

Dalton Transactions

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: F. Scalambra, M. Serrano-Ruiz and A. Romerosa, *Dalton Trans.*, 2017, DOI: 10.1039/C6DT04262G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Water and catalytic isomerization of linear allylic alcohols by $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2]^+$ (PTA = 1,3,5-triaza-7-phosphaadamantane)

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Franco Scalambra,^a Manuel Serrano-Ruiz^a and Antonio Romerosa*^a

The new water soluble complex $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2]^+$ (**1**) (PTA = 1,3,5-triaza-7-phosphaadamantane) has been synthesized and fully characterized by NMR and IR. The crystal structure of **1**(CF₃SO₃)₃·3.5H₂O was characterized by single crystal X-ray determination. The catalytic activity of this complex was evaluated for the isomerisation of linear allylic alcohols from 3-buten-2-ol to 1-octen-3-ol into the correspondent ketones under both inert and air atmosphere, using as solvent: water, the substrate, mixtures of water/substrate, MeOH and mixtures of MeOH/water. An isomerization experiment on a mixture of all the studied allylic alcohols was also carried out.

Introduction

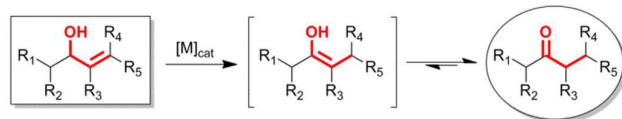
The catalytic redox-isomerization of allylic alcohols mediated by metal complexes constitutes an useful, easy and shorter synthetic route to carbonyl compounds (Scheme 1),¹ which are very important compounds in organic chemistry. The carbon-carbon double bond conversion into the corresponding enolate or enol, which finally tautomerizes to the carbonyl compound, is 100 % atom efficient. The non catalytic isomerization process needs protection-deprotection steps, high reaction temperatures and oxidizing reagents, which are costly and toxic. The best known efficient catalytic systems are based on second and third row metal complexes of ruthenium, rhodium, platinum, palladium and iridium.² Water is the most abundant and accessible solvent on Earth, easily recyclable and therefore very convenient for being used in chemical industry. Therefore, the development of metal-catalyzed allylic alcohols isomerization processes in water under mild reaction conditions is especially attractive. The early work of McGrath and Grubbs using $[\text{Ru}(\text{H}_2\text{O})_6](\text{OTs})_2$ (OTs = p-toluenesulfonate) as catalyst³ started a long-lasting effort to develop a useful and general process to isomerise allylic alcohols in water.⁴ There are, however, several problems to be solved, one of the most

important of which is the insolubility in water of active metal catalysts and organic compounds. Several strategies have been proposed to address these issues, such as the use of water-soluble phosphines as ligands for obtaining water soluble catalytically-active metal complexes.⁵ In water and in biphasic water/organic-solvent systems, the organic reactant interacts with the catalyst to provide the final products that can easily be isolated from the reaction medium.⁶

In the last years we focused our main research activity on the synthesis and study of hydrosoluble metal complexes, mainly with ruthenium, containing water-soluble phosphines. The complexes we have obtained show antiproliferative activity,⁷ optical properties,⁸ and catalytic activity,^{9,10} particularly for the isomerization of allylic alcohols in water under mild conditions.¹¹ The complex $[\text{RuClCp}(\text{PTA})_2]$ was found to be especially interesting as it is easy to synthesize, soluble and stable in water, even if not as much as its parent complexes containing mTPPMS (diphenylphosphinobenzene-3-sulfonic Na salt) and mPTA (N-methyl-PTA).¹² This complex does however exhibit a significantly higher catalytic activity for the isomerization of allylic alcohols compared to its parent complexes. The catalytic properties of $[\text{RuClCp}(\text{PTA})_2]$ depend on its equilibrium with $[\text{RuCp}(\text{PTA})_2(\text{OH}_2)]^+$ (**1**) in water ($K_{\text{eq}} = 6.18 \cdot 10^{-4}$)¹³ in contrast with $[\text{RuClCp}(\text{mPTA})_2]^{2+}$ and $[\text{RuClCp}(\text{mTPPMS})_2]$.^{2-9,11} In fact, complex **1** was proposed to be the real catalytic active species.¹² The lower activity in isomerization of allylic alcohols in water by ruthenium complexes containing mPTA and mTPPMS can however also be explained by other, less evident, reasons.

J. Gimeno, A. Lledos et al. speculated that the excellent catalytic properties of hydrosoluble ruthenium(IV) bifunctional complexes containing pyrazole-based ligands is due to the active participation of water in the catalytic process.¹⁴ DFT studies suggest that putative bifunctional catalytic species forming aqua complexes are involved in the process, which

Scheme 1. Metal catalyzed isomerization of allylic alcohols



^a Área de Química Inorgánica-CIESOL, Facultad de Ciencias, Universidad de Almería, Almería, Spain; Fax: +34 950015008; E-mail: romerosa@ual.es

^c Electronic Supplementary Information (ESI) available: Material and methods, synthesis, NMR and IR spectra, and crystallographic data. See DOI: 10.1039/x0xx00000x

ARTICLE

Journal Name

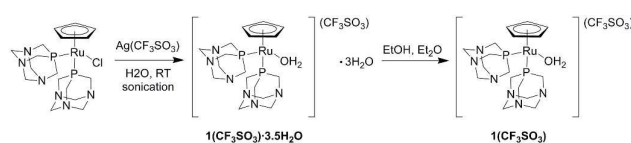
explains the observed large activity and general catalytic properties. Water can coordinate the metal but can also participate in proton-transfer processes and interacts with the N atom of the amine coordinated to the metal, promoting stable intermediate species. This argument stresses the important role of cooperating ligands (pyrazole and water in the Gimeno's paper¹⁴) in catalysis. Despite these interesting results, the effect of possible multiple water-coordinated complexes and the interactions of water with other sites of the species implicated in the catalytic processes have not been discussed.

In this paper we describe a robust synthetic route to **1**(CF₃SO₃)-3.5H₂O, which can provide this complex in large scales. With enough amount of pure catalytically active specie available, a systematic study on how the catalytic isomerization of allylic alcohols from 3-buten-2-ol to 1-octen-3-ol into the corresponding ketones has been carried out at different temperatures, under air and N₂ atmosphere, using either water or the allylic alcohol itself as solvents, mixtures of water/allylic alcohol, MeOH and mixtures of MeOH/water. Our results provide crucial new information on the involvement of water molecules in these isomerization reactions.

Results and discussion

The complex **1**(CF₃SO₃)-3.5H₂O was synthesized (Supplementary Information (S.I.)) by reaction of [RuClCp(PTA)₂] with Ag(CF₃SO₃) in water and the anhydrous complex **1**(CF₃SO₃) by recrystallization under nitrogen atmosphere from dry EtOH (Scheme 2). The NMR spectra of both compounds are the same and in agreement with the composition of **1**. The ³¹P{¹H} NMR in water displays a singlet with the same chemical shift to that observed when [RuClCp(PTA)₂] is dissolved in water at pH = 7, which was proposed to belong to the product of substitution of the Cl by a water molecule.¹³ While in water the aqua-complex is the only observed specie, in ¹⁹F{¹H} NMR (S.I.) only one singlet ascribable to uncoordinated OTf is found, its ³¹P{¹H} and ¹⁹F{¹H} NMR spectra in CD₂Cl₂ (S.I.) show that in organic solvent the water ligand is partially exchanged by a triflate anion. The composition of **1** was finally confirmed by single crystal X-ray diffraction (NMR and IR spectra and X-ray data on S.I.) structural determination. Both compounds are highly soluble in water (S_(H₂O)25°C = 2 g/mL) but also soluble in organic solvents such as EtOH, CHCl₃, CH₂Cl₂ and THF, but also in the studied allylic alcohols. Both complexes in the solid state are stable under inert atmosphere for months but under air atmosphere decompose in 10 days. The decomposition is

Scheme 2 Synthesis of **1**(CF₃SO₃)-3.5H₂O and **1**(CF₃SO₃).



faster in water solution: under air atmosphere the complexes

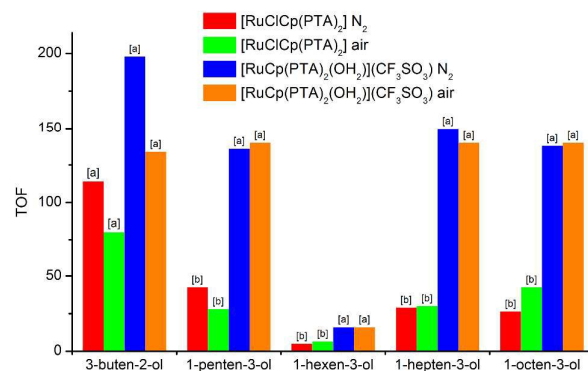


Figure 1. Comparison between the turn over frequencies of **1**(CF₃SO₃)-3.5H₂O and [RuClCp(PTA)₂] in the isomerization of allylic alcohols from 3-buten-2-ol to 1-octen-3-ol. Reactions carried out in H₂O at 80°C, 2 h reaction time. [a] TOF values obtained in this work; [b] TOF values adapted from ref 12.

decompose in two days at room temperature and in 2 h at 80 °C, but need more than 1 month under N₂ at room temperature and 7 days at 80 °C.

Complex **1** was proposed to be the real catalytic active specie for the isomerization in water of the allylic alcohols from 1-octen- to 1-penten-3-ol when complex [RuClCp(PTA)₂] was used as catalyst.¹² This assumption is confirmed by the fact that complex **1** catalyses the conversion of the allylic alcohol only to the ketone significantly better than its precursor [RuClCp(PTA)₂] (Figure 1).

The complex **1** in water is able to isomerize almost 100 eq. of 3-buten-2-ol in 1.5 h. at 40 °C, but needs higher temperatures, and 5 h to isomerize 100 eq. of allylic alcohols from 1-penten-3-ol to 1-octen-3-ol (Figure 2). The complex [RuClCp(PTA)₂] is not able to produce the full conversion of the substrate under the same conditions.¹² The conversion yields (%) under N₂ and air and the corresponding TOF as well as the reaction temperature for all the studied allylic alcohols at 5 h. are summarized in Table 1. The reaction time at which the conversion of 100 eq. of every allylic alcohol was reached at the lowest temperature was 5 h, being this the time used for the comparative study.

The first conclusion obtained from the analysis of the results summarized in Table 1 is that the temperature and atmosphere required to obtain the total isomerization are not apparently correlated with the size of the allyl alcohol: 3-buten-2-ol, 1-penten- and 1-hepten-3-ol are nearly completely converted to the corresponding ketone under N₂ but the conversion of 1-hexen-3-ol was only of 45 %. In contrast under air the conversions of 3-buten-, 1-penten- and 1-hepten-3-ol are below 40 % but for 1-hexen-3-ol is almost the 100 %.

Figure 2 Isomerization (%) of allylic alcohols from 3-buten-2-ol to 1-octen-3-ol vs. reaction time catalysed by complex **1**(CF₃SO₃) (1 mol %) in water (red line = air; black line = N₂). Water/substrate molar ratio = 222.

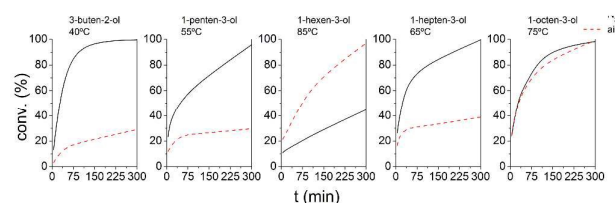


Table 1 Conversion (%) in water of allylic alcohols from 3-buten-2-ol to 1-octen-3-ol into the corresponding ketone catalysed by $1(\text{CF}_3\text{SO}_3)\cdot 3.5\text{H}_2\text{O}$ (1 mol%) in 5h with a water/substrate molar ratio = 222.

Substrate	Product	T [°C]	Yield [%] (TOF [h ⁻¹])	
			N ₂	Air
3-buten-2-ol	butanone	40	>99 (>19.8)	29 (14.5)
1-penten-3-ol	3-pentenone	55	96 (19.2)	30 (6)
1-hexen-3-ol	3-hexanone	85	45 (9)	97 (19.4)
1-hepten-3-ol	3-heptanone	65	>99 (>19.8)	39 (7.8)
1-octen-3-ol	3-octanone	75	98 (19.6)	>99 (>19.8)

The 1-octen-3-ol is similarly converted both under air and N₂. The temperature required for the total conversion of 3-buten-2-ol, 1-penten-3-ol and 1-hepten-3-ol is below 65 °C but the 1-hexen-3-ol requires 85 °C and 75 °C the 1-octen-3-ol.

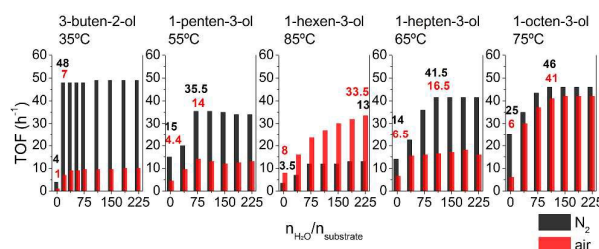
Table 2 Conversion (%) in water of allylic alcohols from 3-buten-2-ol to 1-octen-3-ol into the corresponding ketone catalysed by $1(\text{CF}_3\text{SO}_3)\cdot 3.5\text{H}_2\text{O}$ (0.1 mol%) in 4 and 24 h, under N₂ and air. Water/substrate molar ratio = 22.

Substrate	Product	T [°C]	t [h]	Yield [%] (TOF [h ⁻¹])	
				N ₂	Air
3-buten-2-ol	butanone	40	4	2 (5)	1 (2.5)
			24	14 (5.8)	8 (3.3)
1-penten-3-ol	3-pentanone	55	4	3 (7.5)	1 (2.5)
			24	31 (12.9)	3 (1.3)
1-hexen-3-ol	3-hexanone	85	4	3 (7.5)	32 (80)
			24	9 (3.8)	>99 (>41)
1-hepten-3-ol	3-heptanone	65	4	26 (65)	13 (32.5)
			24	60 (25)	33 (13.8)
1-octen-3-ol	3-octanone	75	4	18 (45)	6 (15)
			24	51 (21.3)	16 (6.6)

As indicated previously, the complex $1(\text{CF}_3\text{SO}_3)\cdot 3.5\text{H}_2\text{O}$ is soluble in water and organic solvent and therefore it was not possible to run recycling experiments in a biphasic reaction system. Isomerization reactions of 1000 eq. of allylic alcohols with 1 eq. of catalyst under both N₂ and air (0.1 mol% catalyst) at the temperatures used with 1 mol% catalyst (Table 2), showed that only the 1-hexen-3-ol is completely isomerized after 24 h but under air, followed by 1-hepten-3-ol under N₂ (60 %). These results suggest that under air the active catalyst could be different than under N₂, which is in agreement with the stability observed for **1** under air and N₂.

Several experiments were made to determine whether the presence of water in the reaction media is mandatory and which amount of water is needed for the catalytic isomerization process. The complex $1(\text{CF}_3\text{SO}_3)$, without crystallization water, was synthesized (S.I.) to accomplish these experiments. This complex dissolves in organic solvents, but also in allylic alcohols with no need of co-solvents. The isomerization conversion was studied at the same temperatures than in water but at 2 h, time in which approximately half of the conversion was observed. The first result showed that without water the rate of isomerization is significantly lower than that found with a large amount of water (Figure 3), but the conversion trend observed for each allylic alcohol under air and N₂ atmosphere is in general similar. Nevertheless, the highest TOF observed was 24 h⁻¹ for the isomerization of 1-octen-3-ol under N₂ at 75 °C (Table 3), quite different to that obtained in water (Table 2). It is particularly interesting to stress that the TOF for the isomerization of 3-buten-2-ol is so low as 5 h⁻¹ under N₂. Newly the 1-hexen-3-ol is isomerized better under air than under N₂ in contrast with those observed for the rest of the allylic alcohols. At least a water molecule is always present in the reaction as the catalyst must release it by exchange with the substrate.

The presence of water in the reaction medium increases significantly the conversion of all the studied substrates, but this improvement is not linear and after adding a minimum amount required to speed up the reaction, further additions of water have only a minor influence (Figure 3). Moreover the amount of water required is different for each of the studied allylic alcohols and in all cases it is larger than that required if a stoichiometric intervention of the water in the catalytic cycle is considered, as proposed by Gimeno.^{14,16} We notice, in particular, that the catalytic isomerization of 3-buten-2-ol improves its TOF from 4 to 48 when the molar fraction of

Figure 3. TOF of the catalytic isomerization of 3-buten-2-ol to 1-octen-3-ol by $1(\text{CF}_3\text{SO}_3)$ (1 mol %) vs. molar fraction of water at the lowest best reaction temperature at 2 h reaction time under N₂ and air.

ARTICLE

Journal Name

Table 3. TOF of the catalytic isomerization of 3-buten-2-ol to 1-octen-3-ol by **1** (CF_3SO_3) (1 mol %) vs. molar ratio of water/allylic alcohol at the lowest best reaction temperature at 2 h reaction time under N_2 and air.

Substrate	Product	T [°C]	t [h]	$n_{\text{H}_2\text{O}}/n_{\text{sub}}^{[a]}$	TOF [h^{-1}]	
					N_2	Air
3-buten-2-ol	butanone	40	2	0	4	1
				18.5	48	7
				222.2	49.5	10
1-penten-3-ol	3-pentanone	55	2	0	15	4
				74.1	35	14
				222.2	34	13
1-hexen-3-ol	3-hexanone	85	2	0	3	8
				74.1	12	23
				222.2	13	34
1-hepten-3-ol	3-heptanone	65	2	0	14	7
				74.1	36	16
				222.2	41	16
1-octen-3-ol	3-octanone	75	2	0	24	6
				111.1	46	42
				222.2	46	41

water vs. the allylic alcohol is increased to 18.5 (Table 3).

A similar experiment was performed using MeOH as solvent (Figure 4), to determine whether also in other solvents the isomerization reaction is influenced by the presence of water. The results show that the presence of a minimum amount of water remains important, even if the overall effect of water may differ slightly from what is observed when only the substrate species is used as solvent.

Catalytic isomerization mechanism.

The catalytic properties of **1** differ from those of $[\text{RuClCp}(\text{PTA})_2]$ in (1) higher catalytic activity, (2) temperature needed for the total isomerization conversion, (3) the

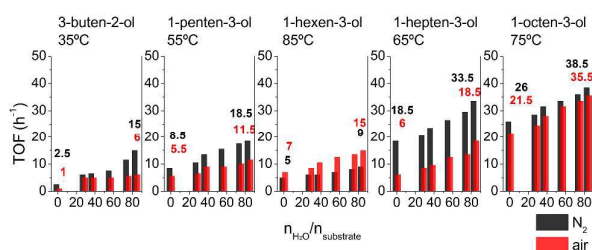
conversion under air and N_2 and (4) the isomerization conversion for each allylic alcohols.¹² Nevertheless also some similarities between both catalysts are observed as both display a comparable qualitative conversion tendency depending of the allylic alcohol size and they reduce and equalize their catalytic activity if an excess of Cl^- is added in the reaction media. Nevertheless the improvement of activity observed using complex **1**, instead of the precatalyst $[\text{RuClCp}(\text{PTA})_2]$,¹² seems to be too huge to be caused just by the activation of the latter upon release of the Cl^- . The equilibrium between **1** and the complex $[\text{RuClCp}(\text{PTA})_2]$ is likely to have an active role in the catalytic mechanism, in addition to providing the catalytic species. Furthermore, the release of Cl^- should be taken in account in the reaction mechanism.

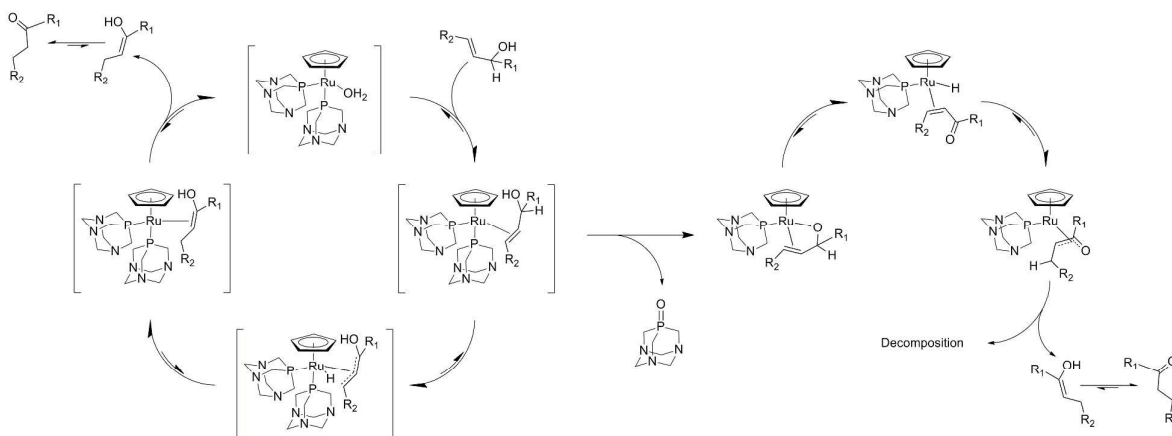
In principle complex **1** can display only one available coordination position generated by substitution of the labile water molecule (Scheme 3). In reaction conditions, it is not possible to substitute the Cp and the phosphines, as confirmed by the general known reactivity of $[\text{RuClCp}(\text{PTA})_2]$ and its parent complexes.^{12,17} Nevertheless, release of the PTA ligand as $\text{O}=\text{PTA}$ was observed in air. Therefore presence of oxygen in the reaction media should be sufficient to oxidise the PTA ligand, which provides an additional coordination site at the metal centre, but can also result in the decomposition of the catalyst. As discussed previously about the catalytic isomerization of the studied allylic alcohols with **1**, the isomerization conversion is lower in the presence of air than under N_2 atmosphere.

Experiments on the catalytic reaction in dry MeOH also suggest that a threshold amount of water is needed to achieve maximum conversion. It is important to point out that at least one water molecule is always present in the reaction, as the catalyst releases a water molecule by exchange with the substrate. This fact could justify the observed residual isomerization conversion.

The obtained results support that more than a few water molecules are participating in the catalytic reaction mechanism: some of them could be involved to assist the isomerization reaction by interaction with the substrate and the metal, but additional ones should also participate probably linked indirectly to the metal, the substrate, N_{PTA} and other atoms of the intermitted species.

We showed that in water solution the $[\text{RuCp}(\text{PTA})_2]-\mu\text{-CN-}^1\text{kC:}^2\text{k}^2\text{N-RuCp}(\text{PTA})_2](\text{CF}_3\text{SO}_3)$ dimer interacts with the water molecules by the N_{PTA} , but also, and in contrast with that thought initially, with Cp ligand atoms.¹⁸ The interaction of water molecules with the Cp has been shown to be sufficiently pronounced to modify the electronic distribution in the dimeric ruthenium complex. Therefore two aspects should be considered in the probable isomerization mechanism mediated by **1** under nitrogen: a) the interaction of water molecules with metal and substrate and b) the probable stabilization of reaction intermediates by the water molecules interacting with N_{PTA} and Cp.

Figure 4 TOF of the catalytic isomerization of 3-buten-2-ol to 1-octen-3-ol by **1** (CF_3SO_3) (1 mol%) vs. $\text{H}_2\text{O}/\text{substrate}$ rate at the lowest temperature for the best conversion of each allylic alcohol at 2 h.



Scheme 3 Possible mechanism for the isomerization of allylic alcohols catalyzed by **1** including the dissociation of a PTA ligand as O=P-TA, in which the participation of water molecules was not included.

For the direct influence of water molecules on metal and substrate a similar mechanism to that proposed by Gimeno et al.,¹⁴ could be considered but with significant differences. First, complex **1** is able to provide under N₂, in which the conversion is significantly larger than in air, only one available coordination position. This fact was supported by NMR spectroscopy, as a significant amount of free PTA and Cp were not observed along the catalytic isomerization reaction. The lack of a second available coordination position prevents the formation of species in which a water molecule could coordinate the metal and then interact with the oxygen of the allylic alcohol. Nevertheless, under air the formation of O=P-TA was observed during the reaction and therefore several coordination positions may be made free, but the catalytic conversions in these conditions are significantly lower than those under N₂ for almost all the alcohols considered.

Taking in account the obtained experimental evidences for complex **1** catalytic behaviour on the studied allylic alcohols and considering what proposed by Gimeno et al., the most probable mechanism should facilitate the direct interaction of

the allylic alcoholic proton to an N_{PTA}, which could be only possible by intervention of a large number of water molecules, due to the far distance and relative geometrical disposition between the metal and the N_{PTA} atoms. Therefore, in complex **1**, being the N_{PTA} far away from the catalytic centre, the cooperative effect of the water molecules can be achieved only if the substrate is suitably oriented and if a network of water molecules is taking part in the reaction. This assumption could also justify the observed dependence of the selective conversion on the size of the allylic alcohols.

To determine if a selective conversion is possible in this reaction, a competitive isomerization experiment among the studied allylic alcohols was performed. In a general experiment 100 eq. of the five studied allylic alcohols (in total 500 eq. of allylic alcohols) were catalysed by 1 eq. (0.2 mol%, considering all the allylic alcohols) of **1** during 2 h at 40, 55, 65, 75 and 80 °C under N₂ and air atmosphere (Figure 5).

At temperature ranging from 50 to 85°C in both catalytic reactions, under N₂ and air, the substrates are differently converted. Under N₂ and below 65°C the isomerization

Figure 5 Selectivity in the conversion (%) in water into the corresponding ketones of an equimolar mixture of allylic alcohols from 3-buten- to 1-octen-3-ol catalysed by **1**(CF₃SO₃) (0.2 mol% against the overall content of alcohols) under N₂ at 40, 55, 65, 75 and 85°C, at 2 h.

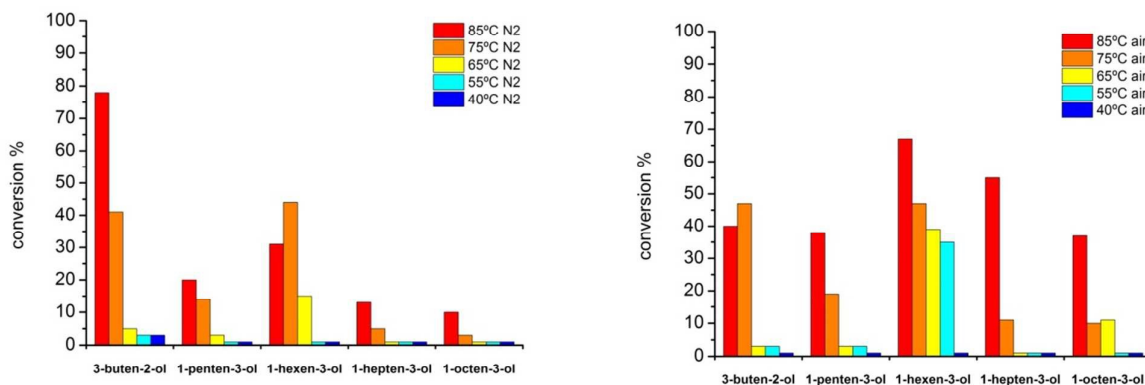
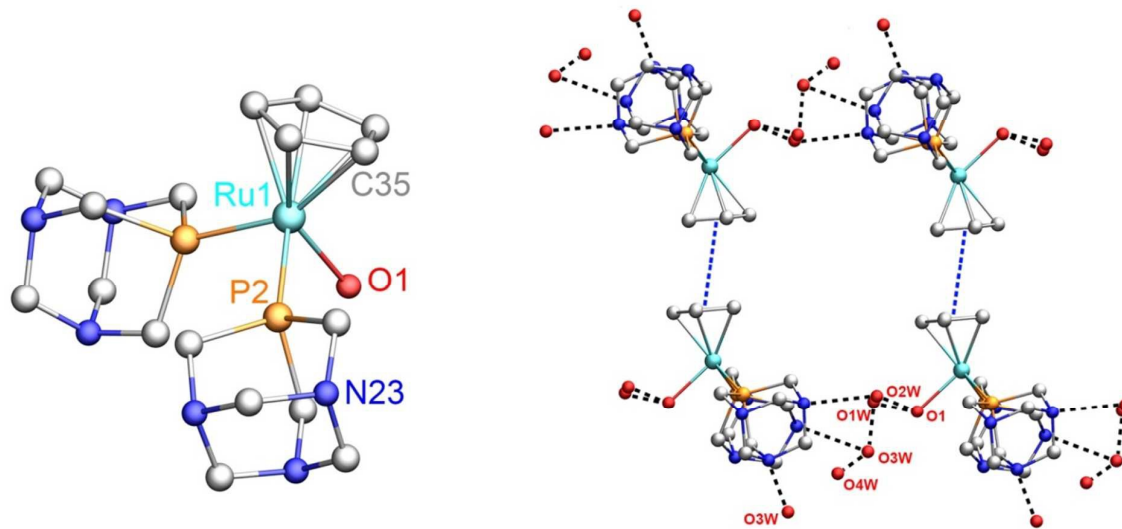


Figure 6. Right: Ball and stick representation of the crystal structure of cation complex **1**. Selected distances and angles: Ru1 - P1 2.2654(10) Å; Ru1 - P2 = 2.2614(8) Å; Ru1 - O1 = 2.1784(16) Å; Ru-Cp_{cent} = 1.837 Å; P2 - Ru1 - P1 = 95.47(2) °. Left: Diagram of **1**(CF₃SO₃)-3.5H₂O highlighting the intermolecular interactions. Hydrogens and anion molecules have been omitted for clarity



conversion rates are lower than those found for pure small alcohols, while under air isomerization of longer-tailed allylic alcohols is preferred. Except at 85°C under N₂, in which the 3-buten-2-ol is largely converted with respect to the rest of allylic alcohols, complex **1** shows a slight selectivity for the isomerization of 1-hexen-3-ol both under N₂ and air at temperatures up to 65°C for N₂ atmosphere and below 55°C for air atmosphere. This experiment therefore supports the hypothesis that the most stable intermediate complex is that obtained by reaction of **1** with 1-hexen-3-ol, which, for this reason, competes with the rest of the studied allylic alcohols and provides the largest amount of intermediated species and finally the largest isomerization conversion.

Crystal structure of **1**(CF₃SO₃)-3.5H₂O.

A concentrate solution of **1**(CF₃SO₃) in water provided single crystal of **1**(CF₃SO₃)-3.5H₂O suitable for X-ray crystal structure determination. The crystal structure of the complex is shown in Figure 6 and selected interatomic distances and angles in the figure caption (more details in SI). The coordination polyhedron around the Ru atom exhibits the expected distorted pseudo-octahedral geometry. The angle P-Ru-P (P2 - Ru1 - P1 = 95.47(2)°) is in the range found for similar ruthenium complexes^{15b,17,19} and similar to that for starting complex [RuClCp(PTA)₂] (Ru1 - P1 = 96.18(7)°), indicating that the substitution of the Cl⁻ by the water molecule does not change significantly the basic distortion of the metal coordination polyhedron. The Ru-P bonds (Ru1 - P1 = 2.2654(10) Å; Ru1 - P2 = 2.2614(8) Å) are somewhat larger than those found in the starting complex [RuClCp(PTA)₂] (Ru1 - P1 = 2.2525(18) Å) and in the range found for similar ruthenium complexes also.^{17,19} Complex **1** is the first piano-stool ruthenium complex containing PTA and a water molecule characterized by single crystal X-ray diffraction. For this reason it is possible only to make comparison with complexes

containing PTA and its derivatives. The Ru-OH₂ distance in **1** is 2.1784(16) Å, which is in the range of those found in literature for ruthenium complexes with PTA and its derivatives.^{17,19,20} The H₂O molecule is a weakly nucleophilic “hard” donor ligand which, therefore, is not strongly attached to most low-valent transition metals. A strong base phosphine like mPTA can therefore shorten its ligand bond with the metal. This effect is not however observed in complex **1**, probably due to the constraints on the angle between OH₂ and the P atoms. The Ru-Cp_{cent} distance (1.837 Å) is also consistent with Ru-Cp_{cent} bond lengths found in bibliography (range 1.836 Å-1.929 Å; mean 1.868 Å).¹² The remaining distances and angles are in ranges found for similar compounds and do not deserve special discussion.¹⁹

The complex is involved in an extended network of hydrogen bonds (Figure 8) with distances larger than 2.5 Å postulated in the literature as weak hydrogen bonds,²¹ being the shorter distance that between O1 and O1W (2.548(18) Å).

Conclusions

The complex [RuCp(H₂O-κO)(PTA)₂]⁺ (**1**) was synthesized, characterized and its catalytic properties explored for the isomerization of lineal allylic alcohols in water and other solvents. As expected complex **1** was found to be an excellent catalyst for the isomerization of linear allylic alcohols, much more active than its parent complex [RuClCp(PTA)₂] both under air and N₂ atmosphere. The catalytic isomerization conversion obtained when **1** was used as catalyst was found to depend on the size of the substrate and the proportion of water in the reaction. Optimal catalytic conversion is achieved with a threshold of water that is different for each studied allylic alcohol. The required amount of water is much larger than what would be expected to obtain the maximum isomerization conversion if water molecules were involved stoichiometrically in the interaction between metal, substrate

and N_{PTA} . The stabilization of reaction intermediates by interaction among all the ligands with water is therefore an important aspect of the reaction mechanism that must be studied as it could be an important factor also in known catalysed isomerization processes in water, some of them faster than presented.²² Theoretical and experimental works are in progress to determine the mechanism of the catalytic isomerization process mediated by **1** and how water and substrate molecules participate in it.

Acknowledgements

Thanks are given to the European Commission FEDER program for co-financing the project CTQ2015-67384-R (MINECO). Thanks are also given to Junta de Andalucía PAI-research group FQM-317 and COST Action CM1302 (WG1, WG2). F. S. is grateful to the University of Almeria for a predoctoral grant. We are very grateful to Marek Jura and Leonardo Bernasconi (Appelton-Rutherford Laboratory, Oxfordshire, U. K.) for facilitating the X-ray determination, suggestions, discussion and checking the paper.

Notes and references

- (a) R. C. van der Drift, E. Bowman and E. Drent, *J. Organomet. Chem.*, 2002, **650**, 1; (b) R. Uma, C. Crévisy and R. Grée, *Chem. Rev.*, 2003, **103**, 27; (c) V. Cadierno, P. Crochet, and J. Gimeno, *Synlett.*, 2008, **8**, 1105; (d) N. Ahlsten, A. Bartoszewicz and B. Martín-Matute, *Dalton Trans.*, 2012, **41**, 1660.
- (a) H. Li and C. Mazet, *Acc. Chem. Res.*, 2016, **49**, 1232; (b) K. Voronova, M. Purgel, A. Udvardy, A. C. Bényei, Á. Kathó and F. Joó, *Organometallics*, 2013, **32**, 4391; (c) G. C. Fu, *Recent Advances in Rhodium(I)-Catalyzed Asymmetric Olefin Isomerization and Hydroacylation Reactions. In Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, Germany, 2005; Chapter 4; (d) N. Ahlsten, A. Bartoszewicz and B. Martín-Matute, *Dalton Trans.*, 2012, **41**, 1660; (e) D. Cahard, S. Gaillard and J. L. Renaud, *Tetrahedron Lett.*, 2015, **56**, 6159; (f) D. B. Grotjahn, C. R. Larsen, G. Erdogan, *Topics in Catalysis* 2014, **57**, 1483.
- D. V. McGrath and R. H. Grubbs, *Organometallics*, 1994, **13**, 224.
- P. Lorenzo-Luis, A. Romerosa and M. Serrano-Ruiz, *ACS Catal.* 2012, **2**, 1079.
- See for example: (a) C. J. Li, *Chem. Rev.*, 2005, **105**, 3095; (b) F. Joó, *Aqueous Organometallic Catalysis*, Kluwer, Dordrecht, 2001; (c) D. J. Adams, P. J. Dyson and S. J. Tavener, *Chemistry in Alternative Reaction Media*, Wiley, Chichester, 2004; (d) P. Servin, R. Laurent, L. Gonsalvi, M. Tristany, M. Peruzzini, J.-P. Majoral and A.-M. Caminade, *Dalton Trans.*, 2009, **23**, 4432; (e) L. Gonsalvi and M. Peruzzini, *Catalysis by Metal Complexes*, 2011, **37**, 183-212.
- A. Mena-Cruz, M. Serrano-Ruiz, P. Lorenzo-Luis, A. Romerosa, Á. Kathó, F. Joó and L. M. Aguilera-Sáez, *J. Mol. Catal. A: Chem.*, 2016, **411**, 27.
- (a) Z. Mendoza, P. Lorenzo-Luis, M. Serrano-Ruiz, E. Martín-Batista, J. M. Padrón, F. Scalambra and A. Romerosa, *Inorg. Chem.*, 2016, **55**, 7820; (b) L. Hajji, C. Saraiba-Bello, A. Romerosa, G. Segovia-Torrente, M. Serrano-Ruiz, P. Bergamini and A. Canella, *Inorg. Chem.*, 2011, **50**, 873; (c) C. Ríos-Luci, L. G. León, A. Mena-Cruz, E. Pérez-Roth, P. Lorenzo-Luis, A. Romerosa and J. M. Padrón, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 4568.
- F. Scalambra, M. Serrano-Ruiz, S. Nahim-Granados and A. Romerosa, *Eur. J. Inorg. Chem.*, 2016, **10**, 1528.
- T. Campos-Malpartida, F. Joó, M. Fekete, Á. Kathó, A. Romerosa, M. Saoud and W. Wojtków, *J. Organomet. Chem.*, 2008, **693**, 468.
- (a) S. Bolaño, L. Gonsalvi, F. Zanobini, F. Vizza, V. Bertolasi, A. Romerosa and M. Peruzzini, *J. Mol. Catal. A: Chem.*, 2004, **224**, 61; (b) M. Saoud, A. Romerosa, and M. Peruzzini, *Organometallics*, 2000, **19**, 4005.
- B. González, P. Lorenzo-Luis, M. Serrano-Ruiz, M. É Papp, M. Fekete, K. Csépe, K. Osz, Á. Kathó, F. Joó and A. Romerosa, *J. of Mol. Catal. A: Chem.*, 2010, **326**, 15.
- M. Serrano-Ruiz, M.; P. Lorenzo-Luis, A. Romerosa and A. Mena-Cruz, *Dalton Trans.*, 2013, **42**, 7622.
- C. A. Mebi, R. P. Nair, R. P. and B. J. Frost, *Organometallics* 2007, **26**, 429.
- L. Bellarosa, J. Díez, J. Gimeno, A. Lledós, F. J. Suárez, G. Ujaque and C. Vicent, *Chem. Eur. J.*, 2012, **18**, 7749.
- (a) A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J. A. Garrido-Cárdenas and F. García-Maroto, *Inorg. Chem.*, 2006, **45**, 1289; (b) D. N. Akbayeva, L. Gonsalvi, W. Oberhauser, M. Peruzzini, F. Vizza, P. Brüggeller, A. Romerosa, G. Sava and A. Bergamo, *Chem. Comm.*, **2003**, 264.
- P. Crochet and V. Cadierno, *Dalton Trans.*, 2014, **43**, 12447.
- See for example: S. S. Bosquain, A. Dorcier, P. J. Dyson, M. Erlandsson, L. Gonsalvi, G. Laurency and M. Peruzzini, *Appl. Organomet. Chem.*, 2007, **21**, 947. (b) A. Rossin, L. Gonsalvi, A. D. Phillips, O. Maresca, A. Lledós and M. Peruzzini, *Organometallics*, 2007, **26**, 3289. Some reviews covering the chemistry of PTA and its derivatives: (c) A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza and M. Peruzzini, *Coord. Chem. Rev.*, 2004, **248**, 955. (d) J. Bravo, S. Bolaño, L. Gonsalvi and M. Peruzzini, *Coord. Chem. Rev.*, 2010, **254**, 555; (e) M. Zablocka, A. Hameau, A. M. Caminade and J. P. Majoral, *Adv. Synth. Catal.*, 2010, **352**, 2341; (f) L. Gonsalvi and M. Peruzzini, *Catalysis by Metal Complexes*, 2011, **37**, 183; (g) L. Gonsalvi, A. Guerriero, F. Hapiot, D. A. Krogstad, E. Monflier, G. Reginato and M. Peruzzini, *Pure Appl. Chem.*, 2013, **85**, 385.
- M. Serrano-Ruiz, S. Imberti, L. Bernasconi, N. Jadagayeva, F. Scalambra, and Romerosa, *Chem. Commun.*, 2014, **50**, 11587.
- (a) B. J. Frost, C. A. Mebi, *Organometallics*, 2004, **23**, 5317; (b) M. S. Ruiz, A. Romerosa, B. Sierra-Martin, A. Fernandez-Barbero, *Angew. Chem. Int. Ed.*, 2008, **47**, 8665; (c) M. Serrano-Ruiz, P. Lorenzo-Luis, A. Romerosa, *Inorg. Chim. Acta*, 2017, **455**, 528.
- (a) R. Girotti, A. Romerosa, S. Mañas, M. Serrano-Ruiz and R. Perutz, *Inorg. Chem.*, 2009, **48**, 3692; (b) R. Girotti, A. Romerosa, S. Mañas, M. Serrano-Ruiz and R. Perutz, *Dalton Trans.*, 2011, **40**, 828; (c) J. Kovács, F. Joó, A. Bényei and G. Laurency, *Dalton Trans.* **2004**, 2336-2340.
- F. Scalambra and A. Romerosa, *Non-covalent Interactions in the Synthesis and Design of New Compounds*; Maharramov, A. M., Mahmudov, K. T., Kopylovich, M. N., Pombeiro, A. J. L., Eds.: John Wiley & Sons, Inc.: Hoboken, NJ, 2015; Chapter 5, 85.
- (a) E. Bolyog-Nagy, A. Udvardy, A. Barczane-Bertok, F. Joo, A. Katho, *Inorganica Chimica Acta*, 2017, **455(2)**, 514-520; (b) H. Horvath, A. Katho, A. Udvardy, G. Papp, D. Szikszai and F. Joo, *Organometallics*, 2014, **33**, 6330-6340; (c) K. Voronova, M. Purgel, A. Udvardy, A. C. Bényei, A. Katho and F. Joo, *Organometallics*, 2013, **32**, 43914401; (d) P. Smolenski, M. V. Kirillova, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Dalton Trans.*, 2013, **42**, 10867-10874; (e) C. J. Brown, G. M.

ARTICLE

Journal Name

Miller, M. W. Johnson, R. G. Bergman, K. N. Raymond and N. Kenneth, *J.A.C.S.*, 2011, **133**, 11964-11966.

Water and catalytic isomerization of linear allylic alcohols by $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2]^+$ (PTA = 1,3,5-triaza-7-phosphaadamantane)

Franco Scalambra,^a Manuel Serrano-Ruiz,^a Antonio Romerosa^a

Área de Química Inorgánica-CIESOL, Facultad de Ciencias, Universidad de Almería, Almería, Spain; Fax: +34 950015008; E-mail: romerosa@ual.es

The new water soluble complex $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2]^+$ has been synthesized and fully characterized. This complex showed to be an excellent catalyst for the isomerization in water of allylic alcohols from 3-buten-2-ol to 1-octen-3-ol. Water was found to be an important factor for obtaining the best conversion.

