Synthesis and catalytic activity of new, water-soluble mono- and dinuclear ruthenium(II) complexes containing 1,3,5-triaza-7-phosphaadamantane: study of the effect of the visible light.

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Abstract

The newly synthesized *mer-trans*-[$RuCl_2(OH_2)(PTA)_3$] (**1**) is the first compound isolated in solid state containing the $Ru(PTA)_3$-fragment (PTA = 1,3,5-triaza-7-phosphatricyclo[3.3.1.$1^{3,7}$]decane). Dissolution of **1** in aqueous HCl leads to *mer*-[$RuCl_3(HPTA)_3$]Cl_2 (**2**) which is stable in the dark but is transformed into *fac*-[$RuCl_3(HPTA)_3$]Cl_2 (**3**) under visible light. Irradiation with visible light of an aqueous solution of **1** at room temperature or refluxing of the same solution in the dark leads to the formation of [{$Ru(PTA)_3$}$_2$(μ-$Cl)_3$]Cl (**4**)**.** The dinuclear complex **4** was also formed upon irradiation of solutions of PTA and various Ru(II)-complexes ([$RuCl_2(DMSO)_4$], [{$RuCl_2(\eta^6$-*p*-cymene)}$_2$]) or *cis-cis-trans*-[$RuCl_2(DMSO)_2(PTA)_2$]). All complexes were characterized by elemental analysis and NMR spectroscopy, furthermore solid state structures of **2**·1.25H_2O, **3**·HCl·2H_2O and **4**·9H_2O were also determined by single crystal X-ray diffraction. We have investigated the influence of the above photochemical processes on reduction of benzaldehyde and cinnamaldehyde with *trans*-[$RuCl_2(PTA)_4$] and *cis-cis-trans*-[$RuCl_2(DMSO)_2L_2$] (L=PTA, (PTA-Me)CF_3SO_3, (PTA-Bn)Cl; Me=methyl, Bn=benzyl) complexes as catalysts. The effect of visible light on benzonitrile hydration with various Ru(II)-PTA catalysts is also reported.

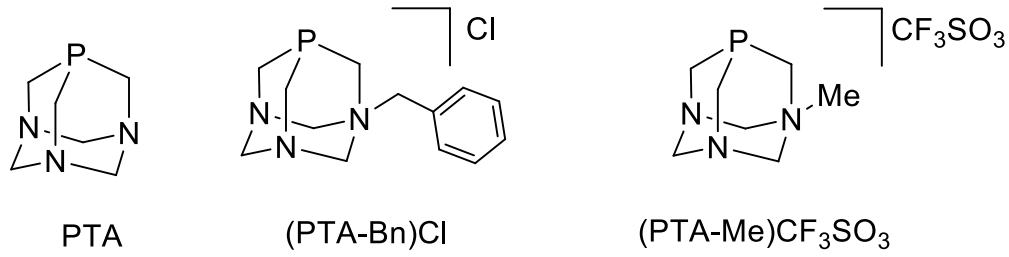
Keywords

ruthenium, visible light, water, hydrogenation, hydration, 1,3,5-triaza-7-phosphaadamantane (PTA)

Introduction

Water is an environment-friendly solvent and has gained increasing application recently in organic synthesis and in homogeneous catalysis.[1-5] Water-soluble transition metal complex catalysts frequently contain tertiary phosphine ligands,[6] although hydrosoluble *N*-heterocyclic carbenes,[7-10] salens and salans[11] also receive attention. Among tertiary phosphines, monosulfonated and trisulfonated triphenylphosphines, usually as their sodium salts (*m*tppms-Na[12,13] and *m*tppts-Na_3,[14,15] respectively) are the most commonly used. In addition, the small aliphatic phosphine, PTA[16-18] (1,3,5-triaza-7-phosphatricyclo[3.3.1.$1^{3,7}$]decane) and its various derivatives have often been used for synthetic and catalytic purposes. Due to the importance of aqueous organometallic catalysis in green chemical processes, a wide range of water-soluble catalysts with ruthenium, rhodium, iridium, palladium, and other metal ions has been investigated.[1-21] The present study is focused on new mono- and dinuclear chloro-Ru(PTA)-complexes prepared from various Ru(II)-complexes such as [$RuCl_2(PPh_3)_3$], *cis*-[$RuCl_2(DMSO)_4$] and [{$RuCl_2(\eta^6$-*p*-cymene)}$_2$].

The first PTA-containing Ru(II)-complex, *trans*-[$RuCl_2(PTA)_4$] was synthesized by refluxing ethanolic solutions of PTA and hydrated $RuCl_3$ or reacting aqueous solutions of PTA (n_{PTA}:n_{Ru}≥4) with toluene solutions of [$RuCl_2(PPh_3)_3$].[16]



PTA (PTA-Bn)Cl (PTA-Me)CF_3SO_3

Scheme 1. Water-soluble phosphines used in this study

In the presence of Na-formate, *trans*-[$RuCl_2(PTA)_4$] proved catalytically active both in transfer hydrogenation of aldehydes[16,22] and in redox isomerization of allylic alcohols.[23] Conversely, reduction of aldehydes by complexes with the general formula *cis*-*cis*-*trans*-[$RuCl_2(DMSO)_2L_2$] (L=PTA, (PTA-Me)CF_3SO_3, (PTA-Bn)Cl; Me=methyl, Bn= benzyl) is

unexplored. The latter complexes showed at least twice as high catalytic activities than *trans*-[$RuCl_2(PTA)_4$] in transformation of oct-1-en-3-ol to octan-3-one. These catalysts were obtained in reactions of the water-soluble *cis*-[$RuCl_2(DMSO)_4$] with PTA and its N-alkylated derivatives and were applied either synthesized in situ or as isolated solid compounds.[23] Light-sensitivity of *cis*-[$RuCl_2(DMSO)_4$] is well known[24] and therefore these catalytic redox isomerization reactions were run with strict exclusion of light unlike several earlier studies[16,22,25] in which no attention was paid to possible photochemical effects.

It has been reported that upon irradiation *trans*-[$RuCl_2(PTA)_4$] can be isomerized to *cis*-[$RuCl_2(PTA)_4$] and the latter can be aquated to *cis*-$[RuCl(OH_2)(PTA)_4]^+$.[26,27] The photoactivity of *trans*-[$RuCl_2(PTA)_4$] brings up the question of the influence of visible light irradiation on the rate or selectivity of the reactions catalyzed by this complex.

Trans-[$RuCl_2(PTA)_4$] efficiently catalyzed the hydration of various nitriles, as well.[28] We have also reported on the catalytic application of *cis-cis-trans*-[$RuCl_2(DMSO)_2L_2$] complexes and that of *trans*-[$RuCl_2(PTA)_4$] in hydration of various nitriles,[29,30] however, these studies did not include investigation of photochemical effects.

In several cases[16,22,25,29,30] the catalytically active species was presumed to be a Ru(II)-trisphosphine complex, however to date such species have not been isolated in pure form. Earlier, $[Ru(OH_2)_3(PTA)_3]^{2+}$ (formed in the reaction of $[Ru(OH_2)_6](tos)_2$ and PTA) was characterized in aqueous solution[21] and very recently *cis-mer*-[$Ru(S)Cl_2(PTA)_3$] complexes were identified in refluxing solutions of *trans*-[$RuCl_2(PTA)_4$] using S = DMSO or CH_3CN as solvents.[27]

We deemed important the synthesis and characterization of Ru(II)-PTA complexes with a PTA:Ru=3:1 ratio including also the study of their photoactivity. In addition, we also investigated the hitherto unexplored photochemistry of *cis-cis-trans*-[$RuCl_2(DMSO)_2L_2$] complexes. This paper describes detailed synthetic investigations on the interconversions of various Ru(II)-PTA complexes under visible light irradiation together with structural characterization of the products both in solution and in the solid state. It is also essential to learn, how these photochemical processes may influence the catalytic reactions. With this aim in mind we have investigated the reduction of benzaldehyde and cinnamaldehyde both in the dark and under light both with *trans*-[$RuCl_2(PTA)_4$] and *cis-cis-trans*-[$RuCl_2(DMSO)_2L_2$] complexes as catalysts. The effect of visible light on benzonitrile hydration with various Ru(II)-PTA catalysts is also reported.

Experimental Section

All reactions were carried out under an N_2 atmosphere using standard Schlenk techniques. Solvents were dried and deoxygenated under nitrogen/vacuum before use. Doubly distilled water was used throughout. PTA,[31] (PTA-Me)CF_3SO_3,[32] (PTA-Bn)Cl,[33] *trans*-$[RuCl_2(PTA)_4]$,[16] *cis*-$[RuCl_2(DMSO)_4]$,[34] $[(DMSO)_3Ru(\mu\text{-}Cl)_3RuCl(DMSO)_2]$,[35] $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ (*p*-cymene = *p*-isopropyltoluene),[36] *cis-cis-trans*-$[RuCl_2(DMSO)_2L_2]$ [23] were prepared according to the literature. UV-Vis spectra of 10^{-3}-10^{-5} M solutions were recorded on a Jasco V-650 spectrometer in quartz cells (10 mm optical path). Specific absorption coefficients were obtained by linear regression over 5-7 points ($R^2 \geq 0.999$). When necessary, the bands were analysed by the Spectra Manager software of JASCO. Elemental analyses (C, H, N) were performed on a Fisons Instrument EA 1108 elemental analyzer or on an Elementar Vario Micro (CHNS) equipment. NMR spectra were recorded on a Bruker AVANCE DRX300 spectrometer operating at ca. 300 MHz (^{1}H), ca. 75.47 MHz (^{13}C) and ca. 121 MHz (^{31}P), respectively and on a BRUKER AVANCE 360 spectrometer operating at 360 MHz (^{1}H), ca. 95 MHz (^{13}C) and ca. 145 MHz (^{31}P). Peak positions were referenced to TMS or 3-(trimethylsilyl)-1-propanesulfonic acid Na-salt, DSS (^{1}H and ^{13}C), H_3PO_4 (0.1 M in D_2O) with downfield values taken as positive and were measured at 293 K (if not stated otherwise). Gas chromatographic measurements were made on an Agilent 7890A gas chromatograph with Chrompack WCOT Fused Silica 30 m×32 mm×0.25 μm CP WAX52CB, column, injector temperature 250 °C, FID (300 °C).

Photolysis

Irradiation of the NMR tubes with broad-band UV-visible light was carried out using a home-made photo-reactor with a built-in standard 150 W halogen lamp[37] and a LOT-Oriel 150 W Xenon lamp. Irradiation at selected wavelengths was carried out with the Xenon system equipped with a water filter (5 cm) and appropriate band-pass or interference filters (Schott). Solutions for photolysis and reactions in the dark were prepared under Ar and transferred to 10 mm path-length quartz cells. During photolysis the solutions were stirred using a small magnetic stirring bar inside the cell.

Synthesis of *mer-trans*-$[RuCl_2(OH_2)(PTA)_3]\cdot 3H_2O$ ($1\cdot 3H_2O$)

A solution of PTA (183.2 mg, 1.166 mmol) in 50 mL of water was mixed with a solution of $[RuCl_2(PPh_3)_3]$ (372.2 mg, 0.388 mmol) in 50 mL of CH_2Cl_2 and stirred at room temperature in the dark overnight. The water phase was separated, filtered and evaporated to dryness to

give a yellow powder which was washed with acetone (2 mL) and Et_2O (6x6 mL) and finally dried under vacuum. Yield: 168.1 mg (65%). $S_{25°C}(H_2O)$ = 190 mg/mL.

Elemental analysis: Found C, 30.03; H, 5.85; N, 17.16 %; $C_{18}H_{38}N_9Cl_2OP_3Ru \cdot 3H_2O$ (715.53) calculated C, 30.22; H, 6.20; N, 17.62 %.

UV-vis $\lambda_{max}(H_2O)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 457 (199), 336 (914).

IR (KBr): ν_{max}/cm^{-1} 3434b (OH), 2930 and 2873m (CH), δ/cm^{-1} 1706w (OH).

^{1}H NMR (300 MHz, D_2O): δ (ppm) 3.94 (bs, 6H, PC*H*$_2$N), 4.24 (bs, 12H, PC*H*$_2$N), 4.49 (bs, 6H, NC*H*$_2$N), 4.55 (bs, 12H, NC*H*$_2$N).

^{13}C{^{1}H} NMR (75.47 MHz, D_2O): δ (ppm) 48.27 (t, $^1J_{CP}$ = 6.4 Hz, P*C*H$_2$N, P$_{trans\text{-}O}$), 53.74 (d, $^1J_{CP}$ = 19.1 Hz, P*C*H$_2$N, P$_{trans\text{-}P}$), 70.62 (d, $^3J_{CP}$ = 6.3 Hz, N*C*H$_2$N, P$_{trans\text{-}P}$), 70.78, (t, $^3J_{CP}$ = 2.4 Hz, N*C*H$_2$N, P$_{trans\text{-}O}$)

^{31}P{^{1}H} NMR (121 MHz, D_2O): δ (ppm) -5.08 (t, $^2J_{PP}$ = 34.6 Hz, P$_{trans\text{-}O}$, 1 P), -46.78 (d, $^2J_{PP}$ = 34.6 Hz, P$_{trans\text{-}P}$, 2 P).

ESI-MS(+) (H_2O): *m/z*=644.072, $[M\text{-}H_2O]H^+$ ($[RuCl_2P_3N_9H_{37}C_{18}]^+$) calculated 644.081.

Synthesis of *mer*-[RuCl$_3$(HPTA)$_3$]Cl$_2$ ·2H$_2$O (2·2H$_2$O)

This complex was obtained by reaction of **1**·3H$_2$O (200 mg, 0.280 mmol) dissolved in 5 mL aqueous 1 M HCl solution. After 15 min at room temperature the resulting bright yellow solution was evaporated to dryness and the powder obtained was washed with EtOH (2x3 mL), Et_2O (2x3 mL) and vacuum dried. Yield 185 mg (83 %).

Elemental analysis: Found C, 27.26; H, 6.12; N, 15.89 %; $C_{18}H_{39}Cl_5N_9P_3Ru \cdot 2H_2O$ (788.85) calculated C, 27.41; H, 5.49; N, 15.98 %.

IR (KBr): ν_{max}/cm^{-1} 3480 and 3377b (OH), 2979 and 2815m (CH), 2726-2071m (NH_{PTA}), δ/cm^{-1} 1706w (OH).

*NMR data of aqueous solutions of mer-[RuCl$_3$(HPTA)$_3$]Cl$_2$ (**2**):*

Two sets of NMR signals are detected in aqueous solutions of **2**: *mer*-$[RuCl_3(HPTA)_3]^{2+}$ and *mer*-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$ are in equilibrium

NMR data of mer-[RuCl$_3$(HPTA)$_3$]$^{2+}$

^{1}H NMR (300 MHz, D_2O): δ (ppm) 4.16 (bs, NC*H*$_2$P$_{trans\text{-}Cl}$, 6 H), 4.46 (bs, NC*H*$_2$P$_{trans\text{-}P}$, 12 H), 4.85 (bs, NC*H*$_2$N$_{trans\text{-}P}$, 12 H), 4.84 (bs, NC*H*$_2$N$_{trans\text{-}Cl}$, 6 H).

^{13}C{^{1}H} NMR (75.47 MHz, D_2O): δ (ppm) 47.85 (t, $^1J_{CP}$ = 6.9 Hz, N*C*H$_2$P$_{trans\text{-}Cl}$), 52.14 (d, $^1J_{CP}$ = 17.2 Hz, N*C*H$_2$P$_{trans\text{-}P}$).

$^{31}P\{^{1}H\}$ NMR (121 MHz, D_2O): δ (ppm) -4.62 (t, $^{2}J_{PP}$ = 33.3 Hz, $P_{trans\text{-}Cl}$, 1 P), -40.62 (d, $^{2}J_{PP}$ = 33.3 Hz, $P_{trans\text{-}P}$, 2P).

NMR data of mer-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$:

^{1}H NMR (300 MHz, D_2O): δ (ppm) 4.12 (bs, $NCH_2P_{trans\text{–}O}$, 6 H), 4.40 (bs, $NCH_2P_{trans\text{-}P}$, 12 H), 4.83 (bs, $NCH_2N_{trans\text{-}O}$, 6 H), 4.89 (bs, $NCH_2N_{trans\text{-}O}$, 6 H).

$^{13}C\{^{1}H\}$ NMR (75.47 MHz, D_2O): δ (ppm) 46.83 (t, $^{1}J_{CP}$ = 6.5 Hz, $NCH_2P_{trans\text{-}O}$) , 52.02 (d, $^{1}J_{CP}$ = 19.3 Hz, $NCH_2P_{trans\text{-}P}$), 70.84 (d, $^{3}J_{CP}$ = 5.60 Hz, $NCH_2N_{trans\text{-}P}$), 70.90 (bs, $NCH_2N_{trans\text{-}O}$).

$^{31}P\{^{1}H\}$ NMR (121 MHz, D_2O): δ (ppm) 2.31 (t, $^{2}J_{PP}$ = 35.6 Hz, $P_{trans\text{-}O}$, 1 P), -36.28 (d, $^{2}J_{PP}$ = 35.6 Hz, $P_{trans\text{-}P}$, 2 P).

UV-vis $\lambda_{max}(H_2O)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 453 (218), 330 (939).

Single crystals of **2**·1.25H_2O were obtained by slow diffusion of 5 mL of isopropanol into a solution of 100 mg **1**·3H_2O in 5 mL aqueous 0.1 M HCl. The resulting orange crystals were filtered and air dried. Yield: 80 mg (74 %). $S_{25°C}(H_2O)$ = 250 mg/mL.

Synthesis of *fac*-$[RuCl_3(HPTA)_3]Cl_2 \cdot HCl \cdot 2H_2O$ (3·HCl·2H_2O)

Single crystals of **3**·HCl·2H_2O were obtained by irradiation with visible light (150 W halogen lamp) of a solution of **2**·1.25H_2O (30 mg, 0,039 mmol) in 1 mL of H_2O at 80 ºC. The crystals were filtered and air dried. Yield: 25 mg (78 %). $S_{25°C}(H_2O)$ = 20 mg/mL.

Elemental analysis: Found C, 26.01; H, 5.49; N, 15.48 %; $C_{18}H_{44}Cl_6N_9O_2P_3Ru$ (825.30) calculated C, 26.20; H, 5.37; N, 15.27 %.

IR (KBr): ν_{max}/cm^{-1} 3392b (OH), 2981 and 2921m (CH), 2773-2535bm (NH_{PTA}), δ/cm^{-1} 1625m (OH).

*NMR data of aqueous solutions of fac-$[RuCl_3(HPTA)_3]Cl_2$ (**3**):*

Two sets of NMR signals are detected in aqueous solutions of **3**: *fac*-$[RuCl_2(OH_2)(HPTA)_3]^{2+}$ and *fac*-$[RuCl_3(HPTA)_3]^{2+}$ are in equilibrium, however, only signals of the latter are observed when 10 eq. of NaCl are dissolved into the solution.

NMR data of fac-$[RuCl_3(HPTA)_3]^{2+}$

^{1}H NMR (300 MHz, D_2O): δ (ppm) 4.27 (bs, $NCH_2P_{trans\text{-}Cl}$, 18 H), 4.75-4.85 (bm, $NCH_2N_{trans\text{-}Cl}$, 18 H).

$^{13}C\{^1H\}$ NMR (75.47 MHz, D_2O): δ (ppm) 51.71-52.07 (m, N*C*$H_2P_{trans\text{-}Cl}$), 70.67 (bs, N*C*$H_2N_{trans\text{-}P}$ and N*C*$H_2N_{trans\text{-}O}$).

$^{31}P\{^1H\}$ NMR (121 MHz, D_2O): δ (ppm) -12.83 (s).

NMR data of fac-[$RuCl_2(OH_2)(HPTA)_3$]$^{3+}$.

^1H NMR (300 MHz, D_2O): δ (ppm) 4.23 (bs, N*C*$H_2P_{trans\text{-}O}$, 6 H), 4.15-4.40 (bm, N*C*$H_2P_{trans\text{-}Cl}$, 12 H), 4.78 (bs, N*C*$H_2N_{trans\text{-}O}$ + N*C*$H_2N_{trans\text{-}Cl}$, 18 H).

$^{13}C\{^1H\}$ NMR (75.47 MHz, D_2O): δ (ppm) 50.86 (t, $^1J_{CP}$ = 8.7 Hz, N*C*$H_2P_{trans\text{-}O}$), 51.71-52.07 (m, N*C*$H_2P_{trans\text{-}Cl}$), 70.67 (bs, N*C*$H_2N_{trans\text{–}P}$ and N*C*$H_2N_{trans\text{–}O}$).

$^{31}P\{^1H\}$ NMR (121 MHz, D_2O): δ (ppm) -4.57 (t, $^2J_{PP}$ = 36.5 Hz, $P_{trans\text{-}O}$, 1 P), -12.49 (d, $^2J_{PP}$ = 36.5 Hz, $P_{trans\text{-}Cl}$, 2 P).

UV-vis $\lambda_{max}(H_2O)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 350 (1715), 312 (1061).

Synthesis of [{Ru(PTA)$_3$}$_2$(μ-Cl)$_3$]Cl·9H$_2$O (4·9H$_2$O)

The complex can be prepared by various procedures:

a) PTA (105.9 mg, 0.674 mmol) was added to an aqueous solution (2 mL) of *cis*-[$RuCl_2(DMSO)_4$] (109 mg, 0.225 mmol) and the solution was irradiated overnight with visible light. The reaction mixture was evaporated to dryness and the residue dissolved in acetone (2 mL). The product was precipitated by adding Et_2O (10 mL). The solid was filtered off and dried under vacuum. Yield: 160 mg (98 %).

b) A solution of *mer-trans*-[$RuCl_2(OH_2)(PTA)_3$]·3H_2O (**1**·3H_2O) (100 mg, 0.140 mmol) in 5 mL of water was irradiated overnight with a 150 W halogen lamp. The initial orange solution changed to pale yellow. The resulting solution was evaporated and the obtained powder washed with EtOH (3x5 mL), Et_2O (5x10 mL) and vacuum dried. Yield: 87 mg (86%).

c) A solution of *mer-trans*-[$RuCl_2(OH_2)(PTA)_3$]·3H_2O (**1**·3H_2O) (100 mg, 0.140 mmol) in 10 mL of water was refluxed for 1 h. The resulting solution was treated as described in b). Yield: 78 mg (77%).

Slow diffusion of 1:1 mixture of isopropanol/Et_2O (5 mL) into 5 mL aqueous solution of 200 mg of the product yielded light yellow single crystals of **4**·9H_2O. Crystals: 90 mg, $S_{25°C}(H_2O)$ = 179 mg/mL.

Elemental analysis: Found C, 30.06; H, 6.09; N, 16.96 %; $C_{36}H_{90}N_{18}O_9Cl_4P_6Ru_2$ (1449.02) calculated C, 29.84; H, 6.26; N, 17.40 %.

UV-vis $\lambda_{max}(H_2O)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 362 (3013).

^{1}H NMR (300 MHz, D_2O): δ(ppm) 4.09 (bs, 36H, NC*H*$_2$N), 4.48 (bs, 36H, NC*H*$_2$P).

^{13}C{^{1}H} NMR (90 MHz, D_2O): δ(ppm) 51.50 (s, N*C*H$_2$P), 70.68 (s, N*C*H$_2$N).

^{31}P{^{1}H} NMR (121 MHz, D_2O): -14.60 (s) ppm.

ESI-MS(+) (H_2O): *m/z* = 1251.163 $[Ru_2Cl_3(PTA)_6]^+$ ($C_{36}H_{72}N_{18}P_6Cl_3Ru_2$), calculated: 1251.177.

Synthesis of *trans*-[RuCl$_2$(PTA)$_4$] (5) from *cis*-[RuCl$_2$(DMSO)$_4$] and PTA

A solution of *cis*-[$RuCl_2(DMSO)_4$] (100 mg, 0.21 mmol) in 5 mL of water was irradiated overnight with visible light from a 150 W halogen lamp. The irradiation was stopped and solid PTA (129.8 mg, 0.83 mmol) was added to the resulting deep green solution. After 1 night in the dark a yellow solution was obtained, which was evaporated to dryness and the residue was dissolved in 2 mL of acetone. Addition of 10 mL of Et_2O gave rise to a yellow precipitate, which was filtered and dried in vacuum. The product was identified as *trans*-[$RuCl_2(PTA)_4$]. Yield: 96 mg (58%).

Reaction of *cis-cis-trans*-[RuCl$_2$(DMSO)$_2$(PTA)$_2$] with PTA under visible light

A deep yellow solution was obtained during an overnight irradiation with a 150 W halogen lamp of a 2 mL aqueous solution of *cis-cis-trans*-[$RuCl_2(DMSO)_2(PTA)_2$] (162 mg, 0.25 mmol) and PTA (37 mg, 0.24 mmol) at room temperature. The solvent was evaporated and the residue was crystallized from acetone/Et_2O. The obtained yellow powder was identified as the dinuclear complex, **4·9H$_2$O**.

Reaction of *cis*-[RuCl$_2$(DMSO)$_4$] and *trans*-[RuCl$_2$(PTA)$_4$] under visible light

A solution of *trans*-[$RuCl_2(PTA)_4$] (10 mg, 0.01 mmol) and *cis*-[$RuCl_2(DMSO)_4$] (2.1 mg, 0.004 mmol) in 1 mL water was introduced into a 5 mm NMR tube. After irradiation with a 150 W halogen lamp overnight the starting compounds were fully transformed into **4**. When the same reaction was made without irradiation no significant transformation of the starting complexes was observed.

Reaction of [(DMSO)$_3$Ru(μ-Cl)$_3$RuCl(DMSO)$_2$] and PTA under visible light

A solution of [$(DMSO)_3Ru(\mu\text{-}Cl)_3RuCl(DMSO)_2$] (10 mg, 0.014 mmol) and PTA (12.8 mg, 0.081 mmol) in 1 mL of water was placed into a 5 mm NMR tube and was irradiated

overnight with a 150 W halogen lamp. The unique compound observed by NMR was **4**. The same reaction in the dark gave rise to a mixture of $[RuCl_2(DMSO)_2(PTA)_2]$ and *trans*-$[RuCl_2(PTA)_4]$.

Reaction of $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ and PTA under visible light

A solution of $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ (5 mg, 0.008 mmol) and PTA (7.7 mg, 0.049 mmol) in 1 mL of water was placed into a 5 mm NMR tube and was irradiated with a 150 W halogen lamp 6 hours. ^{31}P NMR analysis of the resulting solution showed that **4** was the unique compound formed.

Reaction of $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ and *trans*-$[RuCl_2(PTA)_4]$ under visible light

A solution of $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ (2.4 mg, 0.004 mmol) and *trans*-$[RuCl_2(PTA)_4]$ (17.8 mg, 0.02 mmol) in 1 mL of water was placed into a 5 mm NMR tube and was irradiated with a 150 W halogen lamp overnight. ^{31}P NMR analysis of the resulting solution showed that **4** was the unique compound formed. With exclusion of light only the starting complexes were recovered from the same reaction mixture.

Reactivity of 1 in D_2O with NaCl

Compound **1·3H₂O** (15 mg, 0.021 mmol) was dissolved in 0.5 mL of D_2O in a 5 mm NMR tube and the $^{31}P\{^1H\}$ NMR spectrum was recorded. Increasing amounts of NaCl were added into the solution and $^{31}P\{^1H\}$ NMR spectra were recorded in each step. Upon addition of 10 eq of NaCl signals of a new compound, *mer*-$[RuCl_3(PTA)_3]^-$ (20 %) were observed (a triplet around -11.5 ppm and a doublet around -51.3 ppm). With increasing NaCl concentration, the intensities of these resonances increased with a gradual shift of the signals. When the solution arrived close to saturation in NaCl (ca. 80 eq) $^{31}P\{^1H\}$ NMR showed the following data (121 MHz, D_2O): δ (ppm) -10.60 (bt, $P_{trans\text{-}Cl}$, 1 P), -51.30 (bd, $P_{trans\text{-}P}$, 2 P). Nevertheless, signals of *mer*-$[RuCl_2(H_2O)(PTA)_3]^{2-}$ were still observed (34 %) and all efforts on isolation of *mer*-$[RuCl_3(PTA)_3]^-$ in solid form failed.

Reaction of 1 in D_2O with HBF_4

Compound **1**·$3H_2O$ (15 mg, 0.021 mmol) was dissolved in 0.5 mL of D_2O in a 5 mm NMR tube. After recording its $^{31}P\{^1H\}$ NMR spectrum 0.46 mmol HBF_4 (60 μL 48 w/w % solution) was introduced into the solution. The $^{31}P\{^1H\}$ NMR spectrum observed after 15 min showed

the exclusive signals of *mer*-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$: $^{31}P\{^1H\}$ NMR (121 MHz, D_2O): δ (ppm) 2.31 ppm (t, $^2J_{PP}$ = 35.6 Hz, $P_{trans\text{-}O}$, 1 P), -36.28 ppm (d, $^2J_{PP}$ = 35.6 Hz, $P_{trans\text{-}P}$, 2 P).

Study of the behaviour of 1, 2 and 3 in D_2O at 25 ºC, 50 ºC and 80 ºC in the dark

The complexes **1**·$3H_2O$ (10 mg, 0.014 mmol), **2**·$1.25H_2O$ (15 mg, 0.021 mmol) and **3**·HCl·$2H_2O$ (15 mg, 0.018 mmol) were dissolved in 0.5 mL of D_2O each in 5 mm NMR tubes. The $^{31}P\{^1H\}$ NMR spectra obtained at 25 ºC, 50 ºC and 80 ºC showed that complex **1** was stable at 50 ºC for more than 30 min, however, under the same time at 80 ºC the dinuclear complex **4** could also be detected in addition to **2**. In contrast, complex **2** was stable even at 80 ºC. The proportion between *mer*-$[RuCl_3(HPTA)_3]^{2+}$ and *mer-trans*-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$ at room temperature (67/33) was reversibly modified at higher temperatures in favour of *mer*-$[RuCl_3(HPTA)_3]^{2+}$, being 73/27 at 80 ºC. At this temperature no significant modifications in the solution composition were observed after 12 h in the dark, however, under visible light irradiation the *fac*-isomer of complex **2** was slowly formed. Complex **3** is stable at 80 ºC for 12 h both in the dark and under visible light. At this temperature the only signal observed in the $^{31}P\{^1H\}$ NMR spectrum is the singlet corresponding to *fac*-$[RuCl_3(HPTA)_3]^{2+}$.

Catalysis

Aqueous-organic biphasic transfer hydrogenation of aldehydes

Appropriate amounts of the Ru(II)-PTA catalysts containing 0.0625 mmol Ru were placed into a Schlenk tube which was carefully deoxygenated and filled with N_2. The catalyst was dissolved in 5 mL of 5 M aqueous Na-formate solution, followed by addition of 4.92 mmol benzaldehyde or 3.96 mmol cinnamaldehyde in 5 mL chlorobenzene using hypodermic syringes. The reaction mixture was rapidly stirred at T=80 °C for t=3 h using a magnetic stirrer. After this time the mixture was cooled, the phases separated, a sample of the organic phase was passed through a short $MgSO_4$ plug and analyzed by gas chromatography.

In certain cases the catalyst was obtained by 20 min irradiation of a solution of *trans*-$[RuCl_2(PTA)_4]$.

Hydration of nitriles

0.05 mmol of the appropriate complex and the required amount of substrate and additives were placed into a Schlenk tube equipped with a reflux condenser and a bubble counter and

were dissolved in 3 mL water. Under argon atmosphere 1 mmol benzonitrile was added and the tube was immersed into an oil bath of 100-108 °C temperature and refluxed for 3 h. Samples (50 μL) were taken from the hot reaction mixture at 1, 2 and 3 h, and were extracted with 3×2 mL dichloromethane. Part of the combined organic phases was passed through a short plug of anhydrous $MgSO_4$ and analyzed by gas chromatography. The same yields were obtained in reactions carried out under air. In certain cases the catalyst was obtained by 20 min irradiation of a solution of *trans*-$[RuCl_2(PTA)_4]$.

X-ray structure determinations

Crystals of complexes **2·1.25H₂O**, **3·HCl·2H₂O** and **4·9H₂O** suitable for single crystal X-ray structure determination were obtained from water. Crystal data and data collection details are given in Table 1. Data collection for all compounds were performed on a Bruker APEX CCD diffractometer (XDIFRACT service of the University of Almería) in the range $2.82 \leq 2\theta \leq 50.12$, $3.06 \leq 2\theta \leq 50.10$ and $3.66 \leq 2\theta \leq 50.08$ at 150 ºK, 100 ºK and 100 ºK, respectively. No empirical absorption correction was applied for **4·9H₂O** but for **2·1.25H₂O** (T_{min}=0.732; T_{max}=0.949) and for **3·HCl·2H₂O** (T_{min}=0.863; T_{max}=0.906). Structures were determined by direct methods (SIR97[38] or SHELXS-XTL[39]) and refined by least-squares procedures on F^2 (SHELX-XTL). A disordered PTA molecule was found in **2·1.25H₂O** and an average model was refined. All non-hydrogen atoms were anisotropically refined. C-H and hydrogen atoms for all the complexes were placed in riding positions and refined isotropically but N_{PTA}-H in **2·1.25H₂O** were localized by synthesis difference and those for the PTA disordered molecule were not included. The positions of the H atoms of the water molecules coordinated to Ru in **4·9H₂O** were determined and refined altogether isotropically but those for **2·1.25H₂O** could not be localized although there was residual electron density close to the O atom. Final geometrical calculations, the graphical manipulations and the analysis of H-bond network and other crystallographic calculations were carried out with SHELXS-XTL package.

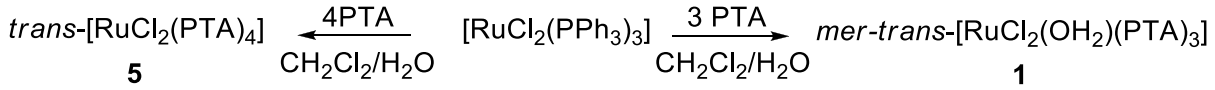
Table 1. Crystal data and structure refinement information for complexes **2·1.25H$_2$O**, **3·HCl·2H$_2$O** and **4·9H$_2$O**.

	2·1.25H$_2$O	**3**·HCl·2H$_2$O	**4**·9H$_2$O
Empirical formula	$C_{18}H_{41.5}Cl_5N_9O_{1.25}P_3Ru$	$C_{18}H_{44}Cl_6N_9O_2P_3Ru$	$C_{36}H_{90}Cl_4N_{18}O_9P_6Ru_2$
Formula weight	775.33	825.30	1449.02
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pccn*	$P2_1/n$	$P\bar{1}$
a (Å)	26.6270(10)	11.1793(8)	13.0395(8)
b (Å)	13.2360(10)	12.2900(9)	15.4809(10)
c (Å)	16.8950(10)	22.3109(16)	17.2746(11)
α (°)	90	90	113.0690(10)
β (°)	90	94.599(2)	111.6010(10)
γ (°)	90	90	93.1250(10)
V (Å^3)	5954.4(6)	3055.5(4)	2901.3(3)
Z	8	4	2
Calculated density (g cm^{-3})	1.695	1.794	1.659
λ / (Å)	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	1.169	1.232	0.935
F(000)	3048	1688	1500
Crystal size / mm	0.290x0.230x0.045	0.165x0.100x0.080	0.148x0.110x0.090
Index ranges	-31≤ h ≤30 -13≤ k ≤15 -20≤ l ≤16	-13≤ h ≤13 -14≤ k ≤14 -13≤ l ≤26	-15≤ h ≤14 -18≤ k ≤16 -10≤ l ≤20
Reflections collected	31517	16207	16165
Reflections unique	4402 (R_{int} = 0.0443)	4769 (R_{int} = 0.0320)	7918 (R_{int} = 0.0286)
Data/restraints/parameters	5279/0/ 328	5370/0/ 357	10154/27/ 733
Final *R* indices [$I>2\sigma(I)$][a,b]	R_1=0.0641, wR_2=0.1675	R_1=0.0445, wR_2=0.1136	R_1=0.0332; wR_2=0.0667
R indices (all data)[a,b]	R_1=0.0757, wR_2=0.1762	R_1=0.0505, wR_2=0.1176	R_1=0.0442; wR_2=0.0692
Goodness-of-fit on F^2	1.052	1.050	0.918
Largest diff. peak; hole (e·Å^{-3})	2.049 and -1.264	1.292 and -1.431	1.436 and -0.919
CCDC	1035047	1035048	1035049

Results and Discussion

Synthesis and properties of *mer-trans*-[$RuCl_2(OH_2)(PTA)_3$] (1)

Reaction of [$RuCl_2(PPh_3)_3$] dissolved in CH_2Cl_2 with 3 equivalents of PTA in aqueous solution immediately gave a dark yellow aqueous phase and a greenish organic phase. The mixture was stirred overnight at room temperature in the dark during which the aqueous phase turned orange yellow. (The organic phase remained pale green probably due to the presence of unreacted [$RuCl_2(PPh)_3$] and/or its oxidized derivatives – this was not investigated in detail.) According to $^{31}P\{^1H\}$ NMR spectra no free PTA was present in the aqueous phase which contained [$RuCl_2(OH_2)(PTA)_3$] (**1**) exclusively. A similar reaction but using of 4 equivalents of PTA over [$RuCl_2(PPh_3)_3$] led to a colorless organic phase and a yellow aqueous phase (Scheme 2); the latter contained *trans*-[$RuCl_2(PTA)_4$] (**5**) in almost quantitative yield.[16]



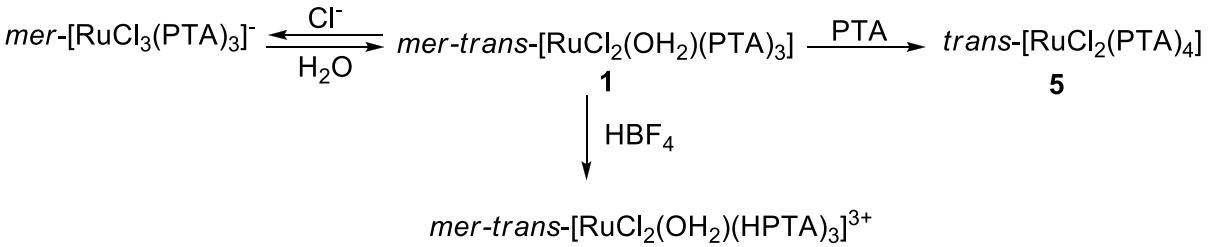
Scheme 2. Formation of *mer-trans*-[$RuCl_2(OH_2)(PTA)_3$] (**1**)

mer-trans-[$RuCl_2(OH_2)(PTA)_3$]·$3H_2O$ (1·$3H_2O$) is the first isolated compound containing a $Ru(PTA)_3$-fragment. Its elemental analysis is in agreement–with this formulation. The IR spectra shows a broad absorption band at 3434 cm^{-1} and a clear sharp band at 1706 cm^{-1}. These absorptions were also observed when the compound was dried at 70 ºC for 1 day, that is in agreement with an OH_2 coordinated to a Ru atom.[26] The $^{31}P\{^1H\}$ NMR spectrum of **1** corresponds to an AM_2 system constituted by a triplet at -5.08 ppm (1P) and a doublet at -46.78 ppm (2P). This indicates two Ru-coordinated PTA ligands *trans* to each other (-57.64 ppm for *cis*-[$RuCl_2(PTA)_4$] and -61.0 ppm for *cis,mer*-[$RuCl_2$(DMSO-S)$(PTA)_3$] [27]).

In similar compounds with *trans* Cl-Ru-PTA structures the chemical shift of the PTA *trans* to a Cl arises at -23.40 ppm.[40] The known complexes containing a water molecule *trans* to a PTA, such as *cis*-$[RuCl(OH_2)(PTA)_4]^+$ [26] and *cis*-$[Ru(OH_2)_2(PTA)_4]^{2+}$ [21] both display the corresponding signal at -16.5 ppm that is far from the chemical shift observed for complex **1** but far also from the normal chemical shift for Ru-coordinated PTA *trans* to a Cl. In contrast, *mer*-$[Ru(OH_2)_3(PTA)_3]^{2+}$ gives rise to a triplet $P_{trans\text{-}OH_2}$ resonance at -7.4 ppm, and a doublet $P_{trans\text{-}PTA}$ resonance at -48.3 ppm;[21] both are close to the relevant resonances of

1. Therefore the most plausible assignation for the triplet signal observed in the $^{31}P\{^{1}H\}$ NMR of **1** is a PTA *trans* to a H_2O coordinated to the metal by the O atom. The presence of a water molecule coordinated to the ruthenium was confirmed by TG analysis that evidenced that in the complexes there are three lattice water molecules that are eliminated below 90 ºC and one above 100 ºC. The ^{1}H NMR spectrum of **1** displays only broad signals in the region determined for the P-CH_2-N and N-CH_2-N protons of known PTA-Ru complexes and its $^{31}C\{^{1}H\}$ NMR data are also in agreement with proposed composition of **1** (ref.[17-18]; and references therein).

Finally, reaction of **1** in water with NaCl showed that the compound was gradually transformed into *mer*-$[RuCl_3(PTA)_3]^-$ upon the increase of salt concentration in the solution. The transformation was not complete within the solubility range of NaCl and it was not possible to isolate the new compound. Addition of H_2O into the solution returned the starting complex, which is in agreement with the initial substitution of the coordinated water molecule by a Cl^- what was reverted as the chloride concentration was reduced (Scheme 3).

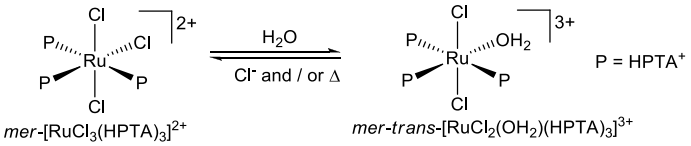


Scheme 3. Reactivity of *mer-trans*-$[RuCl_2(OH_2)(PTA)_3]$ (**1**) in water towards PTA, HBF_4 and Cl^- at room temperature

1 was reacted with PTA and its N-alkylated derivatives [(PTA-Bn)Cl, (PTA-Me)CF_3SO_3] in the dark. Only the neutral PTA afforded a uniform product, the formation of which was followed by UV-vis spectroscopy. Only one new species could be detected in the solution as shown by a single isosbestic point at λ = 322 nm. Accordingly, the $^{31}P\{^{1}H\}$ NMR spectra display a singlet signal (-49.7 ppm) which corresponds to *trans*-$[RuCl_2(PTA)_4]$ (**5**).

Dissolution of **1** in aqueous HCl results in protonation of one nitrogen atom of each of the coordinated PTA ligands yielding *mer*-$[RuCl_3(HPTA)_3]Cl_2$ (**2**). Crystals of **2**·1.25H_2O suitable for single crystal X-ray diffraction were obtained by diffusion of isopropanol to solutions of **2** in aqueous HCl. In *mer*-$[RuCl_3(HPTA)_3]^{2+}$, ruthenium is bonded to the P atoms of three mono-protonated PTA and three Cl in the *meridional* position. The $^{31}P\{^{1}H\}$ NMR in

D_2O showed two sets of signals with relative intensities of 1 to 2, a triplet at 2.31 ppm connected to a doublet at -36.28 ppm and a triplet at -4.62 ppm coupled to a doublet at -40.62 ppm. Ratio of the intensity of these sets of signals varies with the temperature as well as with the amount of added NaCl at room temperature (Scheme 4).



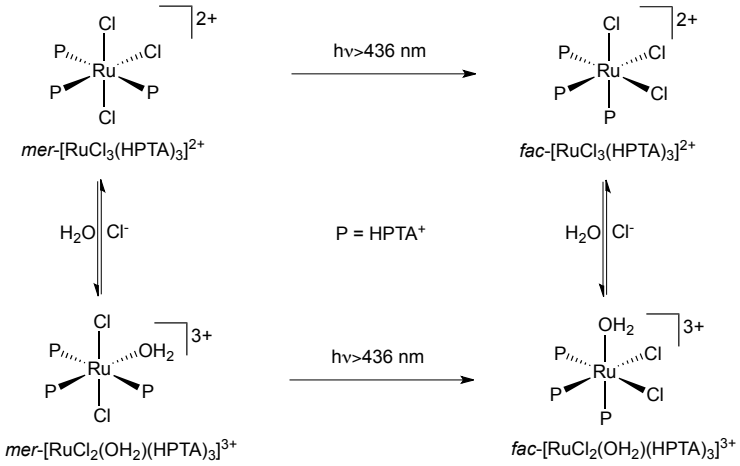
T(°C)	n_{NaCl}/n_{Ru}	Ratio of *mer*-$[RuCl_3(HPTA)_3]^{2+}$: *mer-trans*-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$
25	0	66.6% : 33.3%
25	40	85% : 15%
80	0	75% : 25%

Scheme 4. Aquation of *mer*-$[RuCl_3(HPTA)_3]^{2+}$ as a function of temperature and chloride concentration of aqueous solutions

This behaviour suggests that the main signals at -4.62 ppm and -40.62 ppm correspond to *mer*-$[RuCl_3(HPTA)_3]^{2+}$ and that the other set belongs to *mer-trans*-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$ which is produced by the substitution of a Cl^- in *mer*-$[RuCl_3(HPTA)_3]^{2+}$ by a water molecule. This assumption was confirmed when **1** was reacted with 5 equivalents of HBF_4 in water: the $^{31}P\{^1H\}$ NMR spectrum of the solution showed only the doublet and triplet assigned to *mer-trans*-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$ (Scheme 3).

When a solution of **2** was irradiated by a 150 W halogen lamp[37] single crystals suitable for X-ray determination separated in good yield (see Experimental). The crystal structure showed that the new complex is the *fac*-isomer of **2** isolated as *fac*-$[RuCl_3(HPTA)_3]Cl_2 \cdot HCl \cdot 2H_2O$ (**3·HCl·2H₂O**). Therefore the visible light promotes the isomerization of **2** into **3** in water (Scheme 5).

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of irradiated solutions of **2** showed a triplet at -4.57 ppm and a doublet at -12.49 ppm connected to each other and a singlet at -12.83 ppm. At 80 ºC, $^{31}P\{^1H\}$ NMR of the solution showed only the singlet at -12.83 ppm which is also the only signal observed when NaCl is added to the solution in high excess at room temperature (Scheme 5).



T(°C)	n_{NaCl}/n_{Ru}	Ratio of *fac*-$[RuCl_3(HPTA)_3]^{2+}$: *fac*-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$
25	0	25% : 75%
25	40	99% : 1%
80	0	99% : 1%

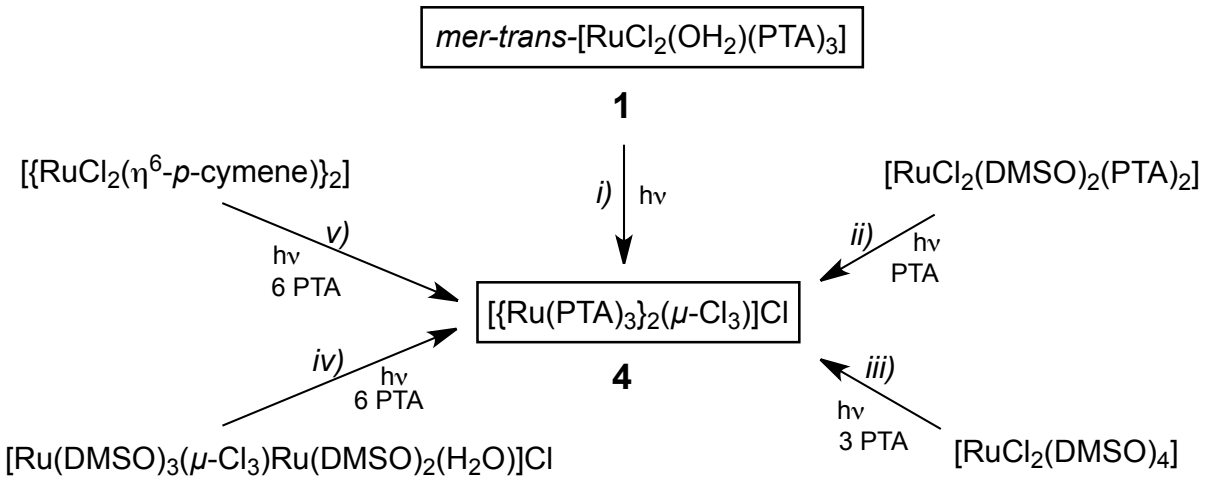
Scheme 5. Synthesis of *fac*-$[RuCl_3(HPTA)_3]^{2+}$ and its aquation in water as a function of temperature and chloride concentration.

The expected signal for **3** should be a singlet as the ligands are in a *fac*-disposition. The chemical shift of the singlet (-12.83 ppm) is very close to that of the doublet (-12.49 ppm) therefore it is reasonable to assign both signals to a $PTA_{trans\text{-}Cl}$, while the observed triplet (-4.57 ppm) at room temperature can be assigned to a $PTA_{trans\text{-}OH_2}$. This is further supported by the triplet's chemical shift being close to the chemical shift of $PTA_{trans\text{-}OH_2}$ in *mer*-$[Ru(OH_2)_3(PTA)_3]^{2+}$ (-7.4 ppm) and in *mer-trans*-$[RuCl_2(OH_2)(PTA)_3]$ (-5.08 ppm).
Altogether these observations show that irradiated solutions of **1** in aqueous HCl contain both *fac*-$[RuCl_3(HPTA)_3]^{2+}$ and *fac*-$[RuCl_2(OH_2)(HPTA)_3]^{3+}$.

Synthesis and characterization of $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ (4)

$[RuCl_2(PR_3)_{3\text{-}4}]$ complexes prepared in the reactions of $RuCl_3$ and aliphatic tertiary phosphines are known to rearrange spontaneously to $[\{Ru(PR_3)_3\}_2(\mu\text{-}Cl)_3]Cl$ in alcohols at reflux temperature.[41] With $P(Bu)_3$ and $P(CH_2OH_3)_3$ the dimerization took place even at room temperature, albeit in slow processes.[42-44]

We have found that [{Ru(PTA)$_3$}$_2$(μ-Cl)$_3$]Cl (**4**) can be obtained in several ways from various Ru(II)-complexes (Scheme 6).



Scheme 6. Formation of [{Ru(PTA)$_3$}$_2$(μ-Cl)$_3$]Cl (**4**) from various precursors at room temperature in water under illumination

[{Ru(PTA)$_3$}$_2$(μ-Cl)$_3$]Cl (**4**) can be prepared by heating of an aqueous solution of [RuCl$_2$(OH$_2$)(PTA)$_3$] (**1**) for 1 hour at elevated temperatures (80 °C) even with exclusion of light. Replacement of the ^{31}P NMR signals of the starting complex (**1**) by a new one at -14.60 ppm in D$_2$O shows the formation of the dinuclear complex. **4** was also obtained in 1 hour already at room temperature when an aqueous solution of **1** was irradiated with white light (150 W halogen lamp) or light of >460 nm (process *i)* on Scheme 6). In comparison, without irradiation, aqueous solutions of *trans*-[RuCl$_2$(PTA)$_4$] are stable in the dark even at 80 °C, while under conditions of process *i)* *trans*-[RuCl$_2$(PTA)$_4$] isomerizes to the thermodynamically stable *cis*-[RuCl$_2$(PTA)$_4$] and small amount of *cis*-[RuCl(OH$_2$)(PTA)$_4$]$^+$ can be also detected[26,27].

Our earlier studies have shown that an aqueous solution of *cis*-*cis*-*trans*-[RuCl$_2$(DMSO)$_2$(PTA)$_2$] obtained in the reaction of *cis*-[RuCl$_2$(DMSO)$_4$] and 2 eq. PTA is stable in the dark.[23] However, upon irradiation (process *ii)* on Scheme 6), the solution turns green, and after addition of 1 eq PTA it becomes lemon yellow; the ^{31}P{^{1}H} NMR spectrum of this yellow solution displays only the signal of **4** at -14.60 ppm. Formation of **4** is facilitated if the solution of *cis*-*cis*-*trans*-[RuCl$_2$(DMSO)$_2$(PTA)$_2$] contains PTA in the ratio (PTA/Ru=3) right from the beginning of irradiation. Increasing the n_{PTA}/n_{Ru} ratio from 3 to 4,

the exclusive product was *trans*-[$RuCl_2(PTA)_4$] in aqueous solution in dark at room temperature, however, upon white light irradiation *cis*-[$RuCl_2(PTA)_4$] was detected as a main product accompanied with $[Ru(OH_2)Cl(PTA)_4]^+$.

Other water-soluble Ru(II)-complexes such as *cis*-[$RuCl_2(DMSO)_4$], [$(DMSO)_3Ru(\mu$-$Cl)_3RuCl(DMSO)_2$] and [{$RuCl_2(\eta^6$-*p*-cymene)}$_2$] were also found suitable for preparation of **4.** In fact, reaction of *cis*-[$RuCl_2(DMSO)_4$] with 3 equivalents of PTA under visible light irradiation (process *iii)*, Scheme 6) provides the simplest synthesis of **4** with almost quantitative isolated yield (98%; see Experimental).

Irradiation with visible light of a solution of the known dinuclear complex [$(DMSO)_3Ru(\mu$-$Cl)_3RuCl(DMSO)_2$] in the presence of 6 equivalents of PTA (process *iv)*, Scheme 6) also led to the formation of **4.** However, with the exclusion of light a 1:1 mixture of *cis*-*cis*-*trans*-[$RuCl_2(DMSO)_2(PTA)_2$] and *trans*-[$RuCl_2(PTA)_4$] (with a 1:2 ratio of $^{31}P\{^1H\}$ NMR integrals) was obtained in the same solution, and no traces of **4** were detected. In comparison, although *cis*-*cis*-*trans*-[$RuCl_2(DMSO)_2$(PTA-Me)$_2$]$(CF_3SO_3)_2$ is also light-sensitive, irradiation by visible light in the presence of 1 eq (PTA-Me)(CF_3SO_3) yields the known[40] *trans*-[$RuCl_2(OH_2)$(PTA-Me)$_3$]$^{3+}$ and *cis*-[$RuCl_2$(PTA-Me)$_4$]$^{4+}$ complexes instead of a dinuclear complex similar to **4**. Irradiation of aqueous solutions of *cis*-*cis*-*trans*-[$RuCl_2(DMSO)_2$(PTA-Bn)$_2$]Cl_2 did not yield uniform products independent of presence or absence of 1 eq (PTA-Bn)Cl.

Finally, the dinuclear compound **4** was formed exclusively upon irradiation or refluxing of an aqueous solution containing [{$RuCl_2(\eta^6$-*p*-cymene)}$_2$] and 6 eq of PTA (PTA/Ru=3) for one hour (the colour of the solution turned from orange to yellow with strong smell of free *p*-cymene) (process *v)*, Scheme 6).

In contrast to the analogous water-soluble dinuclear complex containing $P(CH_2OH_3)_3$,[44] compound **4** is air-stable both in solution and in solid form. Single crystals of **4·9H$_2$O** were obtained by layering 2-propanol on an aqueous solution of the complex.

Crystal structures of 2·1.25H$_2$O, 3·HCl·2H$_2$O and 4·9H$_2$O

The crystal structures of the metal complex units of **2·1.25H$_2$O**, **3·HCl·2H$_2$O** and **4·9H$_2$O** determined by X-ray crystallography are shown in Figures 1, 2 and 3. Crystal data are given in Table 1 (selected bond lengths and angles in Suppl. Table S1).

Complex **2·1.25H$_2$O** is constituted by one cationic *mer*-[$RuCl_3(HPTA)_3$]$^{2+}$, three chlorides and 1.25 lattice water molecules while the asymmetric unit of **3·HCl·2H$_2$O** consists of a *fac*-[$RuCl_3(HPTA)_3$]$^{2+}$ cation, three chlorides, and a protonated water dimer, $H_5O_2^+$. Single crystal

X-ray crystallography showed that the asymmetric unit of **4·9H₂O** consisted of one dinuclear ion $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]^+$, one chloride and nine water molecules. In **2·1.25H₂O**, **3·HCl·2H₂O** and **4·9H₂O**, the C-N distances of the PTA ligands are found to be in the range consistent with those for other PTA complexes. The angles between ligands for a distorted octahedral geometry deviate significantly from 90º in **2** and **4**: the smallest and largest angles in **4** are Cl2-Ru1-Cl1 (79.63(3)°) and P2-Ru1-P1 (97.60(3)º), those in **2** are P1-Ru1-Cl2 (80.60(5)º) and P2-Ru1-P3 (97.31(7)º) while in **3** deviations from 90° are smaller: Cl1-Ru1-Cl2 (85.66(4)º) and P3-Ru1-Cl1 (91.04(4)º).

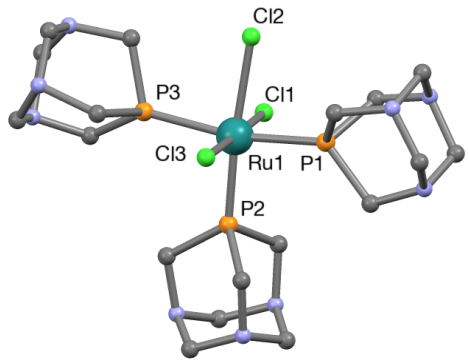


Figure 1. Ball and stick model of the *mer*-$[RuCl_3(HPTA)_3]^{2+}$ cation in **2·1.25H₂O** with partial atom numbering scheme. Hydrogen atoms are omitted for clarity.

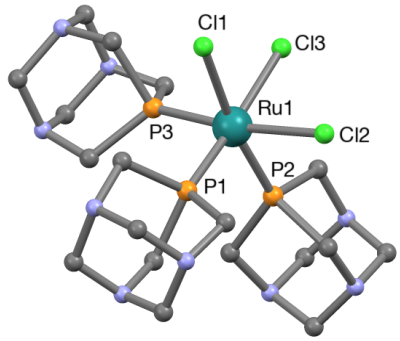


Figure 2. Ball and stick model of the *fac*-$[RuCl_3(HPTA)_3]^{2+}$ cation in **3·HCl·2H₂O** with partial atom numbering scheme. Hydrogen atoms are omitted for clarity.

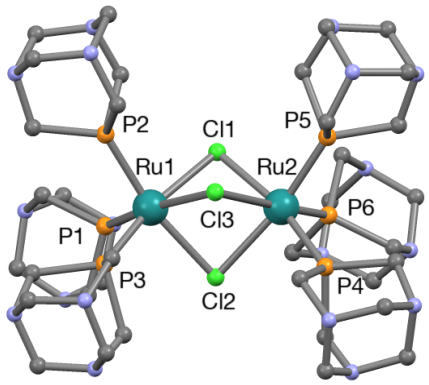


Figure 3. Ball and stick model of the $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]^+$ cation in **4·9H₂O** with partial atom numbering scheme. Hydrogen atoms are omitted for clarity.

The metal ion of **2·1.25H₂O** is in a distorted octahedral environment bound to three chlorides in a *mer*-disposition, completing its coordination geometry by three protonated PTA ligands bonded through the P atoms. The Ru-P bond distances in **2** are in the range from 2.2218(16) Å (Ru-P2; $P_{trans\text{-}Cl}$) to 2.3387(17) Å (Ru-P1; $P_{trans\text{-}P}$) what is similar to those found in *mer*-$[RuCl_3(PTA\text{-}Me)_3]^{2+}$ ($P_{trans\text{-}Cl}$ = 2.220(2) Å - $P_{trans\text{-}P}$ = 2.333(2) Å),[40] showing a similar short distance for the P atom *trans* to the Cl. Nevertheless the Ru-$P_{trans\text{-}Cl}$ distance is longer than those for Ru-$P_{trans\text{-}P}$ and they are quite different from those found in *cis*-$[RuCl_2(PTA\text{-}Me)_4]^{4+}$ (Ru-$P_{trans\text{-}Cl}$ = 2.267(2) Å, 2.277(2) Å; Ru-$P_{trans\text{-}P}$ = 2.375(2) Å, 2.377(2) Å).[40] The three Ru-Cl bond lengths in **2** (Ru1-Cl3 = 2.4033(19) Å, Ru1-Cl1 = 2.4198(18) Å, Ru1-Cl2 = 2.5025(16) Å) are somewhat different but similar to those observed for *mer*-$[RuCl_3(PTA\text{-}Me)_3]^{2+}$ (Ru1-Cl1 = 2.427(1) Å, Ru1-Cl2 = 2.496(1) Å, Ru1-Cl3 = 2.422(1) Å);[40] however, a new feature is that the Ru-Cl distance *trans* to P is the longest.

The ruthenium ion in **3·HCl·2H₂O** is in an octahedrally distorted coordination geometry bonded to three PTA ligands by the P atom and to three Cl^- in a *fac* disposition. The distances Ru-P are more different among them than the Ru-Cl bond lengths and similar to those found in **4** (Ru1-P1 = 2.2494(11) Å; Ru1-P2 = 2.2567(11) Å; Ru1-P3 = 2.2381(11) Å; Ru1-Cl1 = 2.4803 (10) Å; Ru1-Cl2 = 2.4734(11) Å; Ru1-Cl3 = 2.4708(11) Å), what shows the distortion of the molecule.

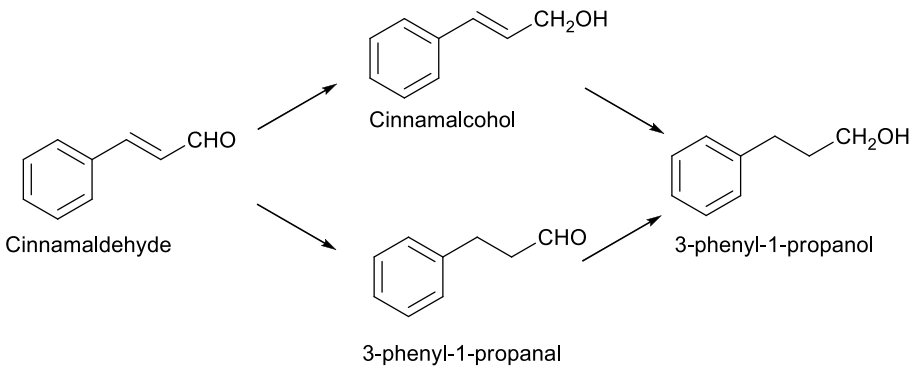
Finally, **4** is constituted by two $\{Ru(PTA)_3\}$ units linked through the metals by three bridging Cl^-; the metal atoms are coordinated in a distorted octahedral geometry to three PTA ligands through the P atoms. According to the Cambridge Structural Database[45] to date only 8 chloro-bridged dinuclear Ru(II)-complexes with monodentate phosphine ligands (similar to

4) have been characterized in solid state [42-44,46-49]. The distances Ru-P and Ru-Cl for the two metals are not the same (Ru1-P1 = 2.2672(9) Å; Ru1-P2 = 2.2601(10) Å; Ru1-P3 = 2.2518(9) Å; Ru2-P4 = 2.2499(9) Å; Ru2-P5 = 2.2438(10) Å; Ru2-P6 = 2.2525(9) Å; Ru1-Cl1 = 2.5335(8) Å; Ru1-Cl2 = 2.4988(9) Å; Ru1-Cl3 = 2.4797(8) Å; Ru2-Cl1 = 2.4857(8) Å; Ru2-Cl2 = 2.5202(9) Å; Ru2-Cl3 = 2.4949(9) Å) showing the distortion of the entire molecule. In the similar dinuclear ruthenium complexes containing trimethylphosphine, $[Ru\{P(CH_3)_3\}_3(\mu\text{-}Cl)_3Ru\{P(CH_3)_3\}_3]X$ ($X=BF_4$[46], Cl[47]) both ruthenium atoms have equal distances to phosphines as well as to chlorides; in the chloride salt the average Ru-P distance (2.266(2) Å) was found larger while the average Ru-Cl distance (2.503(6) Å) almost the same as in **4**. It is known that PTA and $P(CH_3)_3$ have similar cone angles and basicity, therefore the observed differences in the complex structure must be due to the crystal packing of the complex. In fact, complex **4** is involved in an extensive strong hydrogen-bond network made by connections of N atoms of the PTA molecules with the neighbouring molecules (Suppl. Figure S3).

Catalysis

Biphasic reduction of aldehydes catalyzed by water-soluble Ru(II)-PTA complexes

Since upon visible light irradiation *trans*-$[RuCl_2(PTA)_4]$ can be isomerized to *cis*-$[RuCl_2(PTA)_4]$ and the latter can be aquated to *cis*-$[RuCl(OH_2)(PTA)_4]^+$,[26,27] it is important to learn how these photochemical processes may influence the reactions catalyzed by the various Ru(II)-PTA complexes. With this aim in mind we have investigated the reduction of cinnamaldehyde (Scheme 7) and benzaldehyde with aqueous Na-formate as hydrogen donor and with *trans*-$[RuCl_2(PTA)_4]$ as catalyst; the results are shown in Table 2. It was established, that the results of the experiments performed in dark were not different from those obtained under light: benzaldehyde was converted to benzyl alcohol in a fast reaction and cinnamaldehyde was reduced to cinnamalcohol with 100% selectivity (Table 2, entry 1).



Scheme 7. Possible products of hydrogenation of cinnamaldehyde

Reduction of aldehydes was also performed in such a way that an intensively stirred solution of *trans*-[$RuCl_2(PTA)_4$] was irradiated with visible light for 20 min and this solution was then used as catalyst. At this point there was already no *trans*-[$RuCl_2(PTA)_4$] in the solution which, however, contained *cis*-[$RuCl_2(PTA)_4$] and *cis*-[$RuCl(OH_2)(PTA)_4]^+$ in a 1:3 ratio. This in situ prepared mixture was somewhat less active in the reduction of benzaldehyde, leading to 85% conversion instead of 92%. Furthermore, reduction of cinnamaldehyde was less selective than with *trans*-[$RuCl_2(PTA)_4$], and small amounts of 3-phenyl-1-propanal and 3-phenyl-1-propanol could also be detected (entry 3).

Table 2. Biphasic reduction of benzaldehyde and cinnamaldehyde catalyzed by various Ru(II)-PTA complexes using aqueous HCOONa as hydrogen donor.*

	Catalyst	Benz-aldehyde	Cinnamaldehyde			
		Benzyl alcohol (%)	Total conversion (%)	Product yield		
				Cinnam-alcohol (%)	3-phenyl-1-propanal (%)	3-phenyl-1-propanol (%)
1	*trans*-[$RuCl_2(PTA)_4$] (**5**)	92	30	30	-	-
2	*trans*-[$RuCl_2(PTA)_4$] + 5 eq. NaCl	90	29	29	-	-
3	"in situ" *cis*-[$RuCl(OH_2)(PTA)_4$] and *cis*-[$RuCl_2(PTA)_4$]**	85	32	24	5	3
4	*cis*-[$RuCl_2(PTA)_4$] ** (as in entry 3 but + 5 eq. NaCl)	91	29	28	1	-
5	*mer-trans*-[$RuCl_2(OH_2)(PTA)_3$] (**1**)	99	55	55	-	-
6	[{Ru $(PTA)_3\}_2(\mu$-$Cl)_3]Cl$ (**4**)	25	5	5	-	-
7	*cis*-[$RuCl_2(DMSO)_4$]	0	0	-	-	-
8	[$(DMSO)_3Ru(\mu$-$Cl)_3RuCl(DMSO)_2$]	0	0	-	-	-
9	*cis-cis-trans*-[$RuCl_2(DMSO)_2(PTA)_2$]	71	34	16	7	11

10	*cis-cis-trans*- -$[RuCl_2(DMSO)_2(PTA\text{-}Bn)_2]^{2+}$	68	33	28	2	3
11	*cis-cis-trans*- -$[RuCl_2(DMSO)_2(PTA\text{-}Me)_2]^{2+}$	78	40	36	2	2

Conditions: 0.0625 mmol Ru, 4.92 mmol benzaldehyde or 3.96 mmol cinnamaldehyde, 5 mL 5 M aqueous solution of HCOONa, 5 mL chlorobenzene, t = 3 h, T = 80 °C.

*Yields were determined by gas chromatography. ** This catalyst solution was obtained by 20 min irradiation of a solution of *trans*-$[RuCl_2(PTA)_4]$.

Addition of 5 eq NaCl reverted this change almost completely while it had negligible effect on reactions catalyzed by *trans*-$[RuCl_2(PTA)_4]$ with no irradiation (entries 4 and 2). Since already such a small excess of chloride is sufficient to prevent aquation[26,27] this result shows that *cis*- and *trans*-$[RuCl_2(PTA)_4]$ have about the same catalytic activity in this hydrogen transfer reaction. The highest activity in benzaldehyde reduction was shown by the trisphosphine complex, *mer-trans*-$[RuCl_2(OH_2)(PTA)_3]$ (entry 5). The use of the dinuclear $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ (**4**) resulted in 25% benzaldehyde conversion (entry 6). This lower efficiency relative to *mer-trans*-$[RuCl_2(OH_2)(PTA)_3]$ (**1**) may be the consequence of the difficulty of splitting three chloride bridges in $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]^+$ in order to form catalytically active mononuclear complexes.

The Ru(II)-complexes containing only chloride and DMSO ligands were completely inactive in the biphasic hydrogen transfer from aqueous formate (entries 7,8). However, the mixed $[RuCl_2(DMSO)_2L_2]$ complexes showed catalytic activities in reduction of benzaldehyde with 68-78% conversions, and the activity increased in the order L = (PTA-Bn)Cl < PTA < (PTA-Me)(CF_3SO_3).

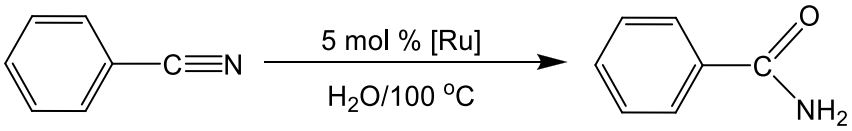
Transfer hydrogenation of cinnamaldehyde was also investigated with the same Ru(II) complexes. The highest catalytic activity was again shown by *mer*-$[RuCl_2(OH_2)(PTA)_3]$ (55% conversion, almost double than that obtained with *trans*-$[RuCl_2(PTA)_4]$; 30%), with 100% selectivity to cinnamalcohol. $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ was a poor catalyst (5% conversion) while $[RuCl_2(DMSO)_4]$ and $[(DMSO)_3Ru(\mu\text{-}Cl)_3RuCl(DMSO)_2]$ did not catalyze the reaction. $[RuCl_2(DMSO)_2L_2]$ complexes showed medium catalytic activity, however, in their cases the reduction was not selective, and the saturated aldehyde and saturated alcohol products were also detected in the reaction mixtures.

From these measurements it can be concluded that visible light has only a small effect on the transfer hydrogenation of aldehydes by $[RuCl_x(OH_2)_y(PTA)_{6-x-y}]$ catalysts (x= 1, y =1; x = 2, y = 0; x=2, y=1) with 5 M aqueous sodium formate as hydrogen source. This

observation may be explained by the fast formation of the same catalytic species from the various Ru(II)-catalyst precursors in the concentrated HCOONa solution (probably Ru(II)-hydrido-complexes, such as those identified in ref.[44]). These results lend further credit to earlier investigations on such catalytic systems with no exclusion of light and suggest that photoactivity of $[RuCl_x(OH_2)_y(PTA)_{6-x-y}]$ catalysts is more likely to influence reactions (such as hydrogenation or redox isomerization) in the absence of a high concentrations of other coordinating ligands such as, for example, $HCOO^-$.

Hydration of nitriles

For hydration of nitriles earlier we applied catalysts formed in situ from –among others– *cis*-$[RuCl_2(DMSO)_4]$ and PTA and (PTA-Bn)Cl.[29,30] The isolated complex, *cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA)_2]$ showed only modest catalytic activity, however, under the same conditions an almost doubled activity was observed with *cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA\text{-}Bn)_2]Cl_2$.[29] Here we report on the catalytic activity of various new, isolated Ru(II)-complexes with PTA-derived ligands as catalysts for benzonitrile hydration (Scheme 8) as well as the effect of light on the catalytic reactions. The results are shown in Table 3 (entries 1-3 and 10 are included for comparison from ref.[29]).



Scheme 8. Hydration of benzonitrile to benzamide

It has been found that addition of 1 eq PTA to *cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA)_2]$ considerably increased the catalytic activity; however an even larger rate increase could be achieved by addition of 1 eq (PTA-Bn)Cl (entries 1-3): with (PTA-Bn)Cl the reaction was practically complete in 1 hour. Similar effects were observed with PTA and (PTA-Bn)Cl as additives applying $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ (entries 4-6), *mer*-*trans*-$[RuCl_2(OH_2)(PTA)_3]$ (entries 7-9) and *trans*-$[RuCl_2(PTA)_4]$ (entries 10,11). In all cases the use of (PTA-Bn)Cl led to ≥90% conversions in 1 hour. We have already observed such a striking accelerating effect of (PTA-Bn)Cl (relative to PTA) with catalysts prepared in situ from *cis*-$[RuCl_2(DMSO)_4]$ and 3 eq (PTA-Bn)Cl.[29] Similarly, an earlier study on catalysis of nitrile hydration with half-sandwich $[RuCl_2(arene)L]$ (L=PTA, (PTA-Bn)Cl, *m*tppms-Na) complexes also showed the PTA-Bn containing catalysts the most effective (independent of the arene ligand).[50] The

catalysts shown in Table 3 entries 3, 6, 9, 11 are approximately twice as active {TOFs = 18-20 h^{-1}; TOF=turnover frequency=(mol product)×(mol catalyst)$^{-1}$×h^{-1}} in hydration of benzonitrile than the best half-sandwich complex, $[RuCl_2\{\eta^6\text{-}C_6(CH_3)_6\}](PTA\text{-}Bn)]Cl$ (TOF=10 h^{-1}) with no microwave irradiation.[51] At present we do not know the origin of this phenomenon. In the cases of entries 3, 6 and 9 one may assume the fast coordination of a $(PTA\text{-}Bn)^+$ ligand to Ru(II), however, this is less likely with the six-coordinated and stable *trans*-$[RuCl_2(PTA)_4]$ (entries 10-11). In separate experiments it was established, that (PTA-Bn)Cl itself had no catalytic effect in hydration of benzonitrile. Furthermore, under the same conditions but in the absence of benzonitrile, attempted reactions of (PTA-Bn)Cl with *cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA)_2]$, *mer*-*trans*-$[RuCl_2(OH_2)(PTA)_3]$ (**1**), $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ (**4**) or *trans*-$[RuCl_2(PTA)_4]$ (**5**) did not yield uniform products as shown by ^{31}P and ^1H NMR measurements. Our efforts to obtain a well defined Ru(II)-PTA-Bn complex from hydrated $RuCl_3$ and PTA-Bn in refluxing ethanol (analogous to the synthesis of *trans*-$[RuCl_2(PTA)_4]$) also failed. Clearly, further experiments are needed to clarify the mechanism of this catalytic nitrile hydration and that of the "magic" effect of (PTA-Bn)Cl.

Table 3. Hydration of benzonitrile catalyzed by various Ru(II)-PTA/PTA-Bn complexes*

	Catalyst	[Ru]:[PTA]:[(PTA-Bn)Cl]	Conversion (%)		
			1 h	2 h	3 h
1	*cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA)_2]$	1:2:0	0	13	46
2	*cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA)_2]$ + PTA	1:3:0	2	56	79
3	*cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA)_2]$ + (PTA-Bn)Cl	1:2:1	99	99	99
4	$[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$	1:3:0	81	84	89
5	$[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ + 2 PTA	1:4:0	96	98	99
6	$[\{Ru\ (PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ + 2 (PTA-Bn)Cl	1:3:1	99	99	99
7	*mer*-*trans*-$[RuCl_2(OH_2)(PTA)_3]$	1:3:0	29	65	80
8	*mer*-*trans*-$[RuCl_2(OH_2)(PTA)_3]$ + PTA	1:4:0	43	91	99
9	*mer*-*trans*-$[RuCl_2(OH_2)(PTA)_3]$ + (PTA-Bn)Cl	1:3:1	90	94	98
10	*trans*-$[RuCl_2(PTA)_4]$	1:4:0	32	65	80
11	*trans*-$[RuCl_2(PTA)_4]$ + [(PTA-Bn)Cl]	1:4:1	94	95	98
12	„in situ"*cis*-$[RuCl(OH_2)(PTA)_4]$ and *cis*-$[RuCl_2(PTA)_4]$**	1:4:0	3	13	29
13	*cis*-$[RuCl_2(PTA)_4]$** (+5 eq. NaCl)	1:4:0	14	47	64
14	*trans*-$[RuCl_2(PTA)_4]$ (+5 eq. NaCl)	1:4:0	17	41	87

Reaction conditions: 0.05 mmol (5 mol%) Ru, 1 mmol benzonitrile, 3 mL H_2O, reflux. *Conversions were determined by gas chromatography. **This catalyst solution was obtained by 20 min irradiation of a solution of *trans*-$[RuCl_2(PTA)_4]$.

The catalytic activity of $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ formed by refluxing or irradiation of aqueous solutions of *mer*-*trans*-$[RuCl_2(OH_2)(PTA)_3]$ is higher than that of the mother mononuclear complex (entries 4 vs 7). The same conclusion can be drawn by comparison of

catalytic activities of **4** and *cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA)_2]$ (or *cis*-*cis*-*trans*-$[RuCl_2(DMSO)_2(PTA)_2]$ + 1 eq PTA; entries 4 vs 1, 2).

We have no evidence on the nuclearity of the active catalytic species in case of $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$ as a precatalyst. However, it is striking that in the presence of 2 eq PTA the activity of the formed catalytic species was much higher than that of *trans*-$[RuCl_2(PTA)_4]$ despite the same overall Ru:Cl:PTA=1:2:4 molar ratio (entries 5 vs. 10), which may refer to the presence of an active dinuclear catalyst.

As discussed above, 20 min irradiation by visible light of aqueous solutions of *trans*-$[RuCl_2(PTA)_4]$ yields a solution containing *cis*-$[RuCl_2(PTA)_4]$ and *cis*-$[RuCl(OH_2)(PTA)_4]^+$ in 1:3 ratio. This solution showed a catalytic activity much inferior to that of *trans*-$[RuCl_2(PTA)_4]$ (entries 12 vs 10). NaCl (5 eq) disfavoured the photochemically assisted formation of *cis*-$[RuCl(OH_2)(PTA)_4]^+$, however, the catalytic activity of *cis*-$[RuCl_2(PTA)_4]$ still did not reach that of *trans*-$[RuCl_2(PTA)_4]$ also measured in the presence of 5 eq NaCl (entries 13 vs 14). In general, NaCl seems to decrease the rate of benzonitrile hydration catalyzed by Ru(II)-PTA species (entries 13, 14 vs 10).

Conclusion

The results described above show that in many cases the composition of in situ prepared Ru(II)-PTA catalysts may critically depend on the ligand/metal concentration ratio and the variety of the obtained complexes is further increased by thermal and photochemical effects. For example, in solutions of [PTA]:$[RuCl_2(DMSO)_4]$=4 concentration ratio, upon irradiation with visible light, in addition to *trans*- and *cis*-$[RuCl_2(PTA)_4]$, *cis*-$[RuCl(OH_2)(PTA)_4]^+$ is also formed via photoaquation. When the [PTA]:$[RuCl_2(DMSO)_4]$ ratio is lowered to 3, visible light irradiation leads to formation of the dinuclear $[\{Ru(PTA)_3\}_2(\mu\text{-}Cl)_3]Cl$. The same dinuclear complex is obtained in aqueous solution from the thermal or photochemical reaction of *mer*-*trans*-$[RuCl_2(OH_2)(PTA)_3]$. However, in aqueous hydrochloric acid solutions *mer*-*trans*-$[RuCl_2(OH_2)(PTA)_3]$ yields *mer*-$[RuCl_3(HPTA)_3]^{2+}$ which is also photoactive and gives *fac*-$[RuCl_3(HPTA)_3]^{2+}$ upon irradiation.

In the catalytic transfer hydrogenation of aldehydes in concentrated aqueous solutions of Na-formate only slight photochemical effects were observed. Conversely, the photochemical activity of the Ru(II)-PTA-type complexes had more pronounced influence on the catalytic hydration of benzonitrile. From the results it can be concluded that irradiation with visible light of *trans*-$[RuCl_2(PTA)_4]$ leads to formation of catalytically less active Ru(II)-

complexes for hydration of nitriles. One must also consider the photochemical or thermal formation of [{Ru(PTA)$_3$}$_2$(μ-Cl)$_3$]Cl which can take place from various Ru(II)-PTA derivatives and which itself is active in benzonitrile hydration especially in the presence of N-benzylated PTA.

Acknowledgement

Thanks are given to the European Commission FEDER program for co-financing the projects CTQ2015-67384-R (MINECO) and P09-FQM-5402 (Junta de Andalucía). Thanks are also given to Junta de Andalucía PAI-research group FQM-317 and COST Action CM1302 (WG1, WG2). The research was supported by the EU and co-financed by the European Social Fund under the project ENVIKUT (TÁMOP-4.2.2.A-11/1/KONV-2012-0043). A.U. acknowledges funding from the Hungarian Academy of Sciences of a postdoctoral fellowship. Thanks are also due to the Hungarian Research, Development and Innovation Office - Hungarian Research Fund (NKFIH-OTKA K101372) for financial support.

Contributions of Dr. Attila Kiss-Szikszai (elemental analyses) and of Dr. Lajos Nagy (ESI-MS measurements) both of the University of Debrecen are thankfully acknowledged.

Appendix A. Supplementary data

CCDC 1035047, 1035048, 1035049 contain the supplementary crystallographic data for compounds **2**, **3** and **4** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif . Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/xxxxxxxxxxxxxxxxx

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