About the mechanism of the catalytic isomerization of 1-penten-3-ol in water: First crystal structure of a η^2-allylalcohol-intermediate.

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The isomerization of the linear allylic alcohol 1-penten-3-ol into 3-pentanone catalyzed by $[RuCp(PTA)_2(H_2O\text{-}\kappa O)](CF_3SO_3)$ (**1**) (PTA=1,3,5-triaza-7-phosphaadamantane) was studied and two intermediates of the process were characterized (**Figure 1**). Complex $[RuCp(exo\text{-}\eta^2\text{-}CH_2{=}CH\text{-}CHOH\text{-}CH_2\text{-}CH_3)(PTA)_2](CF_3SO_3)\cdot 2H_2O$ (**exo-2**) was isolated and characterized by NMR (**Figure 2a,2b**) and single-crystal X-ray diffraction (**Figure 3**), being the first crystal structure of a metal complex containing a η^2-allylic alcohol ligand.

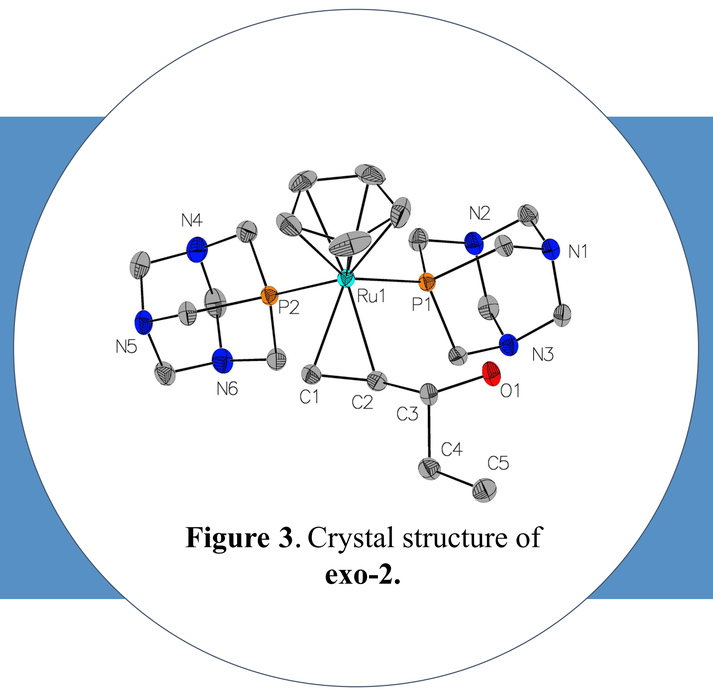

Figure 3. Crystal structure of **exo-2.**

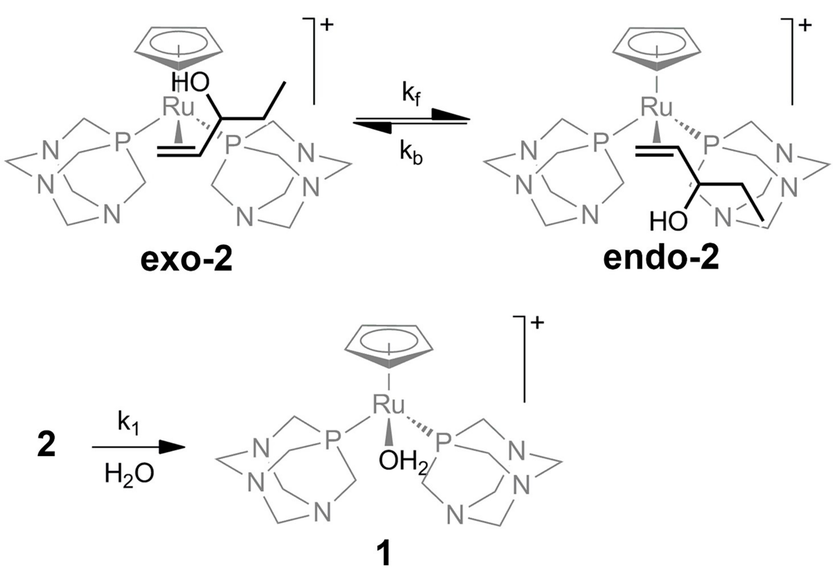

Figure 1. Balance between isomers **exo-2/endo-2**.

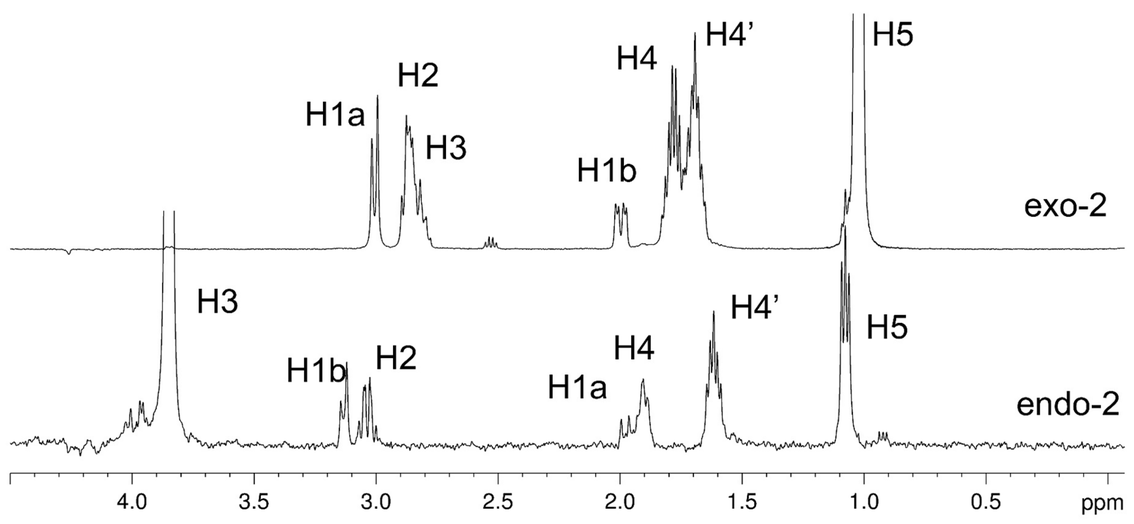

Figure 2a. NMR separation of isomers **exo-2/endo-2**. Stacked selective 1D-TOCSY spectra (CD_3OD/D_2O 5:1, 273 K) irradiated at 1.02 ppm(**endo-2**) and 2.85 ppm(**exo-2**).

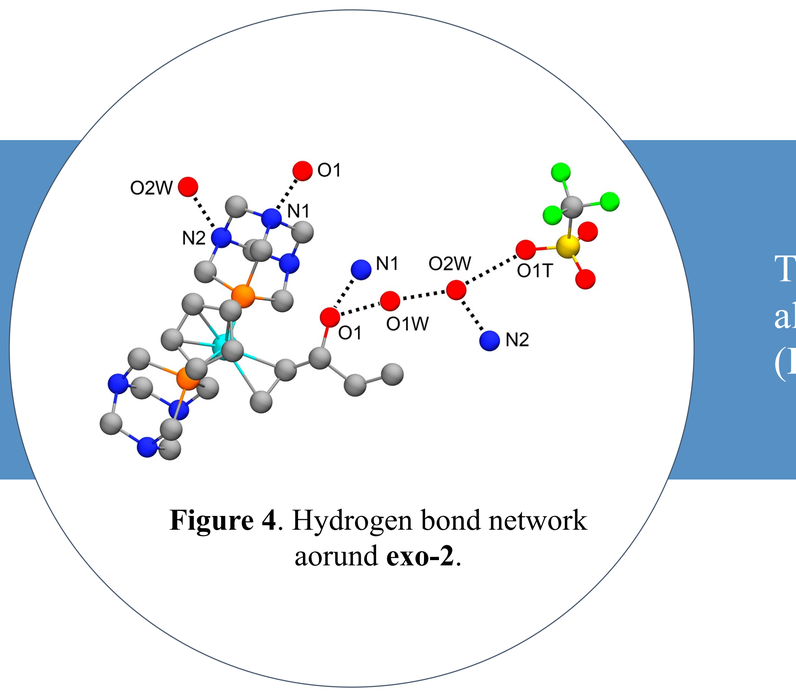

Figure 4. Hydrogen bond network aorund **exo-2**.

The present study evidences that water (**Figure 4**) contributes to the transformation of the allylic alcohol into ketone and that concomitantly as well as **exo-2/endo-2** isomerization takes place (**Figure 5**).

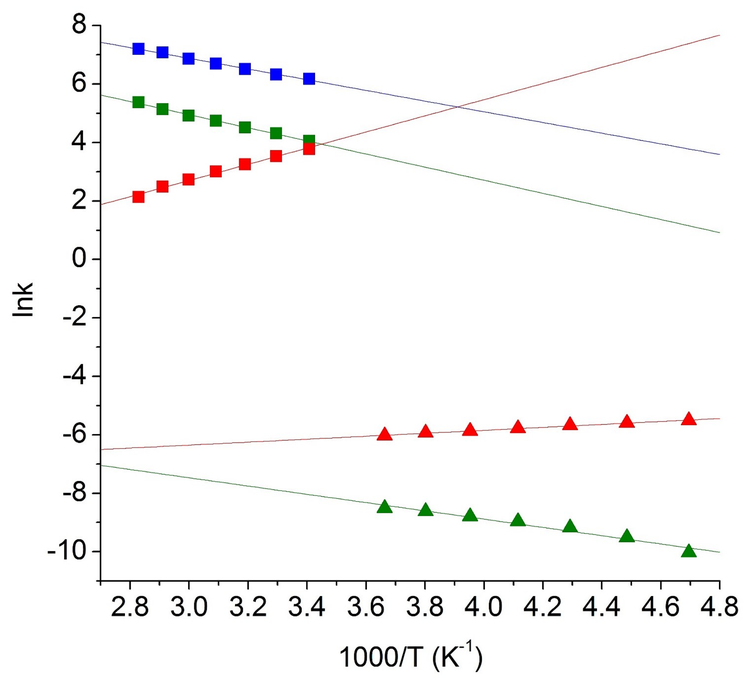

Figure 5. Eyring plots for kf, kb and k1 in D_2O and for kf an kb in CD_3OD/D_2O 5:1. Slope= $-\Delta H^{\pm}/R$; Intercept= $\Delta S^{\pm}$ + ln(kb/h).

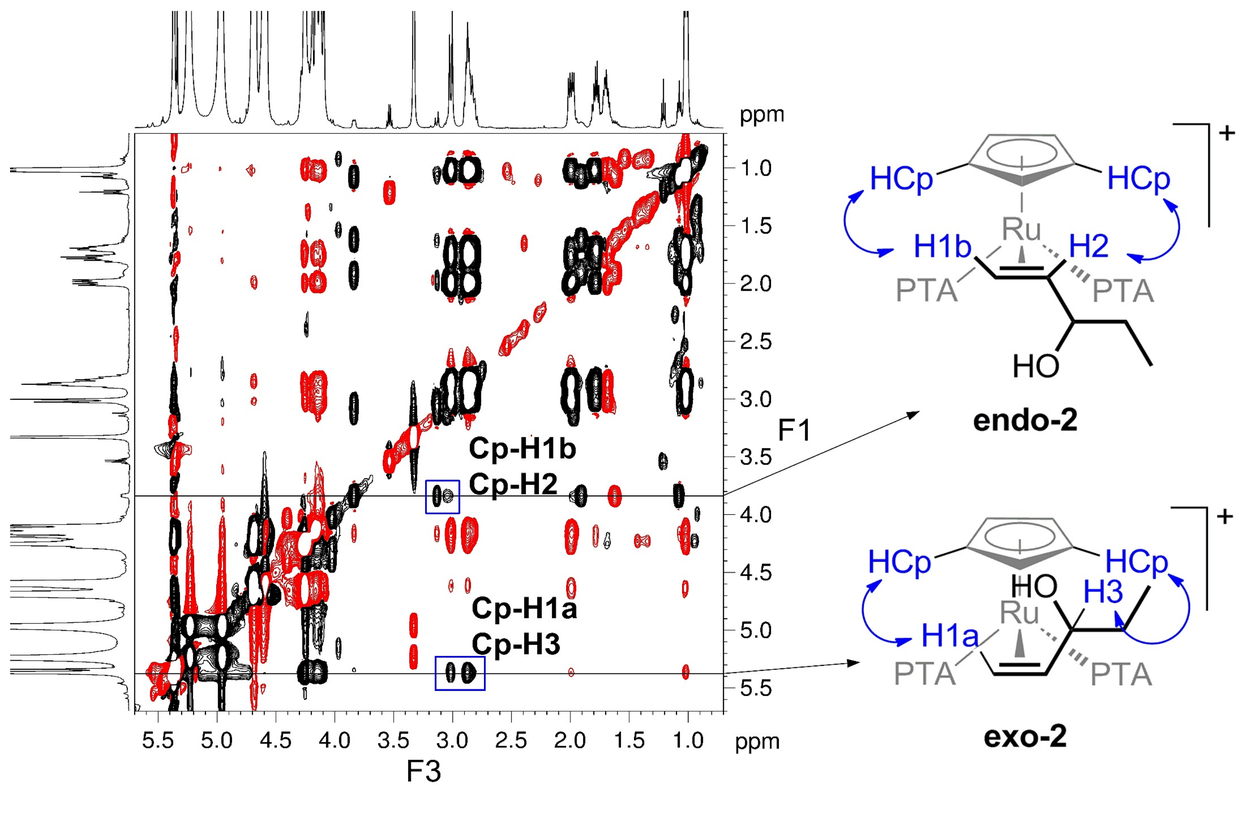

Figure 2b. F1F3 plane of a 3D TOCSY-ROESY (CD_3OD/D_2O 5:1, 273 K) through the resonance chemical shift of the Cp (5.34 ppm). The different spin-lock patterns of **exo-2** and **endo-2** permit to identify the key ROE interactions Cp-H1a, Cp-H3 (**exo-2**) and Cp-H1b, Cp-H2 (**endo-2**).

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References:

[1] Scalambra, F.; Serrano-Ruiz, M.; Romerosa, A., *Dalton Trans.* **2017**, *46*, 5864 - 5871.
[2] Scalambra, F.; López-Sánchez, B.; Holzmann, N.; Bernasconi, L.; Romerosa, A. Article in press.