

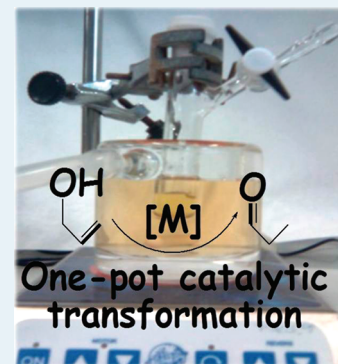
Catalytic Isomerization of Allylic Alcohols in Water

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ABSTRACT: The isomerization of allylic alcohols in water, catalytically mediated by water-soluble metal complexes, is an elegant synthetic procedure for obtaining carbonyl compounds in a completely atom-economical eco-benign process with useful applications in natural-product synthesis and bulk chemical processes. This overview aims to provide a view of the goals attained in catalyzed allylic alcohol isomerization in water and its promising applications.

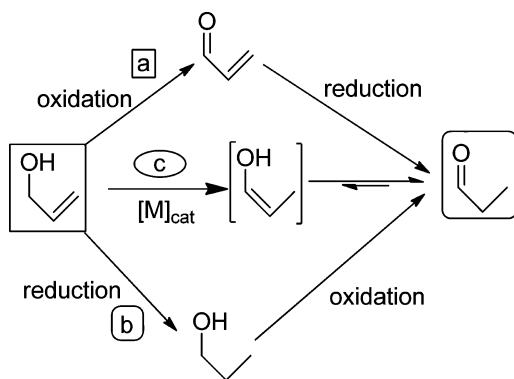


KEYWORDS: allylic alcohol, redox isomerization, homogeneous catalysis, water-soluble metal complexes, catalysis in water, tandem reaction

INTRODUCTION AND SCOPE

Significant efforts have been made in the past decades to develop methods for obtaining carbonyl compounds from allylic alcohols following the seminal works of Blum et al.¹ and Trost and Kulawiec.² The process requires two-step sequences of oxidation (reduction) followed by reduction (oxidation) (Scheme 1: paths (a) and (b)) or more efficient only one-step

Scheme 1. Transformation of Allylic Alcohols to Saturated Carbonyl Compounds



by a catalyzed isomerization process (Scheme 1: path (c)).^{3–6} Sensitive substrates may not survive the conditions of oxidation and/or reduction and therefore catalytic redox isomerizations are especially useful in syntheses requiring mild reaction conditions.^{7–9} Generally, a strong dependence upon the substitution of the C=C allyl alcohol bond has been observed. The reaction becomes more difficult as the number of substituents increases on the double bond. Nevertheless,

interesting and useful catalyzed isomerization processes of substituted allyl alcohols have been reported.

The established mechanisms for metal-catalyzed allylic alcohol isomerization propose alkyl and η^3 -allyl intermediates in acid and neutral environment, and alkoxide intermediate species in basic medium^{2,3,10–12} and in the presence of O₂/H₂O₂.¹³ Nevertheless, scarce experimental evidence has been provided supporting the proposed mechanisms and therefore this is an open subject.^{14,15} Steric as well as electronic factors are expected to play significant roles in the formation of key reaction intermediates that could have an impact on the catalytic process and on the reaction selectivity.^{6,16}

Most of the metal complexes that efficiently catalyze allylic alcohol isomerization processes have been studied in organic solvents.^{7–9} However, water is attracting more and more interest from both industrial and academic perspectives as a replacement for organic solvents.^{17–20} Catalytic reactions in water mediated by aquo-soluble coordination compounds could provide an interesting solution to most of the problems found in catalytic synthesis in organic solvents. Commonly the presence of water provides larger yield, reactivity, and mild reaction conditions than dry solvents. Additionally, the easy catalyst recycling together with the easy separation of the products in water and water/organic biphasic systems make the isomerization of allylic alcohols in the presence of water an economical, eco-benign, and, therefore, very convenient synthetic procedure. Although the results regarding practical applications of allyl alcohol isomerization in water are still in a

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preliminary stage, making the scope of the field still limited, we believe that the efforts carried out over the past few years well deserve an overview.

Despite the potential economic interest and eco-benign aspect of catalyzed isomerization of allylic alcohols in water and notwithstanding that the isomerization processes have been studied for more than 60 years, only recently have significant advances been made in the use of water as an isomerization reaction media. At the moment, only Ru, Rh, and Ni complexes have been shown to be catalytically active in the isomerization reaction of allylic alcohols in water.

The isomerization mechanisms in water have been proposed to be the same as those in organic solvents as no experimental evidence supporting a different mechanism has been found. Excellent experimental data support the inter/intra-molecular characteristics of the metal-catalyzed isomerization of allylic alcohols in water, but it is also evident that complementary studies are necessary to allow in depth understanding of the process and reaching the real mechanism.

There are no examples for asymmetric allylic alcohol isomerization in water, but it can be expected that a novel and more efficient generation of catalysts will be developed soon. Such derivatives could allow a routine use of this economical and powerful atom transformation in synthesis especially for the multistep preparation of natural, as well as non-natural, products. This process in water has broad applications and a bright future.

In this overview, initially, the most significant findings on allyl alcohol isomerization in the presence of water mediated by Ru, Rh, and Ni complexes are presented and discussed. Next, a section focused on "related synthesis" (asymmetric synthesis, tandem redox isomerization-transfer hydrogenation and tandem allylic alcohol isomerization to aldol condensation) presents innovative results on research dealing with the isomerization reactions.

METAL CATALYSTS FOR ALLYLIC ALCOHOLS ISOMERIZATION IN WATER

Reaction of water-soluble ligands with metal salts in water or biphasic conditions provides a convenient strategy for synthesizing water-soluble metal complexes. In the overwhelming majority, the water-soluble transition-metal catalysts contain water-soluble tertiary phosphines such as the monophosphine TPPTS, the sodium salt of sulfonated triphenylphosphine, the diphosphine DPPPS, the sodium salt of sulfonated 1,3-bis-(diphenylphosphino)propane, and the 1,3,5-triaza-7-phosphaadamantane (PTA).^{19,21–23} Biphasic catalysis processes in water/organic-solvent require an accurate experimental control. de Bellefon and co-workers^{24,25} reported a new engineering approach to polyphasic fluid reactions, which are characterized by a novel conception for high-throughput screening that is based on dynamic sequential operations. They studied the isomerization of 1-hexen-3-ol catalyzed by {RuCl₃/TPPTS}, {RhCl₃/TPPTS}, and {Ni(cod)₂/TPPTS} in H₂O/*n*-heptane at 40–80 °C using this new technique. The study concluded the following: (i) the ruthenium and the rhodium species lead to comparable conversions (61% and 53%, respectively); (ii) the nickel species give rise to 1,3-transposition of the allylic alcohol hydroxyl group; (iii) the most interesting, a two-phase reaction has more advantages and efficiency than a water monophasic one: the catalyst separation is easier and can be reused in additional runs, the products can be easily isolated from the reaction media without further

purifications, and the adequate choice of the biphasic system could decant the reaction to a specific product. Biphasic-reaction synthesis, therefore, are expected to be easier, cheaper, and eco-benign synthetic processes.

1.1. Ru(II)-Complexes. Early experiments on the catalytic properties of RuCl₃·*x*H₂O for allylic alcohol isomerization in water provided clear evidence to support the participation of Ru(II)-species in the catalytic process.^{3,4,26} Not long after that, the complex [RuCl₂(PPh₃)₃] (**1**)¹ was found to be an active catalyst for the redox isomerization of allylic and homoallylic alcohol in water.^{2,27,28} Over the past few years interesting water-soluble phosphines such as PTA^{21–23} as well as its derivatives, such as the trihydrazinophosphaadamantane ligand (THPA),²⁹ have received increasing attention as being promising catalysts in aqueous media. We should highlight the work of Joó et al.^{30,31} who described the water-soluble *N*-heterocyclic carbene-complexes [RuCl(X)(1-butyl-3-methylimidazol-2-ylidene)(*p*-isopropyltoluene)]^{*n*+} (2: X = Cl⁻, *n* = 0; 3: X = PTA, *n* = 1) that were the first active catalysts for allylic alcohol isomerization in aqueous–organic biphasic systems. The complex **2** is able to carry out the redox-isomerization of 1-octen-3-ol into 3-octanone in 40 min at 80 °C and 1 bar H₂ pressure (pH solution = 6.9). The total turnover number (TON) obtained after six consecutive runs was 251. It is important to stress that the yield and reaction product distribution strongly depend on the pH and the chloride concentration in the aqueous phase. Complex **3**, containing a PTA molecule, catalyzes the same reaction with 95.6% yield and turnover frequency (TOF) of 135 h⁻¹.

At the beginning of 2004, Cadierno et al.³² showed that the complexes [RuCl₂(η⁶-arene){P(CH₂OH)₃}] (**4**) and [RuCl₂(η⁶-arene){P(CH₂OH)₃}₂]Cl (**5**) (arene = C₆H₆, *p*-cymene, C₆Me₆) are efficient catalysts for the isomerization of allylic alcohols (TOF values up to 600 h⁻¹; TON values up to 782) in biphasic water/*n*-heptane medium (N₂ atmosphere, 75 °C), but the presence of Cs₂CO₃ is mandatory. Two years later, the same research team presented the highly efficient family of catalysts [RuCl₂(η⁶-*p*-cymene){κ-(P)-PPh_{3-*n*}(OCH₂CH₂NMe₃)_{*n*}}[SbF₆]_{*n*}] (**6a**), **2** (**6b**), **3** (**6c**) that isomerizes quantitatively the conversion of 1-octen-3-ol into octan-3-one and can be recycled 3 (**6a**), 7 (**6b**), and 10 times (**6c**) without significant loss of activity.³³ Complex **6c** is one of the most active catalysts for isomerization of allyl alcohol as 1 mol % of complex is able to isomerize 1-octen-3-ol in the presence of 5 mol % of KO-*t*-Bu at 75 °C in water (TON = 990, *t* = 215 min).

The same research team throughout the same year also reported the arene-ruthenium(II) complex [RuCl₂(η⁶-*p*-cymene){P(OEt)₃}] (**7**)⁹ that quantitatively catalyzes in 130 min the isomerization of 1-octen-3-ol into octan-3-one in water (TOF = 46 h⁻¹). The parent complexes [RuCl₂(η⁶-C₆H₅OCH₂CH₂OH)(PR₃)] (PR = (OMe)₃ (**8a**), (OEt)₃ (**8b**), (OPr)₃ (**8c**)) were used by Crochet and co-workers³⁴ for the isomerization of allylic alcohols in aqueous medium. It is important to stress that the complex **8a** is one of the most active catalysts for isomerizing disubstituted allyl alcohol: 1 mol % of complex is able to isomerize 3-penten-2-ol in the presence of 5 mol % of KO-*t*-Bu at 75 °C in water in 30 min. The observed catalytic activity of **8a**, **8b**, and **8c** (TOF values from 200 to 22 h⁻¹) is justified by the increasing steric hindrance when moving from **8a** to **8c** that makes the coordination of the allylic alcohols C=C bond on the metal center more difficult.

A different approach to the problem was made by the Joó and Romerosa groups³⁵ that reported the catalytic properties of $\text{Na}_4[\{\text{RuCl}(\mu\text{-Cl})(\text{mtppms})_2\}_2]$ (**9**), $\text{Na}_4[\{\text{RuCl}(\mu\text{-Cl})(\text{C}=\text{C}=\text{CPh}_2)(\text{mtppms})_2\}_2]$ (**10**), $\text{Na}_2[\text{RuClCp}(\text{mtppms})_2]$ (**11**), and $\text{Na}[\text{Ru}(\text{CO})\text{Cp}(\text{mtppms})_2]$ (**12**) for the isomerization of allylic alcohols in water and in two-phase systems. Complexes showed good to excellent catalytic activities with TOF up to 2226 h^{-1} in the temperature range $50\text{--}80 \text{ }^\circ\text{C}$ and, significantly, under air. However, it was essential to adjust the pH of the aqueous phase in the pH range 4–7 to obtain the optimal conversion. On the basis of the interesting results obtained, the teams carried out an extensive search for the ruthenium complexes that would be more air stable and economical to synthesize. Two new water-soluble complexes $[\text{RuClCp}(\text{mPTA})_2](\text{OSO}_2\text{CF}_3)_2$ (**13**) and $[\text{RuCp}(\text{mPTA})_2(\text{OH}_2\text{-}\kappa\text{O})](\text{OSO}_2\text{CF}_3)_3$ (**14**) were found as active catalysts for the redox isomerization of alk-1-en-3-ols into the corresponding ketones in aqueous or aqueous–organic two-phase environments at $80 \text{ }^\circ\text{C}$.³⁶ Compound **14** was the most active catalyst for the isomerization of oct-1-en-3-ol (TOF = 162 h^{-1}) and showed sharp high activity in water at pH of 4.75. Interestingly, the parent complex **13** displays a catalytic activity largely diminished (TOF = 9.6 h^{-1}) that decreases further monotonically with increasing pH value. The NMR study of the isomerization reaction catalyzed by both complexes showed that components of phosphate buffer, H_2PO_4^- and HPO_4^{2-} , strongly interact with the ionic complex species $[\text{RuClCp}(\text{mPTA})_2]^{2+}$ and $[\text{RuCp}(\text{mPTA})_2(\text{OH}_2\text{-}\kappa\text{O})]^{3+}$.

These results showed unambiguously that the phosphate buffer is not innocent, interacting with the catalytically active metal center and can therefore strongly influence its catalytic properties. It is interesting to stress that **14** remains active in the presence of air, which is an important practical aspect.

Caminade et al.^{37,38} took a step ahead in the use of water-soluble phosphines as ligands for obtaining active catalysts for isomerization of allylic alcohols in water. Dendrimers (1 mol %) containing Ru-PTA complexes as ending groups were active catalysts for the isomerization of 1-octen-3-ol into octan-3-one in a mixture of water–heptane (1:1) at $75 \text{ }^\circ\text{C}$ and in the presence of 2% of Cs_2CO_3 as cocatalyst. It is important to notice that no reaction occurs in the absence of water. At the end of the reaction the phase separation allowed an efficient recycling of the catalyst up to 4 runs. Interestingly a positive dendritic effect was clearly evident as the conversion increased from the monomer (38%) to the third generation dendrimers (98%) under the same conditions.

Active catalysts for the isomerization of allylic alcohols without aquo-soluble phosphines were presented by E. Peris et al.³⁹ The new NHC-complexes $\text{Cs}[\text{Ru}(\kappa^2\text{O},\text{O}-\text{CO}_3)(\eta^6\text{-arene})(\text{NHC})]$ (arene = *p*-cymene (**15a**), hexamethylbenzene (**15b**); NHC = *N,N'*-methyl-(propanesulfonate)imidazolinyldene) were effective and recyclable catalysts in water at $110 \text{ }^\circ\text{C}$ for the isomerization of 1-hepten-3-ol and 1-hexen-3-ol without bases as cocatalyst. The complex **15a** is far more active than **15b**, which is in agreement with the previously observed behavior for this kind of compounds, and can be recycled up to five times without important activity loss (0.5 mol % catalyst; TON = 495; $t = 60 \text{ min}$).

A different approach was proposed by Bergman, Raymond, and co-workers,⁴⁰ who reported the $16\text{CM}_4\text{L}_6$ system, which is composed of the cationic active catalyst $[\text{RuCp}(\text{PMe}_3)(\text{MeCN})_2]^+$ (**16**) encapsulated into $[\text{M}_4\text{L}_6]^{12-}$ ($\text{M} = \text{Al}^{3+}$, Fe^{3+} , Ga^{3+} ; $\text{L} = 1,5\text{-bis}(2,3\text{-dihydroxybenzoylamino})\text{-naphtha-$

lene). Both, **16** and $16\text{CM}_4\text{L}_6$ are active catalysts able to isomerize allyl alcohols completely in water at $42 \text{ }^\circ\text{C}$. The observed lifetime of $16\text{CM}_4\text{L}_6$ (TON = 1070) was higher than that observed for **16** in halogenated organic solvents.⁴¹ This system is a beautiful example of a clever strategy to arrive at a high selectivity and efficiency in a catalytic reaction.

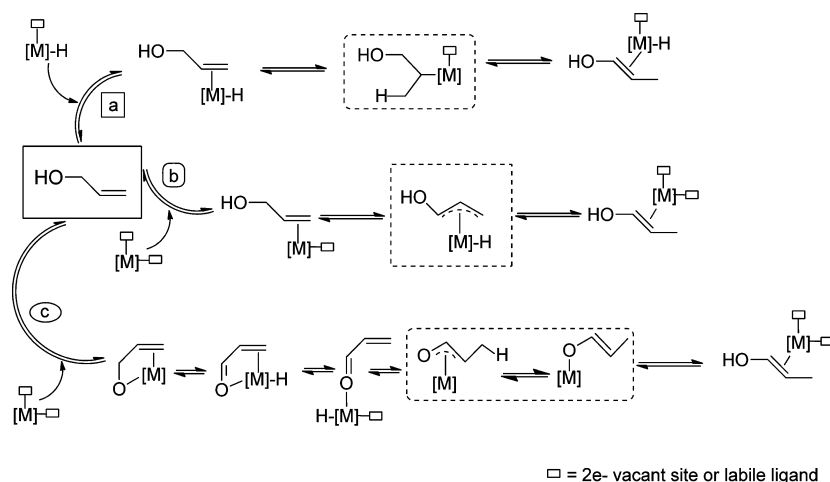
1.2. Ru(IV)-Complexes. Catalytic isomerization of allylic alcohols into carbonyl compounds in aqueous media catalyzed by Ru(IV)-complexes has scarcely been studied up until now. Among some recent examples, we should highlight the works of Gimeno and Cadierno's group who studied the catalytic properties in the isomerization of allyl alcohols of the complexes $[\text{Ru}(\eta^3\text{-}\eta^2\text{-}\eta^3\text{-C}_{12}\text{H}_{18})\text{Cl}_2]$ (**17**),⁴² $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-Cl})\}_2]$ (**18**), $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{L})]$ (**19**) ($\text{C}_{10}\text{H}_{16} = 2,7\text{-dimethylocta-2,6-diene-1,8-diyl}$; $\text{L} = \text{CO}$, PMe_3 , PMe_2Ph , PMePh_2 , $\text{P}(\text{p-C}_6\text{H}_4\text{OMe})_3$, CNTBu , NH_2Ph , NCMe), $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\text{NCMe})_2][\text{SbF}_6^-]$ (**20**),¹⁴ and $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\kappa^2\text{O},\text{O}-\text{CH}_3\text{CO}_2)]$ (**21**).⁴³ Complex **17** is active both in tetrahydrofuran (THF) and H_2O despite of its low solubility in water, in which solvent the isomerization process was found to take place faster. Complex **17** reacts with water to give rise to an aqueous-soluble very active catalyst that is able to isomerize quantitatively 1-octen-3-ol into octan-3-one in 15 min in water at $75 \text{ }^\circ\text{C}$ (TOF = 2000 h^{-1} ; with Cs_2CO_3 in 20 min, TOF = 1500 h^{-1}). The catalytic activity of **17** in water for isomerizing a variety of allyl alcohols showed that this reaction is highly dependent upon the substitution of the carbon–carbon double bond, as previously observed in other catalytic systems. Additionally, the catalyst was able to be recycled more than three times after the conversion of 3-buten-2-ol in butan-2-one, achieving a high catalytic activity of the catalyst at such a lower loading as $10^{-4} \text{ mol } \%$ (100% yield in 20 h; TON = 10^6 ; TOF = 50000 h^{-1}) (vide infra, Section 2.2).

In a further paper, Cadierno's team presented an extensive study of the catalytic properties of the complexes **18**, **19**, **20** in the isomerization of allylic alcohols. Experimental results evidenced that **18** is one of the most active catalyst complexes in water at the moment, useful for isomerizing the monosubstituted alcohols 1-octen-3-ol, 1-hepten-3-ol, 1-hexen-3-ol, 1-penten-3-ol, and 3-buten-2-ol with ruthenium charge of 0.2 mol %, leading to TOF values of $750\text{--}3000 \text{ h}^{-1}$. Its high catalytic activity at lower loading (0.4 mol %) was obtained for the isomerization of 3-buten-2-ol into butan-2-one in water (100% in 24 h; TON = 10^6 ; TOF = 41666 h^{-1})¹⁴ after recycling the catalyst at least four times.

More recently, the complex **21** has been reported as a new highly efficient catalyst in water and ionic liquids. In water 1–2 mol % of **21** isomerizes quantitatively the 1-octen-3-ol at $75 \text{ }^\circ\text{C}$ in only 5 min (TOF = 6000 h^{-1}) and, remarkably, at $35 \text{ }^\circ\text{C}$ in 30 min. It is readily recoverable and remains active up to five runs (in 1.5 or 2 h), leading to cumulative TON values of 495 in water and 487 in ionic liquid ($[\text{BMIm}][\text{BF}_4^-]$) (BMIm = 1-butyl-3-methylimidazolium tetrafluoroborate). Complex **21** catalyzes also very efficiently the isomerization of a broad variety of allylic alcohols; its capability for the isomerization of allyl alcohols in water being the highest in the absence of any cocatalyst reported in literature. Complex **21** can be considered as a genuine example of a pure organometallic catalyst with application in a green chemical process.

1.3. Rhodium Complexes. The use of rhodium complexes for the catalytic isomerization of allylic alcohols has been significantly less extensive than those of ruthenium. Among some older examples on the use of $\text{RhCl}_3\cdot\text{H}_2\text{O}$ for catalyzing

Scheme 2. Proposed Mechanisms for the Metal-Catalyzed Allyl Alcohol Isomerization: (a) via Alkyl-Metal Intermediate, (b) via η^3 -Allyl-Metal-Hydride Intermediate, (c) via Alkoxide Intermediate



the isomerization of allylic alcohol in water, the work published in 1981 by Sasson and co-workers should be highlighted.⁴⁴ This paper reported and discussed the isomerization of 1-octen-3-ol into octan-3-one in benzene/water at 80 °C ($t = 2$ h) catalyzed by RhCl_3 and in presence of onium salts. At the beginning of 1997 the same research team⁴⁵ presented the influence of the carboxylated triarylphosphines CO_2H groups on the isomerization of 1-octen-3-ol catalyzed by the water-soluble complex $[\text{RhCl}(\text{COD})(\text{PAr}_3)]$ (**22**) ($\text{COD} = \text{cycloocta-1,5-diene}$; $\text{PAr}_3 = o-, m-, \text{ and } p\text{-}(\text{Ph})_n\text{P}(\text{C}_6\text{H}_4\text{-COOH})_{3-n}$) in water/toluene. The quaternary phosphonium ion $[(\text{C}_4\text{H}_9)_4\text{P}]\text{Br}$ proved to be somewhat more efficient than the corresponding quaternary ammonium salt $[(\text{C}_4\text{H}_9)_4\text{N}]\text{Br}$. Water does not play a significant part in the isomerization process, justifying that the isomerization of 1-octen-3-ol into octan-3-one can be interpreted in terms of a metal-hydride-addition-elimination mechanism. In 2000, the de Bellefon's group,⁴⁶ reported the catalytic activity of RhCl_3 , $\text{Rh}_2(\text{SO}_4)_3$, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (**23**), and TPPTS (TPPTS = $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$) for the isomerization of allylic alcohols in n -heptane/water and methanol/water, showing that the catalytic activity of the compounds is remarkably different for primary (the best $\text{TOF}_s = 3.1$ to 4.8 h^{-1}) and secondary allylic alcohols (the best $\text{TOF} = 30$ to 2520 h^{-1}).

A different approach to the problem was made by the Bianchini team that used the sulphos phosphine (sulphos = $^-\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{-PPh}_2)_3$) to synthesize the zwitterionic rhodium complex $[(\text{sulphos})\text{Rh}(\text{cod})]$ (**24**) at the beginning of 2001.^{47,48} The interesting and active complex **24** was presented as an efficient catalyst for the chemoselective transformation of both allylic and homoallylic alcohols under aqueous-biphasic reaction as 0.021 mmol of catalyst isomerizes 2.1 mmol of allylic alcohol in 1:1 water/ n -octane (30 mL) within 1 h at 100 °C. The catalyst is able to be reused at least 3 times ($\text{TON} = 1310$; $\text{TOF}_s = 490, 430, \text{ and } 390 \text{ h}^{-1}$) with a slight deactivation (ca. 10%) after each run by the formation of an inactive complex $[(\text{sulphos})\text{Rh}(\text{CO})_2]$. Two years later, Knight and Schull⁴⁹ reported that the water-soluble rhodium bis-phosphine complex $[\text{Rh}(\text{cod})_2]\text{BF}_4/\text{TPPMP}$ (**25**), (TPPMP = $\text{Na}_2[\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-PO}_3)]$) was well active for the aqueous phase isomerization of a variety of allylic alcohols such as $\text{RCH}=\text{CHCH}_2\text{OH}$ ($\text{R} = \text{Ph}; \text{Me}$) at a refluxing temper-

ature. The catalyst could be recycled with a slight loss of activity in every run.

More recently, Martín-Matute and co-workers reported⁵⁰ that $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})_2]\text{BF}_4$ (**26**) catalyzes the fast isomerization of primary and secondary allylic alcohols. Complex **26** (2 mol %) in the presence of the water-soluble phosphine PTA (4 mol %) isomerizes quantitatively the α -vinylbenzyl alcohol (10 mmol) into propiophenone (yield 100%) in only 5 min in water at an ambient temperature. The reaction yield is highly dependent on the Rh/PTA rate as well as on the reaction temperature. Experimental results suggested that a 1,3-hydrogen shift takes place during the reaction, giving rise to Rh-alcohol, -enone, and -enol intermediates. The resulting system **26**/PTA is parallel in catalytic activity to $[\text{Ru}(\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\kappa^2\text{O}, \text{O}-\text{CH}_3\text{CO}_2)]$ (**21**). Both complexes represent the best two excellent examples of active catalysts to isomerize allyl alcohols in water with a low cost and reduced waste production.

Finally, at the beginning of 2007, Bergman, Raymond, and co-workers⁵¹ reported the first remarkable and selective supramolecular encapsulation of discrete organometallic catalysts that display catalytic activity controlled by the size and shape of the cavity host. The cationic active catalyst $[(\text{PMe}_3)_2\text{Rh}(\text{COD})]^+$ (**27**) was encapsulated into Ga_4L_6 to give the $27\text{C}\text{Ga}_4\text{L}_6$ system. A mixture of **27** (10%) and $27\text{C}\text{Ga}_4\text{L}_6$ (10%) isomerizes allylic alcohols in D_2O at 25 °C ($t = 0.5$ h) selectively depending on the size and shape of the substrate that have to be suitable to enter the host cavity.

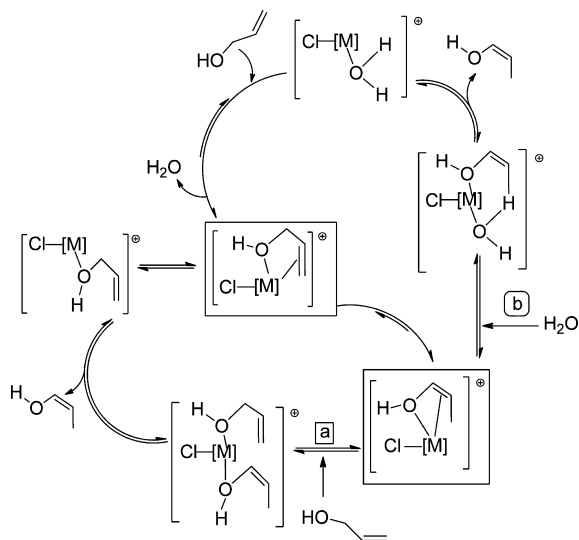
1.4. Nickel Complexes. Despite the promising first results obtained, the isomerization by Ni-catalysts of allylic alcohols in water has not received much attention. In fact, and to our knowledge, the catalytic isomerization of allyl alcohol has been studied in CH_2Cl_2 ,⁵² $\text{HCN}/\text{CF}_3\text{COOH}:\text{benzene}$,⁵³ xylene,⁵⁴ and methanol/xylene,⁵⁵ but only one example in water was published by Monflier et al.⁵⁶ The complex $[\text{Ni}(\text{COD})_2]$ (**28**) is able to catalyze the isomerization of geraniol and prenol to citronellal and isovaleraldehyde in aqua/organic biphasic systems at 110 °C. A similar reaction performed in water led to the 1,3-transposition of geraniol and prenol to afford linalool and 2-methyl-3-buten-2-ol, but the desired redox-isomerization compounds were obtained with poor yields and selectivities. The progressive deactivation of the catalyst was attributed to the reaction of the produced aldehyde with the active intermediate $[\text{Ni}^+]\text{-H}$ or with the π -allyl-/alkyl-nickel

species that are formed by insertion of the starting allylic alcohol into the $[\text{Ni}^+]\text{-H}$ bond across the isomerization catalytic cycle.

1.5. Proposed Mechanisms. There is an exceptional long history associated to the proposed mechanisms for metal catalyzed allyl alcohol isomerization. Thus, Georgoulis et al.²⁶ observed the first chirality transfer in an acyclic system mediated by $\text{RuCl}_3/\text{NaOH}$, proposing that a catalytic process may involve alkoxide-Ru species similarly to those proposed by Sharpless in the epoxidation of the racemic allylic alcohol. Over the years, with regard to the obtained experimental results, three main mechanisms have been proposed for the metal-catalyzed isomerization of allylic alcohols (Scheme 2): (a) the metal-hydride addition–elimination mechanism (also named alkyl mechanism), (b) the π -allyl metal-hydride or η^3 -allyl mechanism, and (c) the mechanism invoking oxygen coordination (also named enone mechanism). The proposed mechanism does not discriminate between catalytic reaction in water and organic solvents.

Near the end of 2011 Varela-Álvarez and co-workers⁵⁷ published an illustrative study of the metal-catalyzed isomerization of allylic alcohols, but labeled substrates were not used, unlike the study made previously by McGrath and Grubbs.⁵⁸ Additionally, a theoretical study on the studied reaction in water and THF under neutral (Scheme 3) and basic conditions

Scheme 3. Proposed Catalytic Isomerization Cycle under Neutral Conditions without (a) and with (b) Water



was also made. The comparison of experimental and theoretical results suggested three fundamental propositions: (i) the general mechanism involves a cationic alcohol complex as the catalytically active species instead of the above proposed neutral alkoxy complex; (ii) in water, the enol decoordination is preferred to be assisted by the coordination to the metal of a water molecule instead of an allylic alcohol, lowering the catalytic energy barrier of the process; and (iii) in basic medium the catalytic reaction is favored in both dry and wet solvents.

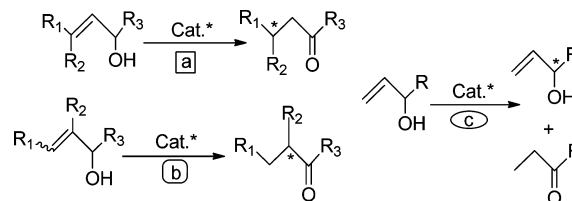
■ RELATED SYNTHESIS USING METAL CATALYSTS IN WATER

2.1. Asymmetric Synthesis. Asymmetric catalysis represents one of the most powerful and cost-effective methods for producing a wide variety of chiral compounds.⁵⁹ Nevertheless,

the general practical application of this synthetic procedure remains limited because the right enantioselectivity of a chemical synthesis can only be often achieved in a restricted range of solvents many of which are environmentally hazardous.^{60,61} After the report at the end of 1980 of the 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) by Takaya, Noyori, et al.⁶² there has been an extensive development of chiral complexes as active catalysts in asymmetric synthesis with excellent results.^{63–67} Catalytic asymmetric isomerization of related compounds such as allylic amines stand out as one of the most accomplished and well-studied reactions in asymmetric catalysis as illustrated by its industrial application.^{3,4,68,69} Examples of highly active and selective catalysts of the asymmetric isomerization of allylamines also remain rare: a few chiral rhodium or ruthenium complexes have been found somewhat active,^{70–73} chiral nickel catalysts being the most used.⁴ A bibliographical look at asymmetric isomerization of allylic alcohols shows that three modes for asymmetric isomerization of chiral allylic alcohols have been reported but none in water.^{3,4}

As depicted in Scheme 4 the chiral isomerization process can occur through the formation of a new stereogenic center at β -

Scheme 4. Possible Products from the Asymmetric Isomerization of Allylic Alcohols by Metal-Chiral-Complexes



(path a) or at α -position (path b), or by the kinetic resolution of the allylic alcohol (path c). The three processes have already been carried out experimentally.^{74,75}

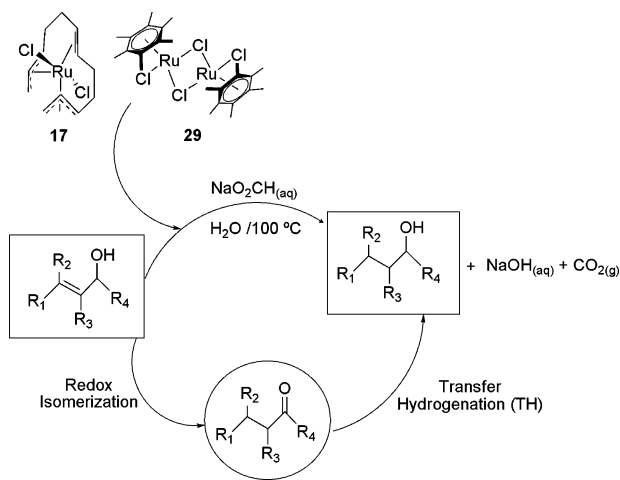
The transposition of allylic alcohols to saturated carbonyls could provide new opportunities to obtain these asymmetric compounds by new catalytic and more convenient procedures.^{76,77} Up until now, there have been no examples of this kind of catalytic reaction in water, but its importance is evident. The extension of the metal-mediated catalytic chiral isomerization in water could be an interesting procedure to obtain complex molecules by more eco-benign and possible economic and convenient procedures. Therefore, this is a virgin research line that could provide interesting results.

2.2. Tandem Redox Isomerization Reactions. When considering sequential tandem reactions, it is often necessary to consider catalyst compatibility with residual material (solvent, additives, and other catalysts) from preceding steps.^{60,78,79} Recently, Cadierno, Gimeno, and co-workers^{6,42,80,81} presented an extensive study of a simple and highly efficient method for the selective reduction of the carbon–carbon double bond in allylic alcohols that is based on a unprecedented redox-isomerization/transfer hydrogenation tandem process catalyzed by a ruthenium complex. The net result is a unique, single-pot method that is a valuable alternative to classical transition metal-catalyzed carbon–carbon double bond hydrogenation: it takes place under relatively mild conditions.

The study was carried out with the highly stable complexes $[\text{Ru}(\eta^3\text{-}\eta^2\text{-}\eta^3\text{-C}_{12}\text{H}_{18})\text{Cl}_2]$ (**17**) and $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_6\text{Me}_6)_2\}]$ (**29**)⁸¹ in organic solvent and water. The hydrogen

source used was sodium formate that reacts with the metal center to give rise to the active $[M]-H$ species⁸² (Scheme 5).

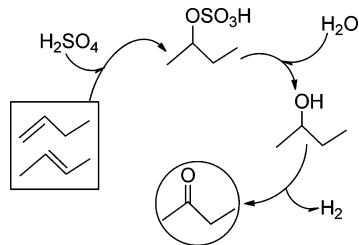
Scheme 5. Isomerization/Transfer Hydrogenation Tandem Process in Aqueous Media



The experimental results show that (i) the transfer hydrogen process (TH) is the determining step of the reaction and **29** is the best catalyst for mediating the isomerization-reduction tandem reaction of monosubstituted- $C=C$ bond allyl alcohols. Additionally, (ii) the redox isomerization becomes the slowest step for the *di*- and *trisubstituted*- $C=C$ bond allylic alcohols, **17** providing the highest activities; in agreement with previous findings (vide supra, Section 1.2). The primary alcohols are less reactive than the secondary ones. Finally, (iii) in water the limiting reaction step is the hydrogenation transfer into the carbonyl intermediate, which favors the isomerization of primary allylic alcohols.^{15,46}

A very interesting tandem reaction catalyzed by a ruthenium catalyst in water has also been described in which an allylic alcohol is the intermediate species. Butanone is a megaton-per-year scale solvent traditionally produced from butenes, but 1,3-butadiene is a most attractive alternative starting material (Scheme 6).

Scheme 6. MEK Synthesis from Butenes by a Tandem Reaction



Drent and co-workers⁸³ reported that in situ mixing of $RuCl_3$, $[Ru(acac)_3]$ (Hacac = pentane-2,4-dione) and 2,2'-bipyridine (bipy) (or 1,10-phenanthroline (phen)) a system is obtained that catalyzes in the presence of H_2SO_4 the direct conversion of 1,3-butadiene to methyl-ethyl-ketone (MEK) in monophasic (water) or biphasic (water/diglyme) reaction conditions with good selectivity (ca. 95%; $T = 155\text{ }^\circ\text{C}$; TON = 1200; $t = 32\text{ h}$). An elegant study focused to determine the influence of the acid in the reaction suggested that coordinative

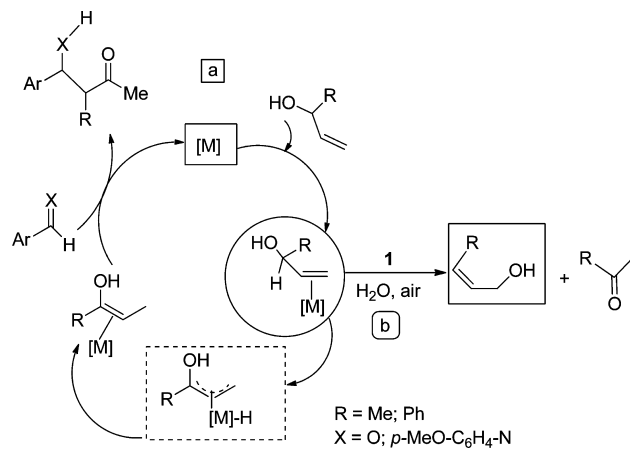
properties of the acid-conjugate base play a decisive role in the catalytic process. Under optimized conditions, Bouwman et al.⁸⁴ reported that a $RuCl_3$ -phen system (TOF = 960 h^{-1} ; TON = 2750; $t = 10\text{ h}$) catalyzes the reaction better than the $[Ru(acac)_3]$ -phen system. Shortly after the same group also described⁸⁵ that the complex *mer*- $[RuCl_3(dmsO)(phen)]$ (**30**) and *cis,cis*- $[RuCl_2(dmsO)_2(phen)]$ (**31**) are active precursors for direct one-pot conversion of 1,3-butadiene to butanone, **30** (TON = 2050; $t = 6\text{ h}$) being the most active (**31**: TON = 1300, $t = 7\text{ h}$). Within this context, it is important to stress that the presence of dienes such as butadiene completely inhibits the catalytic activity of organometallic complexes, and therefore the precedent results are particularly relevant.

2.3. Tandem Allylic Alcohol Isomerization Followed by Aldol Reaction. The aldol and Mannich-type reactions are among the most important C–C bond forming reactions in organic synthesis. According to the literature,^{86–88} complex $[RuCl_2(PPh_3)_3]$ (**1**) catalyzes the *cross-coupling* reactions between allylic alcohols and aldehydes and imines under monophasic (water) or biphasic (water/toluene) conditions. A variety of aromatic aldehydes were examined under similar conditions (H_2O or H_2O /toluene (4:1); $t = 5\text{ h}$).

The desired aldol products were obtained in moderate yields (35–70%, *syn/anti* ratio of 60/40–74/26). However, the results exhibit a reverse trend in the reactivity of aldehydes as compared to aldol condensation in ionic-liquid and aqueous-biphasic. Reactivity between imines and 3-buten-2-ol was carried out at $90\text{ }^\circ\text{C}$ (10 h) to determine the best catalyst for the tandem reaction. As expected, the solvent/catalyst system determined the resulting product. Both in water and in organic solvents the *anti*-product was preferred regardless of the substrate used. Nevertheless the diastereoselectivity of the reaction was not very high, and the electron-rich aldehydes gave a yield lower than electron-deficient substrates.

The tandem olefin migration-aldol- and Mannich-type reactions were described by a typical π -allyl-metal-hydride mechanism. The ruthenium complex isomerizes the allyl alcohol to an enol, which coordinates with the ruthenium catalyst, and an in situ coupling between the enol-ruthenium complexes with the aldehyde (or imine) generates the aldol or Mannich-type product (Scheme 7, path a). The authors described that in the presence of a catalytic amount of **1**,

Scheme 7. Proposed Mechanism for Aldol- or Mannich-Type Catalytic Reaction (a) and Metal-Catalyzed Olefin Migration in Water (b)



functional groups of homoallylic- and allylic alcohols suffered 1,3-rearrangement in air and water, and a side product of the isomerization is also formed (Scheme 7, path b).

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Notes

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