

Important advance about catalytic isomerization of allylic alcohols in water

B. López-Sánchez,¹ F. Scalambra² and A. Romerosa³.

¹Department of Inorganic Chemistry-CIESOL, Faculty of Experimental Sciences, University of Almería, E04120, Almería (Spain); mls505@ual.es.¹

The isomerization of linear^[1] and cyclic allylic alcohols, 2-buten-3-ol, 1-penten-3-ol, 1-hexen-3-ol, 1-hepten-3-ol, 1-octen-3-ol and 2-cyclohexenol in water mediated by [RuCp(PTA)₂(H₂O-kO)](CF₃SO₃) (**1**) (PTA=1,3,5-triaza-7-phosphaadamantane) was successful obtaining. The characterization of the catalytic reaction intermediates showed as they are η^2 -allylic alcohol complexes with formula [RuCp(*exo*- η^2 -CH₂=CH-CHOH-R)(PTA)₂]⁺ (R= CH₃ (**2**), CH₂-CH₃ (**3**), (CH₂)₂-CH₃ (**4**), (CH₂)₃-CH₃ (**5**) or (CH₂)₄-CH₃ (**6**)). The crystal structures of **2**, **3**, **4**, **5** and **6** reveal that Ru atom is coordinated with a distorted pseudo-octahedral geometry by one η^5 -Cp, two PTA, and one *exo*- η^2 -CH₂=CH-CHOH-R ligand (**Figure 1**). The NMR studies showed that the coordinated allylic alcohol is in dissolution thermodynamically in equilibrium between one *exo*- and an *endo*- η^2 -CH₂=CH-CHOH-R conformer, which is strongly influenced by water.^[2] Additionally, complex **1** showed significant catalytic activity for the isomerization of 2-cyclohexenol in solvents such as water (TON=647) and biphasic system (H₂O/Cyclohexane) (TON=3420, occurring up 6 runs) but also in methanol, suggesting that water is not mandatory for accomplishing the isomerization reaction.^[3]

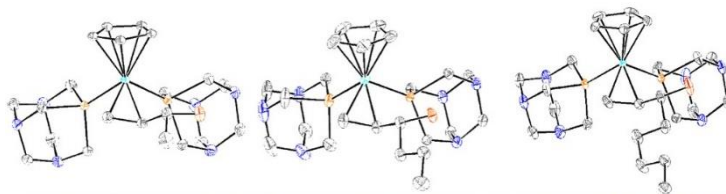


Figure 1. Crystal structures of **2**, **4** and **6**.

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References

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