The dual role of *cis*-[$RuCl_2(dmso)_4$] in the synthesis of new water-soluble Ru(II)-phosphane complexes and in the catalysis of redox isomerization of allylic alcohols in aqueous-organic biphasic systems

Antal Udvardy, Attila Csaba Bényei, Ágnes Kathó*

Department of Physical Chemistry, University of Debrecen, Debrecen, P.O.B. 7, H-4010, Hungary.

* Corresponding author. Á. Kathó: phone: +36-52-512900; fax: +36-52-512915; E-mail: katho.agnes@science.unideb.hu

Abstract

New air-stable, water-soluble Ru(II)-phosphane complexes were synthesized in high purity by the reaction of *cis*-[$RuCl_2(dmso)_4$] with 2 equivalents of 1,3,5-triaza-7-phosphaadamantane (pta) and its *N*-methyl and *N*-benzyl derivatives (pta-Me and pta-Bn, respectively). All new complexes were characterized by elementary analysis and spectroscopic methods (NMR, ESI MS) and the molecular structures of *cis*-*cis*-*trans*-[$RuCl_2(dmso)_2(pta)_2$], *cis*-*cis*-*trans*-[$RuCl_2(dmso)_2(pta\text{-}H)_2]Cl_2$ (obtained in acidic solutions) and that of *cis*-*cis*-*trans*-[$RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)_2$ were determined by single crystal X-ray diffraction.

Under mild conditions, *cis*-[$RuCl_2(dmso)_4$] actively catalyzed the transformation of allylic alcohols into the corresponding ketones with 100 % selectivity while in the same reaction the new Ru(II)-pta complexes showed moderate activity and selectivity.

Highlights

- *cis*-[$RuCl_2(dmso)_4$] (**1**) was used as a water-soluble Ru(II) source for synthesis
- New water-soluble Ru(II)-complexes were obtained from **1** and phosphatriazaadamantanes (L).
- Single crystal X-ray structures evidenced *cis*-*cis*-*trans*-[$RuCl_2(dmso)_2L_2$] geometries.

- **1** and the new complexes actively catalyzed the isomerization of allylic alcohols.

Keywords: water soluble phosphanes, ruthenium, allylic alcohols, isomerization, biphasic catalysis

1. Introduction

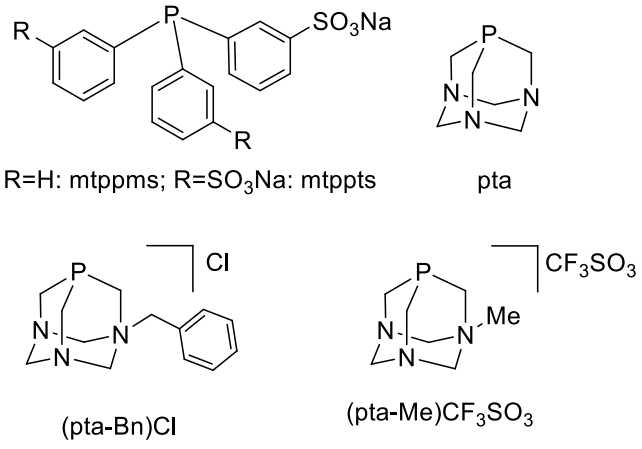
Water is widely considered useful for elimination of hazardous organic solvents in organic synthesis and catalysis. An additional green feature of applying water-soluble catalysts is that the use of aqueous-organic biphasic systems allows recycling of the catalyst under mild conditions by easy phase separation.[1-4]

The chemistry of Ru(II) catalysts containing water-soluble phosphanes as ligands has received considerable attention in recent years.[4] In many cases, Ru(II)-complexes of tertiary phosphanes applied in homogeneous catalysis are synthesized from $RuCl_3 \cdot aq$ as starting material. However, ligand exchange reactions of water-soluble Ru(II)-complexes containing sufficiently labile ligands allow more precise control of the composition and structure of the products.[5] For example, $[Ru(H_2O)_6](tos)_2$ (tos = *p*-toluene-sulfonate) can be efficiently used for this purpose. However, this compound is tedious to synthesize, highly sensitive to oxygen and is stable only in acidic solutions.[6,7]

The ruthenium(II) dimethylsulfoxide complexes, *cis*- and *trans*-$[RuCl_2(dmso)_4]$ are conveniently prepared and easy-to-handle compounds.[8,9] Earlier *cis*-$[RuCl_2(dmso)_4]$, **1** was used as precursor for the synthesis of Ru(II)-complexes with aryl, sulfonated aryl, and cyclohexyl phosphanes**,** both in aqueous and in non-aqueous media.[8, 10-14] In addition, several ligands with N- and O-donor atoms were studied in substitution reactions of both isomers of $[RuCl_2(dmso)_4]$.[15] This was –in part– motivated by the expected biological effects

of the products.[16-19] While **1** itself also shows antitumor and remarkable antimetastatic activity, certain of its substituted derivatives are even more effective.[20]

1,3,5-Triaza-7-phosphadamantane (1,3,5-Triaza-7-phosphatricyclo[3.3.1.1]decane, pta) is a small, aliphatic tertiary phosphane with a cage structure, well soluble in water. Ru(II)-pta complexes such as $[RuCl_2(pta)_4]$ have already been applied in biphasic catalysis[21] and the field is well reviewed.[5, 22,23] In contrast to other tertiary aminoalkylphosphanes where alkylation takes place on phosphorus, pta is alkylated smoothly on one of its nitrogen atoms.[24] The charge and steric bulk of such ligands are changed by quaternarization and this is reflected also in their water-solubility.[25] Coordination properties of alkyl-pta derivatives and catalytic applications of their complexes received less attention than those of pta. Rare examples include the use of (pta-Bn)Cl (Scheme 1) in Rh-catalyzed hydroformylation of higher olefins[26,27] and that of $[(\eta\text{-arene})RuCl_2(pta\text{-}Bn)]Cl$ in hydration of nitriles.[28] $[CpRuCl(pta\text{-}Me)_2](OSO_2CF_3)_2$ and $[CpRu(pta\text{-}Me)_2(H_2O)](OSO_2CF_3)_3$ were found effective catalysts of the redox isomerization of allylic alcohols.[29] In addition, pta has been successfully used for synthesis of anticancer Ru(II)-arene complexes[30]. It is interesting, therefore, that reactions of pta and its derivatives with *cis*- or *trans*-$[RuCl_2(dmso)_4]$ hitherto have not been studied.



Scheme 1. Water-soluble phosphanes used in this study

Herein we report the use of **1** for the synthesis and characterization of several new water-soluble Ru(II)-complexes containing the ligands shown in Scheme 1, and an exploratory study of their catalytic activity in the hydrogenation and isomerisation of allylic alcohols. Strikingly, **1** itself was only scarcely used[31,32] as catalyst in such reactions so its study was also accomplished.

2. Results and Discussion

2.1. Reactions of cis-[$RuCl_2(dmso)_4$] with water-soluble phosphanes

According to the literature,[10] boiling of a toluene suspension of **1** and three equivalents of the water-soluble phosphane, *m*tppms, for 2 h resulted in formation of the mononuclear [$RuCl_2$(dmso)(*m*tppms)$_3$]. However, we found this reaction rather slow and incomplete and ^{31}P NMR indicated the formation of more than one product. No significant improvement/optimization could be reached by varying the ligands (*m*tppms or *m*tppts), ligand to metal ratio (1 to 3), solvents (toluene, methanol or water), reaction time or reaction temperature.

In contrast to the aromatic phosphanes, pta reacted cleanly with **1** in chloroform. The reaction was followed by uv-vis spectrophotometry (Figure 1.). The isosbestic point at λ = 346 nm refers to the formation of a single product (**2**). Formation of **2** became complete in two hour and there were no further spectral changes.

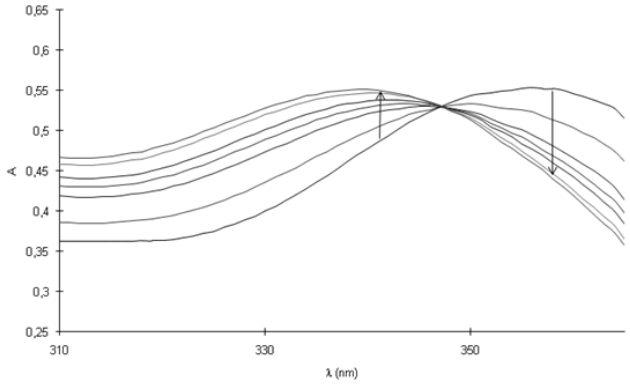
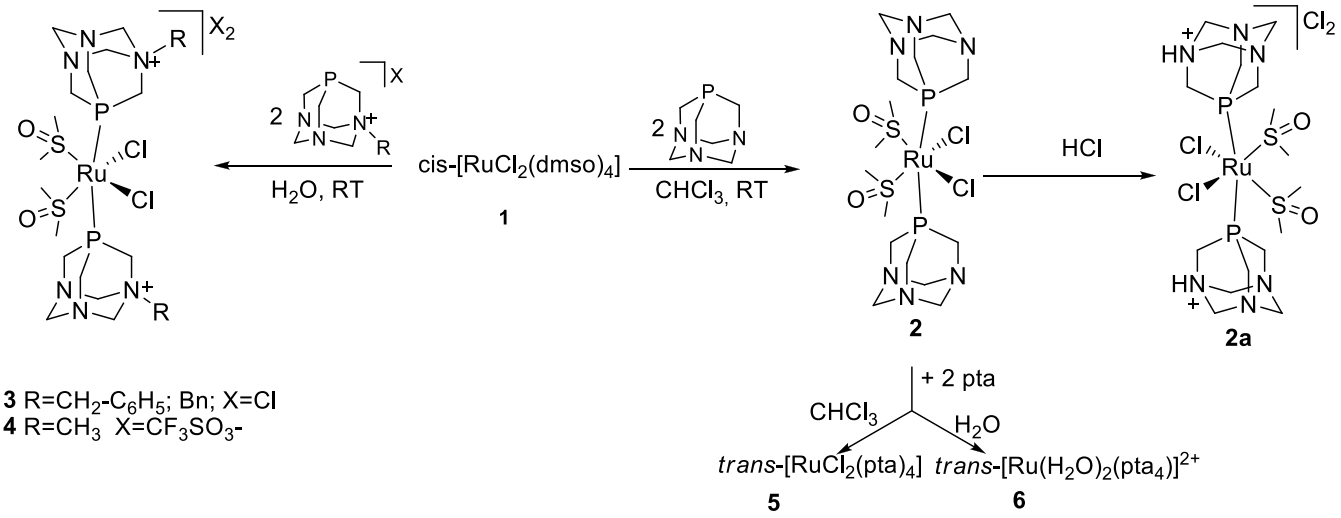


Figure 1. Changes in uv-vis spectra measured in the solution of *cis*-[$RuCl_2(dmso)_4$] (**1**) and 2 pta as a function of time. Conditions: c(**1**) = 0.001 M; T = 25 °C; t = 0, 15, 30, 45, 60, 90 and 120 min.

Only one singlet at δ = -60.7 ppm (in $CDCl_3$) appeared in the ^{31}P NMR spectrum. Based on integrated ^{1}H signal intensities of free and coordinated dmso as well as those of coordinated pta we concluded that the product was [$RuCl_2(dmso)_2(pta)_2$] (**2**). The singlet ^{31}P signal refers to the phosphanes being in trans position each to the other (Scheme 2). This observation is in agreement with that substitution of chloride in this solvent is not favoured. The molecular structure of **2** in solid state was confirmed by single crystal x-ray diffraction (see later).



Scheme 2. Synthesis of Ru(II)-complexes containing triazaphosphaadamantanes

At room temperature, coordination of a further phosphane ligand to **2** is slow and at a 4:1 [pta]:[**1**] ratio only [$RuCl_2(dmso)_2(pta)_2$] (**2**) was formed in the first 90 min of the reaction. During the same reaction time but at reflux temperature, an approximately 3:2 mixture of **2** and the known *trans*-[$RuCl_2(pta)_4$], **5** was obtained (Scheme 2);[21,33] upon further boiling the latter compound precipitated from the solution.

Based on these observations $[RuCl_2(dmso)_2(pta)_2]$ could be synthesized in pure form when $[RuCl_2(dmso)_4]$ and pta were let to react in a 1:2 ratio in chloroform for two hours at room temperature (yield 82 %). In aqueous solution **2** is characterized by a singlet resonance at δ = -57.9 ppm in the ^{31}P NMR spectrum (Table 1).

Table 1. ^{31}P-NMR data of water soluble Ru(II)–phosphane complexes in D_2O

	^{31}P-NMR (ppm)
$[RuCl_2(dmso)_2(pta)_2]$ (**2**)	-57.9*
$[RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)_2$ (**3**)	-38.9
$[RuCl_2(dmso)_2(pta\text{-}Bn)_2]Cl_2$ (**4**)	-36.4
trans-$[RuCl_2(pta)_4]$ (**5**)	-51.6
trans-$[Ru(H_2O)_2(pta)_4]^{2+}$ (**6**)	-52.9

* in $CDCl_3$: δ = -60.7 ppm

Since both pta and **1** are soluble in water, their reaction was studied in aqueous medium, as well. At room temperature, only the characteristic singlet resonance of **2** (δ = -57.9 ppm in D_2O) was observed in the ^{31}P NMR spectra independent of the [pta]:[**1**] ratio being 1 or 2. In contrast, at [pta]:[**1**]=3, albeit in the first 30 min of the reaction exclusively **2** was detected, later a new singlet (δ = -52.9 ppm) grew in gradually. Formation of this new species at room temperature is slow even at higher ligand excess ([pta]:[**1**]=4).The singlet ^{31}P NMR resonance of this new compound is slightly different from that of *trans*-$[RuCl_2(pta)_4]$ (δ = -51.6 ppm in D_2O),[21,33] however, it shows a similar presence of magnetically equivalent phosphane ligands. We reasoned, that during the reaction of **1** with pta in water, aquation could lead to the formation of *trans*-$[Ru(H_2O)_2(pta)_4]^{2+}$ (**6**). This is corroborated by the finding that when $[RuCl_2(dmso)_2(pta)_2]$ (**2**) was reacted first with $AgNO_3$ followed by the addition of 2 equivalents of pta, after a reaction time of 2 h at room temperature only the singlet at δ = -52.9 ppm was observed. The same signal was observed when **1** was

dehalogenated in reaction with $AgNO_3$, followed by addition of 4 equivalents of pta. Furthermore, addition of KCl (5 Cl^-/Ru) to these solutions resulted in the appearance of the ^{31}P NMR signal of *trans*-$[RuCl_2(pta)_4]$ (**5**) on the expense of the one at -52.9 ppm.

Note, that in the reaction of pta and $[Ru(H_2O)_6]^{2+}$ only *cis*-$[Ru(H_2O)_2(pta)_4]^{2+}$ could be detected.[7] The *cis*-$[Ru(H_2O)_2(pta)_4]^{2+}$ compound was also obtained by addition of AgOTf to the product mixture of *cis*-$[RuCl_2(pta)_4]$ and $[RuCl(H_2O)(pta)_4]^+$ formed by visible light irradiation of **5** in water.[34]

It is also worth mentioning, that in contrast to the reaction of $[Ru(H_2O)_6]^{2+}$ and pta, formation of mono- or tris-phosphane complexes was not observed.

In acidic solutions both free and coordinated pta can be protonated on one of the nitrogen atoms. Figure 2 shows the shift of the ^{31}P NMR signal of $[RuCl_2(dmso)_2(pta)_2]$ as a function of the acidity of its aqueous (D_2O) solutions.

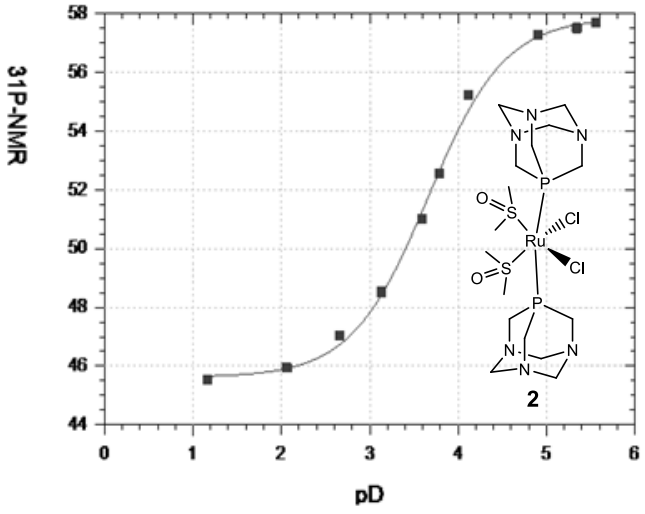


Figure 2. Experimental (squares) and calculated (solid line) ^{31}P NMR chemical shift of $[RuCl_2(dmso)_2(pta)_2]$ *vs* pD.

Henderson-Hasselbach analysis of the data gave pK_a = 3.40 (applying the pH = pD – 0.44 scaling[35]) and the ^{31}P NMR shifts calculated with this value are also shown on Figure 2. Literature values of the pK_a of pta vary in the range of 5.63-6.0,[7, 36-38] so the protonation of coordinated pta in **2** takes place under more acidic conditions relative to the free ligand. Single crystals of **2a** were obtained from hydrochloric acid solutions of **2**. X-ray diffraction analysis of the molecular structure of **2a** (see Supplementary Information: Figure S1) showed that both phosphane ligands had one protonated nitrogen each.

The most intensive peak in the ESI mass spectrum of **2** at m/z = 643.030 belongs to the monoprotonated molecule, conceivably $[RuCl_2(dmso)_2(pta)(ptaH)]^+$ (Figure S2), furthermore, loss of dmso and chloride are also indicated by the signals at m/z = 565.070 ($[RuCl_2(dmso)(pta)(ptaH)]^+$) and at m/z = 607.048 ($[RuCl(dmso)_2(pta)_2]^+$).

The reaction of **1** and (pta-Bn)Cl in aqueous solution at room temperature at a [pta-Bn]:[**1**]=2 ratio yielded **3** with $[RuCl_2(dmso)_2(pta\text{-}Bn)_2]^{2+}$ as the sole product. The uv-visible spectrum of the reaction mixture underwent changes similar to those shown above for the case of **1** with two equivalents of pta, and the spectral parameters of **3** are also similar to those of **2**. The reaction was complete in 1.5 h, and no sign of any other species was detected in the NMR spectra even at higher temperature (up to T = 70 °C).

3 is stable to air and its best solvent is water. Due to its charge solubility of **3** in water is approximately 1.5 times higher than that of the neutral **2** (see Experimental). The most intensive ESI MS peak at m/z = 576.100 belongs to $[RuCl_2(dmso)_2(pta\text{-}Bn)]^+$ (Figure S2). The mono-dmso complex ion, $[RuCl_2(dmso)(pta\text{-}Bn)]^+$ (m/z = 500.003) and chloride-associated ions such as $\{[RuCl_2(dmso)_2(pta\text{-}Bn)_2]Cl\}^+$ (m/z = 860.100) and $\{[RuCl_2(dmso)(pta\text{-}Bn)_2]Cl\}^+$ (m/z = 782.100), could also be identified.

$[RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)_2$ (**4**) was prepared in the reaction of **1** with (pta-Me)CF_3SO_3. This ligand and **1** ([pta-Me]:[**1**]=2) were reacted in water (or methanol) at room

temperature for 2 h yielding exclusively $[RuCl_2(dmso)_2(pta\text{-}Me)_2]^{2+}$ what was isolated as triflate salt.

4 is stable to air and its solubility is approximately the double of that of the neutral **2**, and is somewhat higher than that of **3**The most intensive ESI-MS peak at m/z = 499.947 belongs to $[RuCl_2(dmso)_2(pta\text{-}Me)]^+$ (Figure S2). The mono-dmso complex ion, $[RuCl_2(dmso)(pta\text{-}Me)]^+$ (m/z = 421.947) and triflate-associated ions such as $\{[RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)\}^+$ (m/z = 821.013) and $\{[RuCl_2(dmso)(pta\text{-}Me)_2](CF_3SO_3)\}^+$ (m/z = 743.005), and $\{[RuCl_2(pta\text{-}Me)_2](CF_3SO_3)\}^+$ (m/z = 665.039) could also be identified.

*2.2. Molecular structures of cis-cis-trans-$[RuCl_2(dmso)_2(pta)_2]$ (**2**), cis-cis-trans-$[RuCl_2(dmso)_2(ptaH)_2]Cl_2$ (**2a**) and cis-cis-trans-$[RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)_2$ (**4**) in solid state*

Results of X-ray structure determinations are summarized in Table 2**.**

Search of the Cambridge Structural Database (Ver. 5.33, Update May, 2012)[39] revealed that all $RuCl_2P_2S_2$ complexes in the database contain exclusively bidentate ligands with P-S, P-P or S-S donor pairs. In fact, **2**, **2a** and **4** are the first crystallographically characterized complexes with $RuCl_2P_2S_2$ coordination containing *monodentate* ligands. The two phosphorus atoms are in trans-position, however, the P-Ru-P angles significantly deviate from 180° being 161° in **2,** 168° in **2a** and 165° in **4**. In the vast number of RuP_2 complexes (over 4500 hits in CSD) the P-Ru-P angles rarely deviate from 180° or 90°: in the crystals obtained from $[Ru(H_2O)_6]^{2+}$ with pta or its derivatives[7] (*trans*-$[Ru(H_2O)_4(pta)_2]^{2+}$, *trans*-$[Ru(H_2O)_4(pta\text{-}Me)_2]^{4+}$, *trans*-$[Ru(H_2O)_4(pta\text{-}H)_2]^{4+}$) as well as in *trans*-$[RuI_4(pta\text{-}Me)_2]$[40] and *trans*-$[RuCl_4(pta\text{-}H)_2]$[41] this angle is 180° as ruthenium atom is in the inversion centre of the lattice.

In addition, for $[RuCl_2(PPh_3)_2X]$ (X=further coordinating ligand) complexes the only complex with non-linear P-Ru-P bonds is $RuCl_2(PPh_3)_3$.[42-44] In contrast, Ru(II) complexes containing neutral or protonated pta seem to be more prone for displaying non-linear P-Ru-P angles. For example, earlier we have found[21] 165° in *cis*-$[RuCl_2(pta)_4]$ and 163° for the protonated analog, *cis*-$[RuCl_2(pta\text{-}H)_4]^{4+}$. Later it was shown,[33] that in *trans*-$[RuCl_2(pta)_4]$, too, the P-Ru-P angle for the trans phosphanes significantly differed from 180°. PMe_3-containing Ru(II) complexes behave similarly as pta complexes with bent P-Ru-P coordination, *e.g* 164-165° in $[RuCl_2(PMe_3)_4]$.[45,46] For structures **2**, **2a** and **4** bond distances are in the expected range (see captions of Figures 3 and 4, and Figure S1). CSD data for comparison: in pta-containing Ru(II) complexes the average Ru-Cl and Ru-P distances are 2.44(13)Å and 2.32(16)Å, respectively, and for all RuS_2P_2 complexes Ru-S bond distances are 2.41(41) Å.

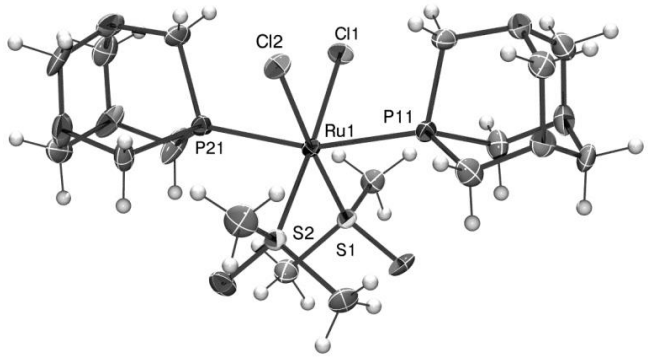


Figure 3. ORTEP view of **2** at 50 % probability level. Solvate chloroform molecule is omitted for clarity. Selected bond length and bond angle data: Ru1 – P11: 2.3866(18) Å ; Ru1 – P21: 2.3623(18) Å ; Ru1 – S1: 2.2522(17) Å ; Ru1 – S2: 2.2644(19) Å ; Ru1 – Cl1: 2.449(2) Å ; Ru1 – Cl2: 2.4292(17) Å ; P21 – Ru1 – P11: 161.53(6)° ; S1 – Ru1 – S2: 89.31(6)° ; Cl1 – Ru1 – Cl2: 89.83(6)°.

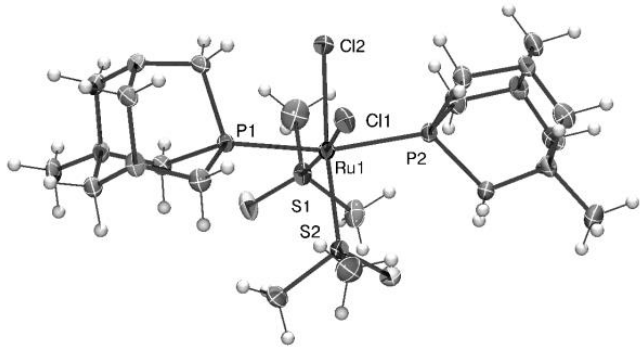


Figure 4. ORTEP view of **4** at 50 % probability level. Water molecules and triflate counter ions are omitted for clarity, only one molecule from the asymmetric unit is shown. Selected average bond length and bond angle data: Ru – P : 2.365(9) Å ; Ru – S: 2.265(6) Å ; Ru – Cl: 2.440(5) Å ; P – Ru – P: 165(5)^o ; S – Ru – S: 90.3(9)^o ; Cl – Ru – Cl: 86(2)^o.

The structure of **4** contains two complexes in the asymmetric unit with the appropriate 4 triflate counter ions. The water molecule in **4** is in two positions with occupancy of 0.5 and various orientation in the channel. The structures of **2** and **4** are stabilized by C-H..O, C-H..N C-H..F or C-H..Cl hydrogen bonds.

The solid state structure of **2a** is also stabilized by both electrostatic and secondary interactions. Extensive hydrogen bond network is formed between water molecules or protonated pta ligands as hydrogen donors and water oxygen atoms or chloride ions as acceptors. However, all five water positions in the structure have partial occupancy of 0.5 resulting in 2.5 equivalents of solvent water per molecules of **2a** complex. The layered structure contains water filled solvent channels.

Table 2. Summary of crystallographic data and structure refinement results for the complexes

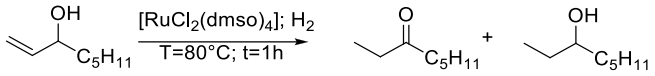
Compound No.	**2**·$CHCl_3$	**2a**·$3H_2O$	**4**·H_2O
Empirical formula	$C_{17}H_{37}Cl_5N_6O_2P_2S_2Ru$	$C_{17}H_{44}Cl_4N_6O_5P_2S_2Ru$	$C_{20}H_{42}Cl_2F_6N_6O_9P_2S_4Ru$
Formula weight/g mol^{-1}	761.91	769.5	986.79
Crystal system, space group	Triclinic, P-1 (No.2)	Monoclinic, P21/n (No. 14)	Triclinic, P-1 (No.2)
a/b/c (Å)	9.074(5), 9.861(5), 17.200(5)	10.022(5), 13.533(2), 22.796(5)	14.164(5), 17.108(5) 17.570(5)
α/° β/° γ/°	95.12 (1), 92.48 (1), 106.90 (1)	90, 95.04(2), 90	74.99 (1), 82. 32(1), 70.16 (1)
V/Å^3	1462.8 (12)	3079.8(17)	3863 (2)
Z	2	4	4

D_{calc}/Mg m^{-3}	1.73	1.66	1.697
μ(Mo-$K_α$)/mm^{-1}	1.27	1.13	0.92
Crystal color / morphology	yellow / prism	yellow / prism	orange / block
Crystal size	0.3 x 0.25 x 0.22	0.3 x 0.25 x 0.2	0.45 x 0.3 x 0.16
T/K	293	293	293
R_{int} / %	2.1	4.1	6.8
Reflections: collected	5884	5962	14753
Reflections unique	5327	5469	14137
Reflections observed , I > 2σ(I)	3578	4798	7873
No. of parameters	358	376	927
R[$F^2 > 2σ(F^2)$] / %	0.051	0.069	0.083
wR(F^2) / %	0.123	0.188	0.23
GOF	0.99	1.13	1.01

2.3. Isomerization of allylic alcohols catalyzed by Ru(II)-dmso complexes

Redox isomerization of allylic alcohols to the respective oxo derivatives is a synthetically valuable procedure since it allows a stepwise transformation (oxidation and reduction of conjugated alcohol and C=C functions, respectively) in a single procedure.[29,47-49] *cis*-[$RuCl_2$(dmso)$_4$] has already been applied as catalyst for isomerization of 3-buten-2-ol to butan-*2*-one in homogeneous water-diglyme solvent mixtures, however, as high temperatures as 130 °C had to be used for meaningful reaction rates.[31] Gimeno et al studied the reduction of 1-octen-3-ol by hydrogen transfer from 2-propanol with **1** as catalyst in homogeneous solution.[32] The reaction yielded octan-3-one as major product together with 16 % octan-3-ol. Furthermore, at a substrate/catalyst ratio of 100 the reaction required 9 h (T = 82 °C) to reach full conversion. These literature reports prompted us to investigate the catalytic properties of **1** in more detail, especially since no investigations were done with this catalyst in aqueous-organic biphasic systems. We also checked the catalytic activities of the pta-containing Ru(II)-complexes **2**-**5**. Under inert atmosphere (Ar or N_2), isomerization of 1-octen-3-ol in a water-toluene biphasic mixture was slow or did not proceed at all. According to the known mechanism of homogeneously catalyzed redox isomerizations the reactions proceed through the transient formation of hydridometal complexes and in many cases the hydrogen source is the substrate allylic alcohol itself. Nevertheless, hydride donors such as H_2, 2-propanol or aqueous formate can facilitate the formation of the catalytically active hydrido species.[47]

Under hydrogen the reaction catalyzed by **1** led to a highly selective conversion of 1-octen-3-ol (in 1 h, TOF = 42 h^{-1}) to octan-3-one (83 %) with only 2 % of the hydrogenated product, octan-3-ol (Scheme 3). This result demonstrates for the first time, that in a dihydrogen atmosphere **1** can be successfully used for redox isomerization of 1-octen-3-ol under mild conditions with high activity and selectivity to octan-3-one.

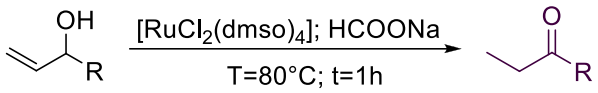


Scheme 3. Hydrogenation and isomerization of 1-octen-3-ol.

Hydrogen gas is flammable and explosive, however, in many cases can be replaced by solutions of Na-formate in water as safe H-donor. Furthermore, catalytic transfer hydrogenation of oxo-compounds from aqueous Na-formate is well studied and the conditions of C=O/C=C selectivity are known. Therefore isomerization activities of **1-5** were also studied in the presence of HCOONa.

An aqueous solution of **1** and HCOONa (1:50) was intensively stirred at 80 °C under argon with a toluene solution of 1-octen-3-ol yielding exclusively octan-3-one in 1 h. In other words, despite the presence of an H-donor, no hydrogenation of the resulting ketone was observed. This is in contrast to the results of Gimeno et al who in the same reaction with the same catalyst observed considerable formation of 1-octen-3-ol in homogeneous 2-propanol solution.[32] In addition, with Na-formate as H-source in aqueous-organic biphasic system the reaction proceeded much faster (1 instead of 9 h for full conversion).

Other allylic alcohols reacted also with 100 % selectivity with respect to the formation of the corresponding ketones (Scheme 4).



R	Yield (%)
CH_3	82
C_2H_5	69
C_3H_7	100
C_4H_9	100
C_4H_{11}	100

Scheme 4. Isomerization of allylic alcohols catalyzed by **1** in the presence of Na-formate. Conditions: 0.01 mmol 1; 0.50 mmol HCOONa in 3 mL water; 0.08 mL 1-octen-3-ol (0.50 mmol) in 1 mL toluene.

Isomerization of 1-octen-3-ol was investigated in detail. Originally the reaction mixture was pale yellow what turned to deeper yellow in the first few minutes of the reaction, routinely run for 1 h. The temperature dependence of the conversion showed (Figure 5) that the reaction proceeded slowly below 60 °C. Therefore further measurements were done at 80 °C.

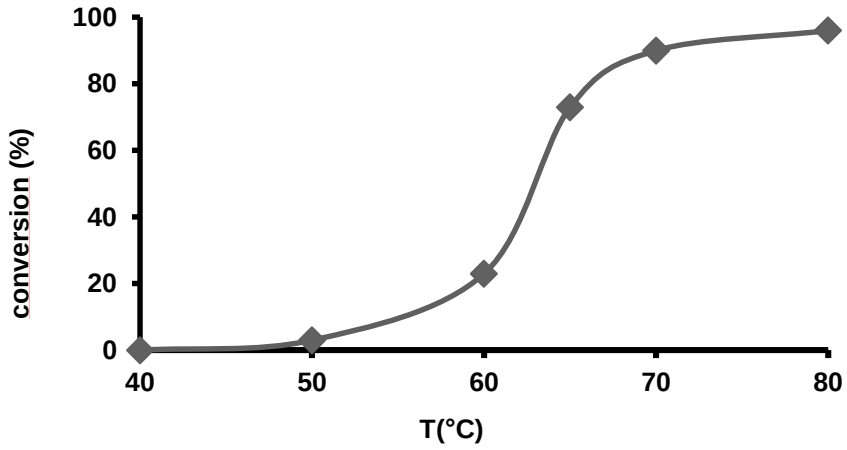


Figure 5. Isomerization of 1-octen-3-ol catalysed by **1** as a function of temperature. Conditions: 0.01 mmol $[RuCl_2(dmso)_4]$; 0.50 mmol HCOONa in 3 mL water; 0.08 mL (0.50 mmol) 1-octen-3-ol in 1 mL toluene, t =1 h.

Recycling of the catalyst was attempted the following way. After 1 h reaction, stirring was stopped, the phases were separated, a new batch of the toluene solution of 1-octen-3-ol was added to the catalyst-containing aqueous phase and the stirring continued. Although the selectivity to octan-3-one remained 100 %, the conversion dropped to 36 % in the second, and to 4 % in the third cycle.

Of the various pta-containing Ru(II)-complexes of this study **2**, **3** and **4** proved less active than **1**, nevertheless they catalyzed the formation of octan-3-one with considerable selectivity (Figure 6). However, in case of $[RuCl_2(pta)_4]$ (**5)** only a slight activity was determined (6 % conversion in 1 h). This is in agreement with the known low catalytic activity of this tetrakisphosphino-Ru(II) complex in other catalytic reactions (hydrogenation, hydrogen transfer from formate).[21]

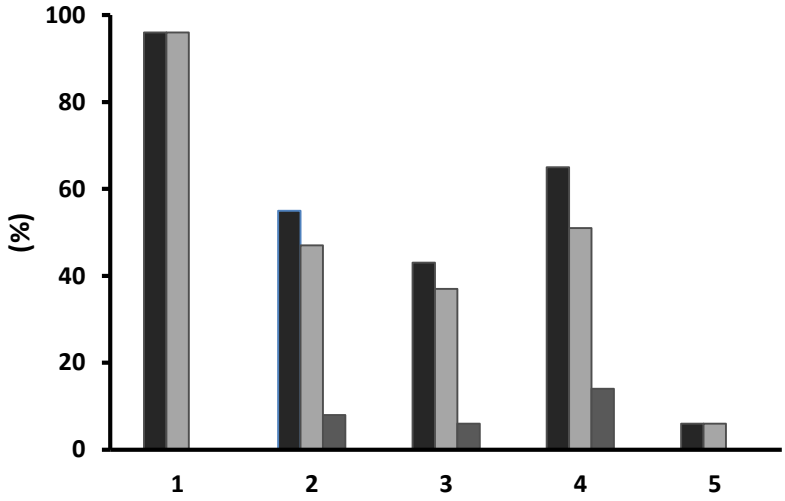


Figure 6. Reduction and/or isomerization of 1-octen-3-ol catalysed by complexes **1-5** using Na-formate as a H-source. Conditions: 0.01 mmol Ru-complex; 0.50 mmol HCOONa in 3 mL water; 0.50 mmol 1-octen-3-ol in 1 mL toluene; T = 80 °C, t =1 h (♦conversion, ♦ketone, ♦alcohol)

Concerning the reaction mechanism, one of the possible pathways is the isomerization of allylic alcohols to saturated ketones followed by hydrogenation of the latter to saturated alcohols. However, in independent reactions no hydrogenations of the respective ketones occurred (either with H_2 or with formate), therefore with the catalysts described above we consider isomerization and hydrogenation of allylic alcohols as parallel reactions.

3. Conclusions

The easily available *cis*-[$RuCl_2(dmso)_4$] is useful as a Ru(II)-source not only in organic solvents, but in water, as well. 1,3,5-Triaza-7-phosphaadamantane (pta) is soluble in both types of media and its reactions with *cis*-[$RuCl_2(dmso)_4$] resulted in the same product, *cis*-*cis*-*trans*-[$RuCl_2(dmso)_2(pta)_2$] (**2**) in both $CHCl_3$ and water. *N*-alkyl derivatives of pta (L = {pta-Bn}Cl; {pta-Me}CF_3SO_3) also easily replace two dmso ligands in trans positions of *cis*-[$RuCl_2(dmso)_4$] in aqueous solution to form air-stable, *cis*-*cis*-*trans*-[$RuCl_2(dmso)_2(L)_2$] complexes (**3, 4**). Of the new compounds, **2**, **2a** and **4** are the first crystallographically characterized complexes with $RuCl_2P_2S_2$ coordination containing *monodentate* ligands. The P-Ru-P angles in these *trans*-bisphosphane complexes significantly deviate from 180° (161° in **2**, 168° in **2a** and 165° in **4**).

It was shown here for the first time, that apart from its useful role in the synthesis of water-soluble Ru(II)-complexes, *cis*-[$RuCl_2(dmso)_4$] is an excellent catalyst for aqueous-organic biphasic isomerization of allylic alcohols. The reactions proceeded with 100 % to the respective ketones using Na-formate as a H-source. Under the same conditions the activities of **2**, **3** and **4** are 45-65 % of that of *cis*-[$RuCl_2(dmso)_4$], and the reactions are also less selective leading to the formation of small amounts of octan-3-ol, too.

4. Experimental Section

4.1. General Remarks

Allylic alcohols (Aldrich) and other reagents and solvents were commercially available and used as received. The water-soluble phosphane ligands, *m*tppms,[50] *m*tppts (*m*tppts = $P(C_6H_4$-3-$SO_3Na)_3$),[51] pta,[52] (pta-Bn)Cl (1-benzyl-1-azonia-3,5-diaza-7-phosphaadamantyl chloride),[36] and cis-$[RuCl_2(dmso)_4]$ (**1**),[8] were prepared according to the literature. (pta-Me)CF_3SO_3[25] was kindly supplied by Prof. A. Romerosa (U. Almería, Spain). **1** is a light sensitive compound,[9,53] therefore its reactions were studied with the careful exclusion of light.

All reactions and manipulations were carried out under argon atmosphere. Reaction mixtures were analyzed by gas chromatography (HP5890 Series II; Chrompack WCOT Fused Silica 30m*32mm CP WAX52CB; FID; carrier gas: argon). The products were identified by comparison to known compounds. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker Avance 360 MHz spectrometer and referenced to 3-(trimethylsilyl)propanesulfonic acid Na-salt (DSS). ESI mass data were collected on a BRUKER BioTOF II ESI-TOF spectrometer. Solubilities were determined by incremental addition of the compounds to water. Complete dissolution was checked by laser light scattering.

4.2. Synthesis and characterization of Ru(II) complexes

4.2.1. Preparation of *cis-cis-trans*-$[RuCl_2(dmso)_2(pta)_2]$, (**2**)

In the dark, a mixture of **1** (400 mg 0.82 mmol) and pta (259 mg, 1.64 mmol) in chloroform (5 mL) was stirred for 2 h at room temperature. Then most of the solvent was removed under vacuum and the residue was triturated with diethyl ether to provide a pale yellow solid. This was washed with acetone and with diethyl ether and dried under Ar to result in a strongly hygroscopic solid. Yield 527 mg (82 %). X-ray quality crystals were grown by slow diffusion of diethyl ether into a chloroform solution of **2** at -15 °C . Anal. calc. for

$RuC_{16}Cl_2H_{36}N_6O_2P_2S_2$ (**2**·0.5 $CHCl_3$) (M=642.30) C 28.22, H 5.23, N 11.97, S 9.13 %; found C 28.67, H 5.40, N 12.17, S 9.98 %. $S_{25\ °C}$=34 mg/mL water. $\lambda_{max}(H_2O)$/nm 338 (ε/$dm^3mol^{-1}cm^{-1}$ 449)

^{1}H NMR: (360 MHz, $CDCl_3$, 25 °C) δ = 3.35 (s, 12 H, S-dmso, C*H*$_3$), 4.43 (s, 12 H, PC*H*$_2$N), 4.52 (s, 12 H, NC*H*$_2$N) ppm; ^{1}H NMR: (360 MHz; D_2O, 25 °C) δ = 3.31 (s, 12 H, S-dmso, C*H*$_3$), 4.26 (s, 12 H, PC*H*$_2$N), 4.43 (s, 12 H, NC*H*$_2$N) ppm; ^{13}C NMR (90 MHz, $CDCl_3$, 25 °C) δ = 51.18 (s, S-dmso, *C*H_3), 51.39 (t, J_{PC}= 7 Hz P*C*H_2N), 73.07 (s, N*C*H_2N), ppm; ^{31}P{^{1}H} NMR (145 MHz, 25 °C) in $CDCl_3$ δ = -60.7 (s), in D_2O δ = -57.9 (s) ppm. MS (ESI+): m/z observed 643.030, calcd. 643.031 for $[RuCl_2(dmso)_2(pta)(pta\text{-}H)]^+$.

Crystals of *cis*-*cis*-*trans*-$[RuCl_2(dmso)_2(ptaH)_2]Cl_2$, (**2a**) were obtained by dissolving 10 mg of **2** in 1 mL of 0.1 M HCl and then it was layered with 1 mL of ethanol. Anal. calc. for $RuC_{16}Cl_4H_{38}N_6O_2P_2S_2$ (**2a**·3H_2O) C 24.97, H 5.76, N 10.92, S 8.33 %; found C 24.91, H 5.53, N 10.82, S 8.33 %.

4.2.2. Preparation of *cis*-*cis*-*trans*-$[RuCl_2(dmso)_2(pta\text{-}Bn)_2]Cl_2$, (**3**)

1 (200 mg 0.41 mmol) dissolved in 3 mL of water was added to an aqueous solution (2 mL) of (pta-Bn)Cl (234 mg, 0.82 mmol). The mixture was stirred for 2 h at room temperature in the dark. Then the solvent was removed under vacuum and the residue was redissolved in a small amount of methanol. Diethyl ether was added to the solution whereupon a yellow solid precipitated. This was washed with acetone and with diethyl ether and dried under Ar. Yield 246 mg, 66 %. Anal. calc. for $RuC_{30}Cl_4H_{50}N_6O_2P_2S_2$ (**3**·2H_2O) (M=895.71) C 38.67, H 5.84, N 9.02 %; found C 38.25, H 6.17, N 8.79 %. $\lambda_{max}(H_2O)$/nm 341 (ε/$dm^3\ mol^{-1}\ cm^{-1}$ 691) .

^{1}H NMR: (360 MHz, D_2O, 25 °C) δ =3.29-4.27 (m, 8 H, NC*H*$_2$P), 3.64 (s, 12 H, S-dmso, C*H*$_3$), 4.19 (m, 4 H, N^+C*H*$_2$Ph), 4.31 (m, 4 H, N^+C*H*$_2$P), 4.51-4.61 (m, 4 H, NC*H*$_2$N), 4.92-5.09 (m, 8 H, N^+C*H*$_2$N), 7.57-7.46 (m, 10 H, Ph) ppm; ^{13}C NMR (90 MHz, D_2O, 25 °C), δ =

47.25 (t, J_{PC}=8 Hz, N*C*H_2P), 50.16 (s, S-dmso, *C*H_3), 51.99 (d, J_{PC}=8 Hz, N^+*C*H_2P), 66.37 (s, N*C*H_2N), 69.80 (s, N^+*C*H_2Ph), 78.71 (s, N^+*C*H_2N), 124.22 (s, Ph), 129.46 (s, Ph), 131.18 (s, Ph), 132.83 (s, Ph) ppm; $^{31}P\{^1H\}$ NMR (145 MHz, D_2O, 25 °C) δ = -36.4 (s) ppm. MS (ESI+): m/z observed 860.100, calcd. 860.265 for $\{[RuCl_2(dmso)_2(pta\text{-}Bn)_2]Cl\}^+$. $S_{25\ °C}$= 50 mg/mL water.

4.2.3. Preparation of *cis-cis-trans*-$[RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)_2$, (**4**)

In the dark, **1** (100 mg 0.21 mmol) and (pta-Me)(CF_3SO_3) (132.7 mg, 0.41 mmol) was dissolved in 5 mL of water. The solution was stirred for 4 h at room temperature and then the solvent was removed under vacuum. The residue was dissolved in a small amount of methanol and **4** was precipitated with diethyl ether to yield a pale yellow solid. This was washed with acetone and with diethyl ether and dried under Ar. Yield 134 mg, 67 %. X-ray quality crystals were obtained by slow diffusion of methanol into aqueous solution of **4**. Anal. calc. for $RuC_{20}Cl_2F_6H_{42}N_6O_8P_2S_2$ (**4**·$2H_2O$) (M=906.62)) C 23.86, H 4.60, N 8.34, S 12.74 %; found C 23.99, H 4.53, N 8.18, S 13.00 %. $\lambda_{max}(H_2O)$/nm 344 (ε/$dm^3mol^{-1}cm^{-1}$ 480). ^1H NMR: (360 MHz, D_2O, 25 °C), δ = 2.84 (s, 6 H, N^+-C*H*$_3$), 3.38 (s, 12 H, S-dmso, C*H*$_3$), 4.32 (s, 8 H, NCH_2P), 4.44-4.38 (4 H, m, N^+C*H*$_2$P), 4.52 (m, 4 H, NC*H*$_2$N), 4.91-5.10 (m, 8 H, N^+C*H*$_2$N) ppm; ^1H NMR: (360 MHz, MeOD, 25 °C), δ = 4.31 (s, 6 H, N^+-C*H*$_3$), 4.81 (s, 12 H, S-dmso, C*H*$_3$), 5.83 (m, 8 H, NC*H*$_2$P), 5.90 (m, 4 H, N^+C*H*$_2$P), 5.95 (m, 4 H, NC*H*$_2$N),6.61-6.69 (m, 8 H, N^+C*H*$_2$N) ppm; ^{13}C NMR (90 MHz, D_2O, 25 °C) δ = 46.97 (t, J_{PC}= 7 Hz, N*C*H_2P), 49.43 (s, N^+-*C*H_3), 50.14 (s, S-dmso, *C*H_3), 55.38 (t, N^+*C*H_2P), 68.79 (s, N*C*H_2N), 79.99 (s, N^+*C*H_2N), 121.34 (m, *C*$F_3SO_3^-$) ppm; $^{31}P\{^1H\}$ NMR (145 MHz, 25 °C) in D_2O δ = -39.61 (s), in MeOD δ = -37.67 (s) ppm; $^{19}F\{^1H\}$ NMR (283 MHz, D_2O, 25 °C) δ = -79.10 (s, $CF_3SO_3^-$) ppm. MS (ESI+): m/z observed 821.013, calcd. 821.022 for $\{[RuCl_2(dmso)_2(pta\text{-}me)_2](CF_3SO_3)\}^+$. $S_{25\ °C}$=63 mg/mL water.

4.3. ^{31}P-NMR pH titrations

A pH-dependent series of ^{31}P-NMR spectra were recorded on a Bruker 360 MHz instrument at 25 °C and 0.2 mol/dm^3 KNO_3 ionic strength. D_2O was used as a solvent. The pH measurements in the pH range 1.1-7.0 for $[RuCl_2(dmso)_2(pta)_2]$, **2** were performed in 0.5 cm^3 vessels at a complex concentration of 0.01 mol/dm^3. Small amounts of cc. NaOD and DNO_3 solutions were used to adjust the pH measured using a Radelkis OK117 pH meter and a combined electrode.

4.4. X-ray crystallographic studies

X-ray data collection was performed using a Bruker-Nonius MACH3 diffractometer equipped with a point detector using graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å. The structures were solved by the SIR-92 program[54] and refined by full-matrix least-squares method on F^2, with all non-hydrogen atoms refined with anisotropic thermal parameters except in the solvent region in **2** since chloroform in two orientations occupies a channel in the lattice (Figure S1.a). Refinement was performed using the SHELXL-97 package;[55] publication material was prepared with the WINGX suite.[56] Hydrogen atoms were located geometrically and refined in the rigid mode or found at the difference Fourier map. Solvent water molecules in **2a** and **4** (Figure S1.b and S1.c) have partial occupancy and can have various orientations forming different hydrogen bond networks with acceptors resulting shift and errors even in the last stage of the refinement.

4.5. General Procedure for Catalytic Isomerization of Allylic Alcohols

Under an inert atmosphere, the catalyst precursor (0.01 mmol) and Na-formate (0.5 mmol) were dissolved in 3 mL of deoxygenated water. The solution was then heated to the indicated

temperature and then allylic alcohol (0.5 mmol, in 1 mL of toluene) was introduced. The system was rapidly stirred for one hour and then was cooled to room temperature. The separated organic phase was filtered through a short silica gel column and was subjected to gas chromatography.

Supplementary material

CCDC 859702- 859704 contain the supplementary crystallographic data for the ruthenium complexes **2**, **2a** and **4**. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data-request/cif. Supplementary data related to this article can be found in the online version, at doi….

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