

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

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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 $\text{Na}_4[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$ 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 $\text{Na}[\text{Ru}(\text{CO})\text{Cp}(\text{mtppps})_2]$ as well as $\text{Na}_4[\{\text{RuCl}(\mu\text{-Cl})(\text{C}=\text{C}=\text{CPh}_2)(\text{mtppps})_2\}_2]$ and $\text{Na}_2[\text{RuClCp}(\text{mtppps})_2]$ also showed good to excellent catalytic activities for redox isomerisations in aqueous systems at 50–80 °C under inert atmosphere.

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1. Introduction

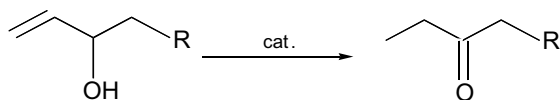
Catalytic isomerisation of allylic alcohols (e.g. Scheme 1) is an attractive strategy for the synthesis of saturated carbonyl compounds [1–4]. Such internal redox reactions (transpositions) show 100% atom economy and therefore much effort has been spent on the study of these processes following the seminal 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, $[\{\text{Ru}(\eta^3\text{-}\text{C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$ ($\text{C}_{10}\text{H}_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diy) catalysed the isomerisation of oct-1-en-3-ol in THF at 75 °C with a turnover frequency (TOF) as high as $62\,500\text{ h}^{-1}$ [$\text{TOF} = (\text{mol converted substrate})/(\text{mol catalyst})^{-1}\text{ h}^{-1}$] [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, $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_6\text{Me}_6)\}_2]$ [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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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 (*mtppps*-Na [19,20] and *mtppts*-Na₃ [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 *mtppps* (such as Na₄[[RuCl₂(*mtppps*)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, Na₃[RuHCl(*mtppps*)₃] and Na₃[RuH₂(*mtppps*)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(H₂O)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(η^3 -C₁₀H₁₆)(μ -Cl)Cl]₂] [12], [RuCl₂(η^6 -*p*-cymene){ κ -(*P*)-PPh_{3-*n*}(OCH₂CH₂NMe₃)_{*n*}}] [SbF₆]_{*n*} (*n* = 1, 2 or 3) [30], [RuCl₂(η^6 -*p*-cymene){ κ -(*P*)-PPh_{3-*n*}(OCH₂CH₂NMe₂)_{*n*}}] (*n* = 1,2 or 3) [30], [RuCl₂(η^6 -arene){P(CH₂OH)₃}] [31] and [RuCl₂(η^6 -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 Rh₂(SO₄)₃ and *mtppts*-Na₃ (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 Na₄[[RuCl₂(*mtppps*)₂]₂] (1), Na₄[[RuCl(μ -Cl)(C=C=CPh₂)(*mtppps*)₂]₂] (2), [42] and Na₂[[RuClCp(*mtppps*)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(*mtppps*)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 Na₄[[RuCl₂(*mtppps*)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 *mtppps*; the results are

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