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Evaluation of catalytic activity of [RuClCp(dmoPTA)(PPh_3)](OSO_2CF_3) in the isomerization of allylic alcohols in water (dmoPTA = 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane)

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ABSTRACT

The catalytic activity of [RuClCp(HdmoPTA)(PPh_3)](OSO_2CF_3) (**1**) and the dimeric complexes [RuClCp(PPh_3)-μ-dmoPTA-1κ*P*:2κ^2*N*,*N*'-MCl_2] (M = Ni (**2**), Co (**3**), Zn (**4**)) for the isomerization in water under Ar and ambient atmosphere of 1-octen-3-ol, 1-hepten-3-ol and 1-hexen-3-ol was investigated. A detailed study was devoted to the catalytic activity under Ar of **1** for the isomerization of 1-octen-3-ol.

1. Introduction

Metal complexes are useful catalysts for the isomerization of allylic alcohols under mild reaction conditions. This attractive reaction takes place via an enol-intermediate which irreversibly tautomerizes to a saturated carbonyl (Scheme 1) [1].

Large efforts have been done in the last years to develop a useful and general process to isomerise allylic alcohols in water [2] starting with the early work of McGrath and Grubbs using [Ru(H_2O)$_6$](tos)$_2$ (tos = *p*-toluenesulfonate) as catalyst [3]. Water is a universal solvent and provides important advantages over organic solvents: it is cheap, easily available, eco-benign, inflammable, etc. A few years ago we have targeted our research activity to the synthesis and characterization of aqua-soluble ruthenium complexes containing phosphines with possible biological [4] and catalytic properties in water [5,6].

Recently we have reported on the synthesis and catalytic activity of [RuCpCl(mPTA)$_2$](OSO_2CF_3)$_2$ and [RuCp(mPTA)$_2$(OH_2 − κ*O*)](OSO_2CF_3)$_2$ (Cp = η^5-cyclopentadienyl, mPTA = *N*-methyl-1,3,5-triaza-7-phosphaadamantane). These complexes can be obtained by easy synthetic procedures and display considerable solubility in water [6,7]. The favourable catalytic activity of [RuClCp(mPTA)$_2$](OSO_2CF_3)$_2$ for the isomerization of allylic alcohols in water was rationalized by the easy displacement of Cl^- by H_2O and the substrate molecule. Notwithstanding, in water the removal of chloride from [RuClCp(mPTA)$_2$](OSO_2CF_3)$_2$ required addition of AgOTf (OTf = $^-OSO_2CF_3$).

In contrast, in water at room temperature the parent complex [RuClCp(PTA)$_2$] exchanges the Cl by a water molecule affording the cationic complex [RuCp(PTA)$_2$(OH_2)]$^+$ in significant extension ($K_{eq} = 6.18 \times 10^{-4}$) [8].

We also showed that –despite of its lower solubility- the catalytic activity of [RuClCp(PTA)$_2$] in isomerization of allylic alcohols is higher than that of the analogous complexes containing mTPPMS and mPTA (mTPPMS = diphenylphosphinobenzene-3-sulfonic acid Na salt) [9].

The fact that a moderate water solubility of the metal complex does not hinder its catalytic application in aqueous media, allowed the investigation of [RuClCp(HdmoPTA)(PPh_3)](OSO_2CF_3) (**1**) (Scheme 2) [10] as catalyst in redox isomerisation of allylic

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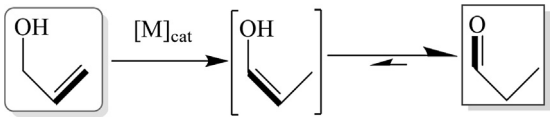
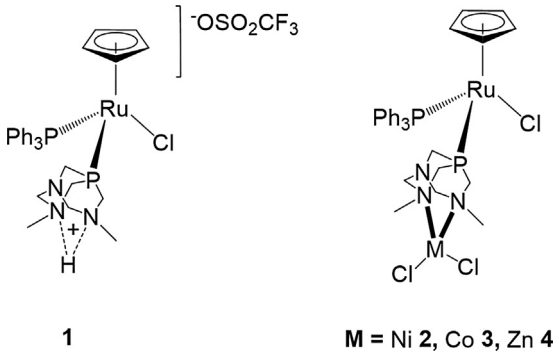


Scheme 1. Metal catalyzed isomerization of allylic alcohol.



1 **M = Ni 2, Co 3, Zn 4**

Scheme 2. Water soluble piano–stool ruthenium complexes.

alcohols. The favourable catalytic activity of this complex for the isomerization of 1-octen-3-ol in water urged us to study the catalytic properties of the bimetallic complexes [RuClCp(PPh_3)-μ-dmoPTA-1κ*P*:2κ^2*N*,*N*'-MCl_2] (M = Ni (**2**), Co (**3**), Zn (**4**)) (Scheme 2) [11], with the aim to distinguish the possible influence of the heterometal on the catalytic properties of the {CpRu} moiety.

2. Experimental

2.1. Materials and methods

All chemicals were reagent grade and, unless otherwise stated, were used as received from commercial suppliers. The reactions were performed in a pure argon atmosphere by using standard Schlenk-tube techniques with freshly distilled and oxygen-free solvents. The dimethyl-derivative of PTA (dmPTA), the complexes [RuClCp(PTA)(PPh_3)], [RuClCp(HdmoPTA)(PPh_3)](OSO_2CF_3) (**1**) and [RuClCp(PPh_3)-μ-dmoPTA-1κ*P*:2κ^2*N*,N'-MCl_2] (M = Ni (**2**), Co (**3**), Zn (**4**)) were prepared as described in the literature [10,11]. Appropriate amounts of $NaH_2PO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}7H_2O$ and $Na_3PO_4{\cdot}6H_2O$ were used to prepare 0.1 M solutions, and phosphate buffer solutions of the desired pH were obtained by mixing corresponding volumes of these solutions. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AV300 and AV500 spectrometers operating at 300.13 and 500.13 MHz (^{1}H), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet ($^{13}C\{^1H\}$). Chemical shifts for $^{31}P\{^1H\}$ NMR spectra were measured relative to external 85% H_3PO_4. Gas chromatographic measurements were made on a Hewlett-Packard HP 5890 Series II equipment using a Varian CP-Wax 52CB, 30 m, 0.32 mm, 0.25 m (CP884) column and FID, and on a Varian CP-3380 GC gas chromatograph equipped with a Factor Four VF23 capillary column and flame ionization.

2.2. Catalytic reactivity of the complexes *1–4* in water for the isomerization of 1-octen-3-ol

In a standard experiment, complex **1** (7.8 mg, 9.9×10^{-3} mmol) and the bimetallic complexes **2–4** (9 mg, 9.9×10^{-3} mmol) were dispersed in 4.5 mL of water with strong stirring before addition of 1-octen-3-ol (180 L, 1.17 mmol).

The resulting mixture was placed into a water bath at 80 °C controlled by a circulator; this was considered the starting time of the reaction. After the required time, the solution was cooled to room temperature in a water bath and extracted with $CHCl_3$ (2×2 mL). The chloroform extracts were combined and passed through $MgSO_4$ and Silica, and analysed by GC. Two sets of reactions were carried out for each catalyst either under nitrogen or an air atmosphere.

2.3. Isomerization of 1-octen-3-ol catalyzed by *1* in a mixture of MeOH/phosphate buffer

Complex **1** (6 mg, 7.60×10^{-3} mmol) was dissolved in 1.5 mL of a mixture of phosphate buffer (0.1 M, pH 6.75) and MeOH in variable proportions: 1.5/0, 1.2/0.3, 1.05/0.45, 0.9/1.1, 0.75/1.25 and 0/1.5 mL. In each experiment 1-octen-3-ol (80 μL, 5.18×10^{-1} mmol) was added and the reaction kept at 70 °C for 3 h. The final products were worked up and analyzed by the general procedure described above.

2.4. Isomerization of 1-octen-3-ol, 1-hepten-3-ol and 1-hexen-3-ol catalyzed by *1* as a function of pH

Complex **1** (6 mg, 7.6×10^{-3} mmol) was introduced into a mixture of 0.4 mL of MeOH and 1.6 mL of a phosphate buffer solution (0.1 M) in the pH range 1.85–9.00. Then 105 μL of 1-octen-3-ol (6.80×10^{-1} mmol), or 95 μL of 1-hepten-3-ol (6.96×10^{-1} mmol) or 82 μL of 1-hexen-3-ol (6.83×10^{-1} mmol), respectively, were added and the reaction mixture was kept at 70 °C for 1 hour and processed as indicated above

2.5. Isomerization of 1-octen-3-ol catalyzed by *1* as a function of reaction time at pH 2.75 and 6.77

In a Schlenk tube, complex **1** (6 mg, 7.6×10^{-3} mmol) was dissolved in a mixture of 1.6 mL of phosphate buffer (0.1 M, pH 2.75 or pH 6.75) and 0.4 mL of MeOH. 1-Octen-3-ol (105 μL, 6.80×10^{-1} mmol) was added and the reaction mixture was stirred at 70 °C. After the desired reaction time the resulting solution was cooled to room temperature and analysed as described above.

2.6. Conversion of isomerization as a function of 1-octen-3-ol / *1* molar ratio

Complex **1** (6 mg, 7.6 × 10–3 mmol) was dissolved in a mixture of 1.6 mL of phosphate buffer solution (0.1 M, pH 2.75) and 0.4 mL MeOH. Then at 70 °C 1-octen-3-ol was added (105, 210, 420 and 840 μL; 0.68, 1.36, 2.72 and 5.44 mmol, respectively; ranging from 0.34 to 2.72 M) and the reaction mixture was strongly stirred. After 3 h the resulting solutions were worked up as described above.

2.7. Study of the effect of chloride concentration on the isomerization of 1-octen-3-ol and 1-hepten-3-ol catalysed by *1* at pH 2.75

Isomerization of both allyl alcohols at three different NaCl concentrations were studied by the same procedure. Into a mixture of 1.6 mL of phosphate buffer (0.1 M, pH 2.75) and 0.4 mL of MeOH was added **1** (6 mg, 7.6×10^{-3} mmol), 1-octen-3-ol (105 μL, 6.80×10^{-1} mmol), or 1-hepten-3-ol (95 μL, 6.96×10^{-1} mmol) together with NaCl (0.0, 11.7 and 35.1 mg; 0.0, 2.0×10^{-1} and 6.0×10^{-1} mmol). The resulting mixture was stirred at 70 °C for 3 h, worked up and analysed by the procedure described above.

2.8. Study of the behaviour 1-4 in water at 70 °C

Complexes **1–4** (7 mg; 8.8×10^{-3} for **1** and 7.7×10^{-3} mmol for **2–4**) were placed into a 0.5 mm NMR tube with 0.5 mL of D_2O and kept at 80 °C. The solutions were checked by $^{31}P\{^1H\}$ NMR periodically. The dimeric complexes displayed two doublets at 49.8 ppm and 1.1 ppm ($^2J_{PP}$ = 50.9 Hz) which are similar to those for [RuClCp(dmoPTA)(PPh_3)], the parent deprotonated complex of **1**.

In contrast, the $^{31}P\{1H\}$ NMR spectrum of the solution of **1** showed also a doublet of doublets but at 46.6 ppm and −4.2 ppm ($^2J_{PP}$ = 42.5 Hz). All attempts to isolate the product were unsuccessful, in all the cases a mixture of compounds was obtained in which the main component was **1**. Nevertheless, the fact that **1** is not enough soluble in water to display a clear $^{31}P\{^1H\}$ NMR spectrum suggests that the obtained clear solution contained [Ru(H_2O)Cp(HdmoPTA)(PPh_3)]$^{2+}$, which formed by substitution of Cl^- in **1** by H_2O.

2.9. Study of the reaction between 1-octen-3-ol and *1* in water at 70 °C under air

Under air, complex **1** (3.5 mg, 4.4×10^{-3} mmol) was added into 0.75 mL of a mixture of D_2O/MeOD (4:1). Air was bubbled into the solution for 5 min and then the tube was soldered and kept at 70 °C. After 1.5 h the $^{31}P\{^1H\}$ NMR spectrum of the resulting solution showed the presence of almost one equivalent of $OPPh_3$ and a new product, which could not be isolated and characterized.

2.10. Reaction of *1–4* with $AgCF_3SO_3$ in D_2O

Into a 5 mm NMR tube were added the complexes **1–4** (7 mg; 8.8×10^{-3} for 1 and 7.7×10^{-3} mmol for **2–4**, respectively) in 0.5 mL of D_2O. At room temperature 1 eq. of $AgCF_3SO_3$ was added to the solution. Complex **1** was transformed quantitatively into a new compound that displayed two doublets at 46.1 ppm and 1.7 ppm ($^2J_{PP}$ = 46.1 Hz). Addition of the silver salt until 3 eq. did not produce further changes. Complexes **3–4** were transformed into **1** and new species when 3 eq. of $AgCF_3SO_3$ were added. In addition to **1** signals a couple of doublets appeared at 50.15 and 1.8 ppm for **2**, at 46.55 and −3.4 ppm for **3** and at 46.21 and −8.6 ppm for **4**.

3. Results and discussion

3.1. Catalytic activity of *1–4*

The catalytic activity of complexes **1** [10] and **2–4** [11] (*vide supra*, Scheme 2) were assessed initially for the isomerisation of 1-octen-3-ol in H_2O at 70 °C both under argon and ambient atmosphere at atmospheric pressure. The isomerization of 1-octen-3-ol usually is the standard reaction to check the possible catalytic properties of a metal complex for isomerization of allylic alcohols [12].

As shown in Fig. 1 the catalytic activity of **1** for the isomerization of 1-octen-3-ol is significantly larger than those for the heterodinuclear complexes **2–4**. We obtained 3-octanone as exclusive isomerization product for all the experiments.

Under argon the isomerization was not complete in the checked reaction time but under air complex **1** was able to fully isomerize 1-octen-3-ol in 3 h.

In identical reaction conditions in water, **1** showed comparable or higher catalytic activity for the redox isomerization of 1-octen-3-ol than the related water soluble complexes [RuClCp(mPTA)$_2$](OSO_2CF_3)$_2$, [RuCp(mPTA)$_2$(OH_2-O)](OSO_2CF_3)$_3$ [6], and [RuClCp(PTA)$_2$] [9].

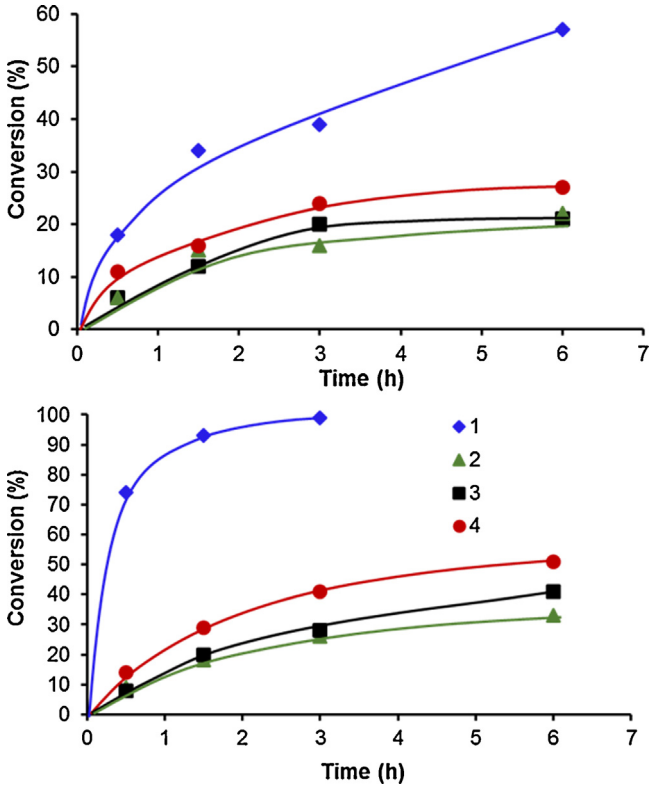


Fig. 1. Isomerisation of 1-octen-3-ol catalysed by the complexes **1–4**, under argon (upper graph) and ambient atmosphere (lower graph). Conditions: 7.8 mg **1** (9.9×10^{-3} mmol); 9 mg **2–4** (9.9×10^{-3} mmol), 180 μL (0.117 mmol) of 1-octen-3-ol; 4.5 mL H_2O, 80 °C.

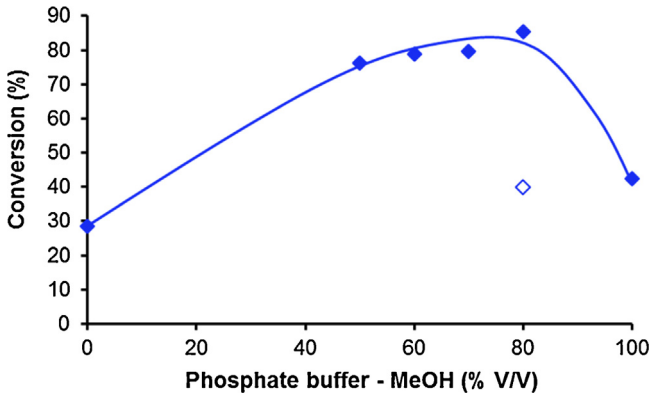


Fig. 2. Conversion of 1-octen-3-ol as a function of solvent composition. Conditions: 6 mg **1** (7.6×10^{-3} mmol), 80 μL 1-octen-3-ol (5.18×10^{-1} mmol), 70 °C, Ar, 3 h reaction time, 1.5 mL 0.1 M buffer/MeOH (4:1 v/v) pH 6.75, (solid diamond) or 1.5 mL H_2O/MeOH (4:1 v/v) (empty diamond).

3.2. Study of the catalytic activity of *1* for the isomerization of 1-octen-3-ol under Ar in H_2O-MeOH mixtures

Isomerization of 1-octen-3-ol was also studied under argon atmosphere in water-methanol mixtures in which complex **1** and the substrate are mostly soluble [10].

The catalytic isomerization of 1-octen-3-ol by **1** was carried out at 70 °C for 3 h in different mixtures of phosphate buffer/MeOH. In pure methanol the observed conversion at 70 °C was 28.5% (Fig. 2) which is significantly lower than the observed conversion in buffer (42.5%). However, as shown on Fig. 2, **1** displays an increasing catalytic activity for the isomerization of 1-octen-3-ol depending on the percentage of aqueous buffer solution added to the reac-

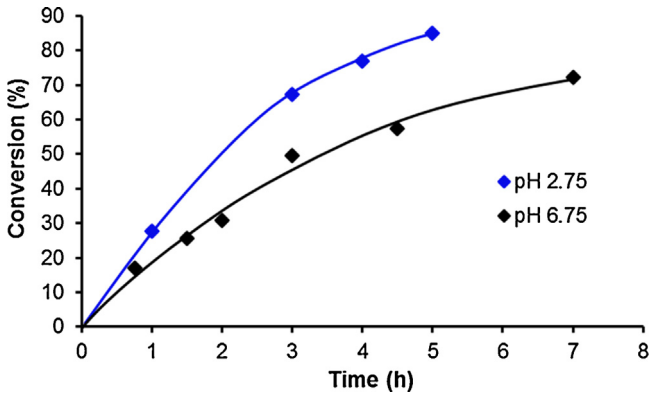


Fig. 3. Isomerization of 1-octen-3-ol catalyzed by **1** at pH 2.75 and 6.75. Conditions: 6 mg **1** (7.6×10^{-3} mmol), 105 μL of 1-octen-3-ol (6.80×10^{-1} mmol), 70 °C, 1.6 mL 0.1 M buffer/methanol (4:1v/v), Ar atmosphere.

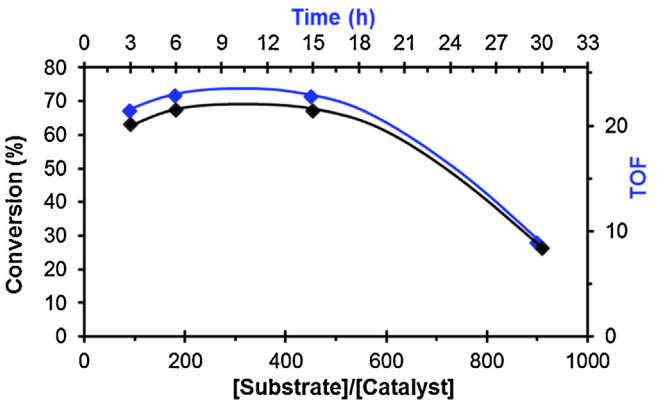


Fig. 4. Conversion of 1-octen-3-ol as a function of the substrate/**1** ratio (black-solid diamond) and TOFs vs. time (blue-solid diamond) for the corresponding experiments. Conditions: 6 mg **1** (7.6×10^{-3} mmol), 105, 210, 420 and 840 μL of 1-octen-3-ol (0.68, 1.36, 2.72 and 5.44 mmol), 70 °C, 2 mL 0.1 M phosphate buffer/methanol (4:1 v/v), pH 2.75, Ar atmosphere.

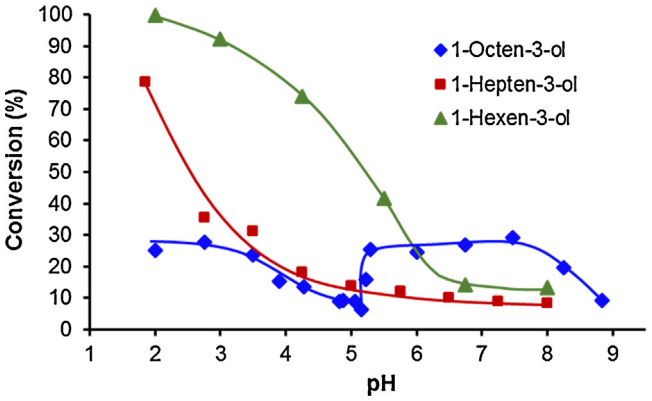


Fig. 5. Isomerization of 1-octen-3-ol, 1-hepten-3-ol,and 1-hexen-3-ol as a function of the pH.Conditions: 6 mg **1** (7.6×10^{-3} mmol), 105, 95 and 82 μL (0.68, 0.70, and 0.68 mmol) of 1-octen-3-ol,1-hepten-3-ol,and 1-hexen-3-ol, respectively, 70 °C, 2 mL 0.1 M phosphate buffer/MeOH (4:1 v/v),), Ar atmosphere, 1 h.

tion media, with the largest conversion (85.5%) obtained with a 4:1 (v/v) mixture of phosphate buffer/MeOH. The similar reaction but carried out in (unbuffered) H_2O/MeOH (4:1 v/v) provided isomerization with only 40% conversion. Note, however, that in H_2O/MeOH (4:1 v/v) the substrate 1-octen-3-ol dissolves only partially. Consequently, the presence of the ionic buffer affects both the solubility of the substrate and the catalyst.

Fig. 2 suggests that water is not only a suitable solvent for the reaction, but it is beneficial for high yields of isomerization as shown by the increasing trend in conversion with the water percentage. However, in pure buffer the conversion drops because at such solvent compositions 1-octen-3-ol and **1** dissolves only partially into the reaction mixture. This fact also indicates that the acid proton (*vide supra*, Scheme 2) of the ligand HdmoPTA may have some influence on the reaction since in water this proton could be released easily [10]. This possibility was evaluated in mixtures H_2O/MeOH (4:1 v/v, both unbuffered and buffered at pH 6.75). The obtained data show a 50% drop of the activity in a MeOH/H_2O (unbuffered) mixture (empty dot, Fig. 2).

This result contrasts the findings obtained with $[RuClCp(mPTA)_2]^{2+}$ and $[RuClCp(PTA)_2]$ as catalysts for the same reaction: in phosphate buffer there were notably lower conversions than in water (4 vs 22% and 40 vs. 90%, respectively). This latter behaviour was rationalized by the interaction of the phosphate ions with the ruthenium, hindering an effective interaction of the allylic alcohol with the catalyst and therefore leading to smaller conversions in isomerization of 1-octen-3-ol [6,9]. Therefore, the fact that complex **1** isomerizes 1-octen-3-ol faster in MeOH/buffer than in MeOH/H_2O, supports our suggestion that pH could strongly influence the isomerization processes catalysed by **1**.

On the basis of the results discussed in this section, for the following experiments we used as standard reaction conditions the parameters leading to the largest isomerization conversion of 1-octen-3-ol by 1 under Ar (i.e., phosphate-buffer/MeOH (4:1 v/v), 70 °C).

3.3. Influence of the pH on the isomerization of 1-octen-3-ol catalysed by 1 under Ar

Previous publications on the catalytic isomerization of allyl alcohols in water showed the significant influence of the pH of the medium on the resulting conversion into the corresponding ketone [6,9]. The isomerization of 1-octen-3-ol catalysed by **1** was studied at pH 6.75 and 2.75 (Fig. 3). At pH 6.75 a 72.3% conversion of 1-octen-3-ol was found after 7 h while at pH 2.75 the conversions were 67.2% at 3 h and 85.0% at 5 h. The data on Fig. 3 clearly support the influence of the pH on the isomerization of 1-octen-3-ol catalysed by **1**.

The effect of the substrate/catalyst concentration ratio on the redox isomerization of 1-octen-3-ol catalysed by **1** at pH 2.75 was also studied (Fig. 4). According to Fig. 4, 1 equivalent of **1** is able to isomerize 71.3% of 1-octen-3-ol with a substrate/1 ratio of 450. This corresponds to a turnover number TON = 320 in 17 h (TOF = 21.4 h^{-1}). With an S/C ratio of 900, 28% conversion was detected in 30 h (TON = 252, TOF = 8.4 h^{-1}). Accordingly, the catalyst is quite stable under the reaction conditions, however, high substrate loadings result in lower catalytic activities.

3.4. Influence of the pH on the isomerization of 1-octen-3-ol, 1-hepten-3-ol and 1-hexen-3-ol catalyzed by 1 under Ar

The isomerization of 1-octen-3-ol, 1-hepten-3-ol, 1-hexene-3-ol catalysed by **1** was studied as a function of the pH at the reaction conditions optimized for 1-octen-3-ol (see Section 3.2). The conversions determined at 1 h (Fig. 5) shows that complex **1** displays a different catalytic activity for each of the three allylic alcohols; similar observations were already made for related complexes [6,9]. The conversions at 1 h also show significant dependence on the pH.

In acidic solutions, high conversions were determined for 1-hepten-3-ol (78.6% at pH 1.85) and for 1-hexen-3-ol (99.9% at pH 2), which strongly decreased with increasing pH. In contrast, the catalytic isomerization of 1-octen-3-ol is moderately dependent on

the pH. In acidic solutions (pH 2–3.5) the conversion was around 24-28%, which dropped to 6.4% at pH 5.15. Further small increase of the pH brought about a sharp increase in conversion (25.5% at pH 5.3).

The conversion then remained fairly constant until pH 7.5 and then -with increasing basicity- fell to the same level as observed with 1-hexene-3-ol and 1-hepten-3-ol.

At the moment we do not have a clear explanation for the different response of the reaction outcomes to the changes in the pH of the reaction mixture in the case of the three related allyl alcohol substrates. It can be assumed that in the middle pH range the monoprotonated complex is dominant and this may interact with the anionic components of the phosphate buffer similar to the case of $[RuCpCl(mPTA)_2](CF_3SO_3)_2$ [6]. However, the different solubility of the substrates in the catalyst-containing buffer phase at different pH may also influence the reaction rates.

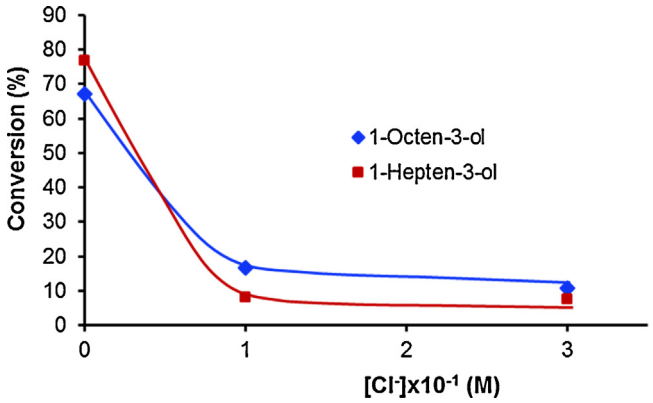


Fig. 6. Effect of the chloride concentration on the isomerization of 1-octen-3-ol and 1-hepten-3-ol catalyzed by **1**, under argon atmosphere. Conditions: 6 mg **1** (7.6×10^{-3} mmol), 105 μL 1-octen-3-ol (6.80×10^{-1} mmol) and 95 μL 1-hepten-3-ol (6.96×10^{-1} mmol), 70 °C, 2 mL 0.1 M buffer/methanol (4:1 v/v), pH 2.75.

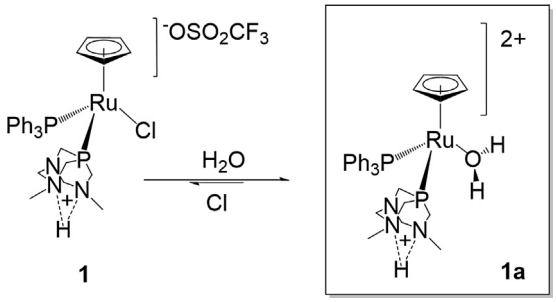
3.5. Catalytic isomerization mechanism

Our previously published results [6,9] on the isomerization of allylic alcohols catalyzed by water soluble piano-stool ruthenium complexes [RuCpClLL'] (L, L' = water-soluble phosphine) suggested that the real catalytic species is not the starting complex but a new one obtained by substitution of the chloride anion bonded to the ruthenium by a molecule of water. The allylic alcohol is able to replace easily the water molecule, starting the catalytic isomerization process (Scheme 3).

This mechanistic suggestion was supported, among others, by the experimental results disclosed in [6,9] on the substitution of the H_2O ligand by phosphate. Since coordinated phosphate is not as easily replaced by the allylic alcohol as water, the catalytic process may be hindered or stopped by phosphate (or by any of H_2PO^{4-}, HPO_4^{2-}at a given pH).

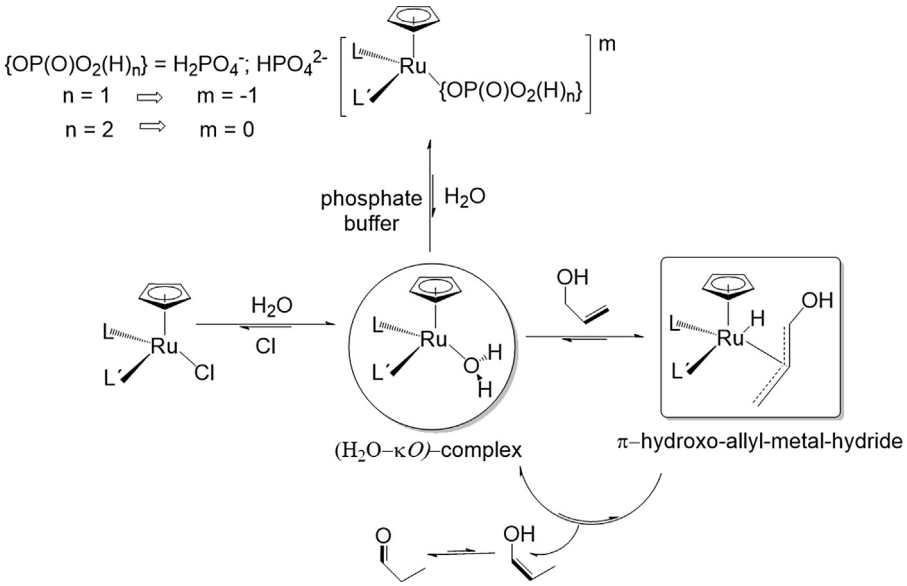
However, in the present work, in contrast to the expectations, a positive influence (relative to pure water) of the phosphate buffer (pH 6.75) was observed on the isomerization of 1-octene-3-ol catalysed by **1**.

The $^{31}P\{^1H\}$ NMR spectra of complex **1** did not significantly change at 70 °C in phosphate buffer. Nevertheless, the presence of chloride in the reaction media produced a clear and significant reduction of the isomerization of 1-octen-3-ol and 1-hepten-3-ol catalysed by **1** (Fig. 6).

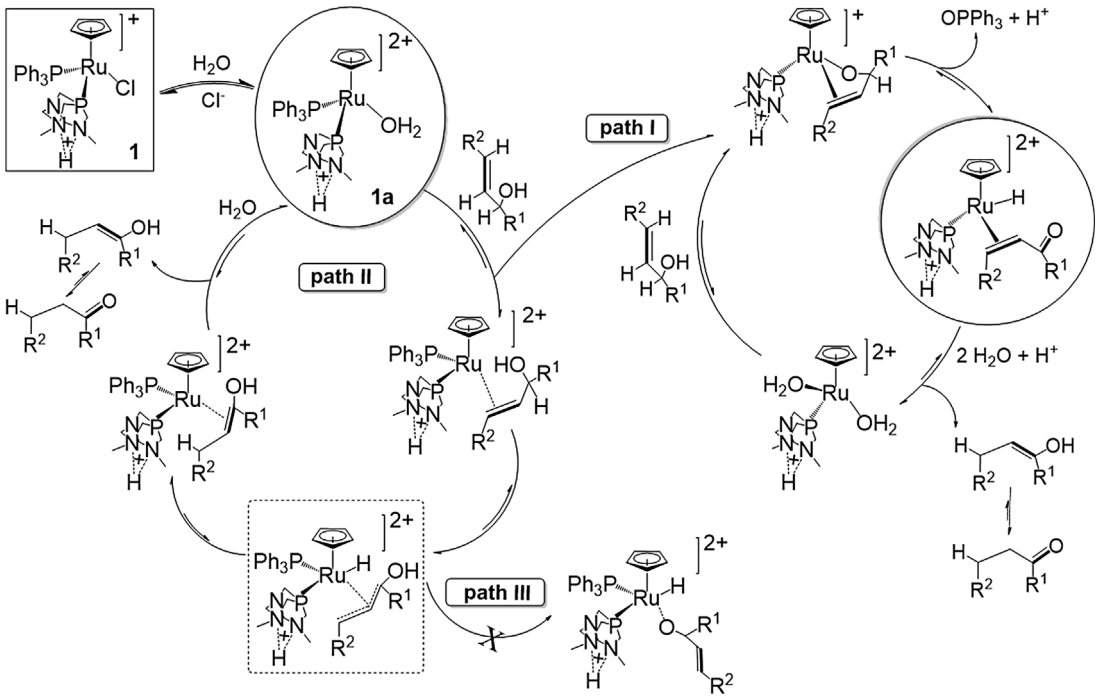


Scheme 4. Replacement of Cl^- by H_2O in **1** providing the probable catalytically active species $[Ru(OH_2-\kappa O)Cp(HdmoPTA)(PPh_3)]^{2+}$**(1a)** for the isomerization of allylic alcohols.

Consequently, we assume that prior to the catalytic isomerization of the allylic alcohol complex **1** undergoes substitution of its Cl^- by a H_2O molecule, providing the real catalytic species, probably $[Ru(OH_2\text{-}^{*}O)\ Cp(HdmoPTA)(PPh_3)]^{2+}$ (**1a**) (Scheme 4).



Scheme 3. Proposed intermediate species in the isomerization of allylic alcohols catalyzed by water soluble piano–stool ruthenium complexes [RuCpClLL'] (L, L' = water soluble phosphine.



Scheme 5. Proposed mechanism for the isomerization of allylic alcohols catalysed by **1** including the dissociation of a PPh_3 ligand as $OPPh_3$.

These results also suggest that the low catalytic activity observed for **2–4** for the isomerization of 1-octen-3-ol in H_2O at 70 °C could be the consequence of the transformation of these complexes into non-catalytic species. The study of the behaviour of **2–4** in water at 70 °C by NMR showed that these complexes decompose to give [RuClCp(dmoPTA)(PPh_3)] by elimination of the {MCl_2} moiety (M = Ni, Co, Zn). As a result, under the isomerization reaction conditions there is free Cl^- in the reaction media, which could hinder formation of the active catalytic species **1a** (Scheme 4).

Therefore, to evaluate the effect of a heterometal on the {CpRu(dmoPTA)(PPh_3)} moiety in catalytic isomerization of allylic alcohols, synthesis of new bimetallic complexes is necessary, which do not eliminate the heterometal under isomerization reaction conditions.

The obtained results suggest also that the most probable mechanism for the catalytic isomerization of the studied allylic alcohols by **1** is similar to that previously proposed for [$RuCpCl(PTA)_2$] [9]. (Scheme 5) but without including the influence of the phosphate buffer.

The large catalytic activity observed in presence of air is explained by the fact that under oxygen the PPh_3 in **1** is eliminated as oxide, which was observed by $^{31}P\{^1H\}$ NMR. In this way an additional coordination position is created which can facilitate a more efficient catalytic isomerization (path I, Scheme 5). In this case the allylic alcohol is chelated to the metal and the β-hydride elimination from the coordinated alkoxide is possible, leading to an active enone-hydride complex. Migration of the hydride then yields the active π-oxo-allyl-metal species, which upon protonation releases the enol. The enol then tautomerizes to the carbonyl derivative.

Under argon, the complex including a coordinated η^2-allylic alcohol on the metal is obtained by substitution of OH_2 formed in a previous step by replacing the Cl^- anion in **1** by a water molecule.

The migration of the hydrogen linked to the carbinol-center to the metal gives rise to a π-hydroxo-allyl-metal-hydride (path II). Therefore, the possible incorporation of a hydride ligand into the hydroxo-allyl ligand leads to a η^2-enol complex that generates the starting catalytic species and the carbonyl compound through the tautomerization of the previously formed enol.

The alternatively associative mechanism (path III) should be improbable for complex **1**, since the close dmoPTA-H^+ should react easily with the H, hindering this path. A possible evidence for supporting this assumption could be the fact that complex **1** displays a large catalytic activity in buffered aqueous solutions, however, additional experiments are needed to clarify the fine details of the reaction mechanism.

4. Conclusions

We have explored the catalytic properties of a series of piano-stool Ruthenium(II) complexes, [RuClCp(HdmoPTA)(PPh_3)](OSO_2CF_3) (**1**) and the related dimeric complexes [RuClCp(PPh_3)-μ-dmoPTA-1κ*P*:2κ^2*N*,*N*'-MCl_2] (M = Ni (**2**), Co (**3**), Zn (**4**)) in the isomerization of 1-octen-3-ol, 1-hepten-3-ol and 1-hexen-3-ol in water. Complex **1** is more active for the isomerization of allylic alcohols in water than **2–4** both under air and Ar atmosphere. In contrast to the behaviour previously observed for [RuClCp(mPTA)$_2$](OSO_2CF_3)$_2$, [RuCp(mPTA)$_2$(OH_2-O)](OSO_2CF_3)$_3$ and [RuClCp($PTA)_2$], complex **1** displays a higher catalytic activity for the isomerization of 1-octen-3-ol in phosphate buffer than in water. The possible coexistence of two different catalytic cycles both useful for the isomerization of allylic alcohols under air but only one of those operating under Ar could explain the larger catalytic activity observed under air. In any case, the active species is not complex **1** itself but the corresponding aqua complex [Ru(OH_2-κ*O*) Cp(HdmoPTA)(PPh_3)]$^{2+}$ (**1a**), which is generated in aqueous solution by the substitution of the Cl^- anion in **1** by a water molecule.

Complexes **2–4** decompose under the catalytic reaction conditions by elimination of the {MCl_2} (M = Ni, Co, Zn) moieties with release of Cl^-, which, in turn, hinders the formation of the catalytically active aqua species. Further studies are needed to synthesize new bimetallic piano-stool complexes containing dmoPTA to determine the heterometal-effect on the catalytic properties of the [Ru(OH_2-κ*O*)Cp(HdmoPTA)(PPh_3)]$^{2+}$ moiety, which are in progress in our laboratories.

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