Yield: 66.8%; S_{25,H_2O}: 70 mg/cm^3. Elemental analysis for $C_{42}H_{33}O_7P_2S_2NaRu \cdot H_2O$ (918.019): Found: C, 54.72; H, 3.80; S, 6.69%; Calc. C, 54.90; H, 3.84; S, 6.97. IR (KBr, cm^{-1}): 1975 ν(CO), 1189, 1224 $\nu(SO_3)$; ^{1}H NMR (300.13 MHz, CD_3OD, T = amb.): δ = ppm 2.32 (s, CH_3Ph, 3H), 5.20 (s, Cp, 5H), 6.93–8.02 (m, aromatic, 28H); $^{13}C\{^1H\}$ NMR (75.494 MHz, CD_3OD, T = amb.): δ = ppm 203.02 (t, $^2J_{CP}$ = 17.80 Hz, RuCO), 126.35–145.40 (m, aromatic), 90.86 (s, Cp); $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_3OD, T = amb.): δ = ppm 43.41 (s, *m*tppms).

3.2.3. Stability study of 4 in water

Complex **4** (10 mg, 0.01 mmol) was dissolved in 0.5 mL of water in a 5 mm NMR tube. The $^{31}P\{^1H\}$ NMR spectrum was recorded from 25 to 95 °C, in which temperature range it was not appreciably modified.

3.3. General procedure for catalytic isomerisation of allylic alcohols

Under an inert atmosphere the catalyst precursors (0.005–0.01 mmol, 0.5–1 mol%), the allylic alcohol (1 mmol) and 3 mL of deoxygenated Na-phosphate buffer of appropriate pH were introduced into a Schlenk tube. The mixture was then heated and rapidly stirred at the indicated temperature. The resulting mixture was cooled to room temperature and extracted by hexane, filtered on silica gel and subjected to gas chromatography. The indentity of the ketones was assessed by comparison with commercially available pure samples. The conversion of allyl alcohol was determined by ^{1}H NMR spectroscopy. Turnover frequencies were calculated from the yields of isomerized products obtained in the given reaction times (usually 0.5–1.0 h).

4. Conclusion

$Na_4[\{RuCl_2(mtppms)_2\}_2]$ (**1**), $Na_4[\{RuCl(\mu\text{-}Cl)(C{=}C{=}CPh_2)(mtppms)_2\}_2]$ (**2**), $Na_2[RuClCp(mtppms)_2]$ (**3**), and $Na[Ru(CO)Cp(mtppms)_2]$ (**4**) showed good to excellent catalytic activities (with turnover frequencies up to 2226 h^{-1}) in the transpositions of simple allylic alcohols in homogeneous aqueous solutions or in two-phase reactions. Replacement of chloride in **3** by a strongly bound CO led to a substantial drop in the catalytic activity which shows the need for an easy-to-substitute ligand for good catalytic activity. It is also essential to adjust the pH of the aqueous phase to its optimum value which for the above catalysts was found in the range of 4–7.

Acknowledgements

The authors are grateful for the financial support provided by the Junta de Andalucía (PAI), the Ministerio de Ciencia y Tecnología of Spain (MCYT) (Project CTQ2006-06552/BQU.MCRTN), the European Comission Research Directorate General Human Resources and Mobility (AQUACHEM Project; MRTN-CT-2003-503864), the European Cooperation in the Field of Science and Technology (COST) Actions D17 and D29, the Hungarian-Spanish Intergovernmental Collaboration in Science and Technology (TéT E-10/2005; HH2005-0001) and the Hungarian National Research and Technology Office – National Research Fund (NKTH-OTKA K 68482). T.C.-M. thanks the Ministerio de Asuntos Exteriores y de Cooperación – Agencia Española de Cooperación Internacional (MAE-AECI) for a predoctoral fellowship. W.W. is grateful for an AQUACHEM ER fellowship. The travel grants provided by COST Action D29 for M.F. and T.C.-M. are gratefully acknowledged.

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