Electronic Supporting Information

Water and catalytic isomerization of linear allylic alcohols by [RuCp(H₂O-κO)(PTA)₂]⁺
(PTA = 1,3,5-triaza-7-phosphaadamantane)

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Contents

1. Materials and methods

1.1. Synthesis of [RuCp(OH₂)(PTA)₂](CF₃SO₃)·3.5H₂O (1(CF₃SO₃)·3.5H₂O)
1.2. Synthesis of [RuCp(OH₂)(PTA)₂](CF₃SO₃) (1(CF₃SO₃))
1.3. Stability of 1(CF₃SO₃)·3.5H₂O and 1(CF₃SO₃) under air in solid state and water solution.
1.4. Stability of 1(CF₃SO₃)·3.5H₂O and 1(CF₃SO₃) under N₂ and air atmosphere.
1.5. Reactivity of 1(CF₃SO₃)·3.5H₂O with NaCl
1.6. General procedure for catalytic isomerisation of allylic alcohols

2. Characterization of [RuCp(H₂O-κO)(PTA)₂](CF₃SO₃)·3H₂O

2.1. NMR spectra of [RuCp(H₂O-κO)(PTA)₂](CF₃SO₃)·3H₂O

Figure S1: ¹H NMR (300.13 MHz, 22 °C, D₂O) of [RuCp(H₂O-κO)(PTA)₂](CF₃SO₃)·3.5H₂O
Figure S2: ¹³C{¹H} NMR (75.47 MHz, 22 °C, D₂O) of [RuCp(H₂O-κO)(PTA)₂](CF₃SO₃)·3.5H₂O
Figure S3: ³¹P{¹H} NMR (121.49 MHz, 22 °C, D₂O) of [RuCp(H₂O-κO)(PTA)₂](CF₃SO₃)·3.5H₂O
Figure S4: ¹⁹F{¹H} NMR (282.40 MHz, 22 °C, D₂O) of [RuCp(H₂O-κO)(PTA)₂](CF₃SO₃)·3H₂O
Figure S5: ³¹P{¹H} NMR (121.49 MHz, 22 °C, CD₂Cl₂) of [RuCp(H₂O-κO)(PTA)₂](CF₃SO₃)·3.5H₂O
Figure S6: ¹⁹F{¹H} NMR (282.40 MHz, 22 °C, CD₂Cl₂) of [RuCp(H₂O-κO)(PTA)₂](CF₃SO₃)·3H₂O
2.2. IR spectrum of [RuCp(H$_2$O-$\kappa$O)(PTA)$_2$](CF$_3$SO$_3$)$\cdot$3H$_2$O

**Figure S7:** IR (KBr) of [RuCp(H$_2$O-$\kappa$O)(PTA)$_2$](CF$_3$SO$_3$)$\cdot$3H$_2$O

3. References

1. Materials and methods

All chemicals were of reagent grade and, unless otherwise stated, were used as received from commercial suppliers. Likewise all reactions were carried out in a pure argon atmosphere by using standard Schlenk-tube techniques. Water was deoxygenated prior to use and organic solvents have been dried through standard methods. The complex [RuClCp(PTA)$_2$] was prepared as described in the literature.\textsuperscript{1} \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300.13 MHz (\textsuperscript{1}H) and 75.47 (\textsuperscript{13}C), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (\textsuperscript{1}H) or the deuterated solvent multiplet (\textsuperscript{13}C). \textsuperscript{31}P\{\textsuperscript{1}H\} and \textsuperscript{19}F\{\textsuperscript{1}H\} NMR spectra were recorded on the same instrument operating at 121.49 and 282.40 MHz, respectively. Chemical shifts for \textsuperscript{31}P\{\textsuperscript{1}H\} NMR were measured relative to external 85% H$_3$PO$_4$ and for \textsuperscript{19}F\{\textsuperscript{1}H\} NMR to CFCl$_3$ with downfield values taken as positive in both cases. All NMR spectra were obtained at 25 °C. Infrared spectra were recorded as KBr disks using a Bruker Vertex 70 FT-IR spectrometer. Elemental analyses (C, H, N, S) were performed on a Fisons Instrument EA1108 elemental analyser. Gas chromatographic measurements were made on a Shimadzu GC-2010 Plus using a Supelco SP-2330 30 m, 0.25 mm, 0.2 μm column and flame ionization detector.

1.1 Synthesis of [RuCp(H$_2$O-$\kappa$O)(PTA)$_2$](CF$_3$SO$_3$)$\cdot$3.5H$_2$O (1(CF$_3$SO$_3$)$\cdot$3.5H$_2$O).
Into a solution containing complex \([\text{RuClCp (PTA)}_2]\) (1.0 g, 1.94 mmol) dissolved in 50 mL of water was added a solution of \(\text{AgCF}_3\text{SO}_3\) (493.5 mg, 1.92 mmol) in 20 mL of water. The resulting mixture was sonicated for 2 h at room temperature and then the precipitated AgCl was filtered through celite. The solvent was removed to dryness giving rise to an orange powder, which was washed with \(\text{Et}_2\text{O}\) (3 x 30 mL) and dried under vacuum. Brown-orange crystals of the complex suitable for single crystal X-ray diffraction grew from an aqueous 1.3 M solution after three days. Crystals yield: 1.17 g, 85%. \(S_{25,\text{H}_2\text{O}}\) (g/mL): 2. Elemental analysis for powder sample \(\text{C}_{18}\text{H}_{38}\text{F}_3\text{N}_6\text{O}_{7.5}\text{P}_2\text{RuS}\) (710.6 g·mol\(^{-1}\)): Found C: 30.21; H 5.43; N 11.50; calcd. C 30.42; H 5.39; N 11.82. IR (KBr, cm\(^{-1}\)): 3082 (m); 2925 (m), 2896 (m); 1446 (m); 1412 (m), 1036 (s), 1014 (s), 972 (s); 1281 – 1260 (s), 1171 (s), 1098 (m); 948 (m), 893 (m), 803 (m), 644 (m); 575 (s). \(^1\text{H}\) NMR (300.13 MHz, 22 °C, \(\text{D}_2\text{O}\)): \(\delta\) 4.06 (m, NCH\(_2\)P, 12H), 4.53 (m, NCH\(_2\)N, 12H), 4.71(s, Cp, 5H). \(^{13}\text{C}\{\text{\textit{1}}\text{H}\}\) RMN (75.467 MHz, 22 °C, \(\text{D}_2\text{O}\)): \(\delta\) 53.70 (t, \(^{1}J_{\text{CP}} = 8.4\) Hz, NCH\(_2\)P), 70.61 (s, NCH\(_2\)N), 75.45 (s, Cp). \(^{31}\text{P}\{\text{\textit{1}}\text{H}\}\) NMR (121.49 MHz, 22 °C, \(\text{D}_2\text{O}\)): \(\delta\) -24.75 (s). \(^{19}\text{F}\{\text{\textit{1}}\text{H}\}\) NMR (282.40 MHz, 22 °C, \(\text{D}_2\text{O}\)): \(\delta\) -78.908 (s).

1.2 Synthesis of \([\text{RuCp(H}_2\text{O-κO})(\text{PTA})_2](\text{CF}_3\text{SO}_3)\) (1(CF\(_3\)SO\(_3\))).

The complex \(1(\text{CF}_3\text{SO}_3)\cdot3.5\text{H}_2\text{O}\) (100 mg, 0.14 mmol) was dissolved in 10 mL of dry EtOH and then the solvent fully eliminated. The dissolution and evaporation process was repeated with the obtained powder for 3 more times. The final resulting yellow powder was stored under N\(_2\).

1.3 Stability of 1(CF\(_3\)SO\(_3\))·3.5H\(_2\)O and 1(CF\(_3\)SO\(_3\)) under air in solid state and water solution.
Crystalline $\text{1(CF}_3\text{SO}_3)\cdot3.5\text{H}_2\text{O}$ (7 mg) and $\text{1(CF}_3\text{SO}_3)$ were kept under air at room temperature, the $^{31}\text{P}\{^{1}\text{H}\}$ NMR (D$_2$O) showed that the compound decomposes slowly under this conditions, achieving the total decomposition after 10 days. The stability in water solution was evaluated by dissolution of crystals of $\text{1(CF}_3\text{SO}_3)\cdot3.5\text{H}_2\text{O}$ (7 mg) and powder $\text{1(CF}_3\text{SO}_3)$ (7 mg) in 0.5 mL of D$_2$O, the obtained solution cooled over ice and then air was bubbled during 2 min. The complete decomposition of the complex was observed before 3 days at room temperature and 2 h at 80 ºC. For both experiments the unique final compound observed by $^{31}\text{P}\{^{1}\text{H}\}$ NMR was O=PTA.

1.4 Stability of $\text{1(CF}_3\text{SO}_3)\cdot3.5\text{H}_2\text{O}$ and $\text{1(CF}_3\text{SO}_3)$ under N$_2$ and air atmosphere.

In 5 mm NMR tubes the complex $\text{1(CF}_3\text{SO}_3)\cdot3.5\text{H}_2\text{O}$ (14 mg, 0.02 mmol) and $\text{1(CF}_3\text{SO}_3)$ (13 mg, 0.02 mmol) were dissolved in 0.5 mL of D$_2$O under N$_2$. The NMR tubes were cooled at 5 ºC and air bubbled for 5 minutes. The solutions were checked by $^{31}\text{P}\{^{1}\text{H}\}$ NMR at room temperature showing that complex 1 is stable in water solution under N$_2$ for one month but under air was decomposed in 1 hour, being the main signal observed by $^{31}\text{P}\{^{1}\text{H}\}$ NMR due to PTA=O.

1.5 Reactivity of $\text{1(CF}_3\text{SO}_3)\cdot3.5\text{H}_2\text{O}$ with NaCl

Crystals of $\text{1(CF}_3\text{SO}_3)\cdot3.5\text{H}_2\text{O}$ (14 mg, 0.02 mmol) were dissolved in 0.5 mL of D$_2$O into a 5 mm NMR tube and then NaCl (1.2 mg, 0.02 mmol) was added. After 5 min the $^{31}\text{P}\{^{1}\text{H}\}$ NMR showed a singlet that only could be ascribable to [RuClCp(PTA)$_2$], which was the unique remaining signal after 2 h.
1.6 General procedure for catalytic isomerisation of allylic alcohols

In a typical reaction a variable volume of the studied substrate (or a mixture of substrates) was introduced into a solution of $1$(CF$_3$SO$_3$)$\cdot$3.5H$_2$O (9.7 mg, 0.15 mmol) in 6 mL of water and/or MeOH. Experiments were also performed using the substrate as solvent without and with variable amounts of water. In this case the water/allylic alcohol mixtures were composed using calibrated micropipettes. The preparation was made under air and under N$_2$, in this last case the used solvent was previously bubbled with N$_2$. The mixture was kept at desired reaction temperature in a sealed tube and stirred regularly (1000 rpm). At the chosen time the reaction was cooled at room temperature and extracted with CHCl$_3$ (5 x 1.5 mL for 1 mol% catalyst; 5 x 3 mL for 0.1 mol% catalyst). The collected organic phases were passed through a column (5 x 50 mm) packed with 60 mesh silica gel. The conversion of allylic alcohol into ketone was determined by gas chromatography. The identity of the ketones was assessed by comparison with commercially available pure samples. Reactions were checked by $^{31}$P{$^1$H} NMR by extracting some aliquots at regular reaction time.

1.7 Catalytic isomerisation of allylic alcohols with 1(CF$_3$SO$_3$) in presence of NaCl.

Using the general procedure indicated previously the substrates were catalysed in water with 1(CF$_3$SO$_3$) in presence of 5 eq. of NaCl. The observed isomerization conversions were similar to that produced by the complex [RuClCp(PTA)$_2$] in presence of NaCl.$^2$

1.8 X-ray structure Determination.

Data of compound 1(CF$_3$SO$_3$)$\cdot$3.5H$_2$O was collected on an Oxford Diffraction Xcalibur diffractometer (Rutherford Appleton Laboratory. Oxfordshire, U.K.), using monochromated Mo
Kα radiation (λ = 0.7107 Å) at 100 K. The crystal parameters and other experimental details of the data collections are summarized in Table 1. The structures were solved by direct methods SHEL97 and refined by full-matrix least squares methods with SHEL-XTL and refined by least-squares procedures on $F^2$ and final geometrical calculations and graphical manipulations were carried out with the SHELXS-XTL package. All the non-hydrogen non-disordered atoms were refined with anisotropic atomic displacement parameters. Three 0.5 disordered (refined isotropically) water molecules were found. All hydrogen atoms, except for disordered water molecules, were included in calculated positions and refined using a riding model. Crystallographic data for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 1511862.

**Table S1.** Selected Crystallographic Data for 1(CF$_3$SO$_3$)$\cdot$3.5H$_2$O

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2. Characterization of $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2](\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$

2.1 NMR spectra of $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2](\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$

Figure S1: $^1\text{H}$ NMR (300.13 MHz, 22 °C, D$_2$O) of $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2](\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$

Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, 22 °C, D$_2$O) of $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2](\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$
**Figure S3**: $^{31}\text{P}^{1\text{H}}$ NMR (121.49 MHz, 22 °C, D$_2$O) of [RuCp(H$_2$O-$\kappa O$)(PTA)$_2$](CF$_3$SO$_3$)-3H$_2$O

**Figure S4**: $^{19}\text{F}^{1\text{H}}$ NMR (282.40 MHz, 22 °C, D$_2$O) of [RuCp(H$_2$O-$\kappa O$)(PTA)$_2$](CF$_3$SO$_3$)-3H$_2$O
Figure S5: $^1$H NMR (300.13 MHz, 22 °C, CD$_2$Cl$_2$) of [RuCp(H$_2$O-κO)(PTA)$_2$](CF$_3$SO$_3$)·3.5H$_2$O
**Figure S6:** $^{31}$P NMR (121.49 MHz, 22 °C, CD$_2$Cl$_2$) of [RuCp(H$_2$O-κO)(PTA)$_2$](CF$_3$SO$_3$)·3H$_2$O

![P NMR Spectrum](image)

**Figure S7:** $^{19}$F{$^1$H} NMR (282.40 MHz, 22 °C, CD$_2$Cl$_2$) of [RuCp(H$_2$O-κO)(PTA)$_2$](CF$_3$SO$_3$)·3H$_2$O

**2.2 IR spectrum of [RuCp(H$_2$O-κO)(PTA)$_2$](CF$_3$SO$_3$)·3H$_2$O**

![IR Spectrum](image)

**Figure S8:** IR (KBr) of [RuCp(H$_2$O-κO)(PTA)$_2$](CF$_3$SO$_3$)·3H$_2$O
3. References