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Visible-Light Photoisomerization and Photoaquation of *trans*-[Ru(1,3,5-triaza-7-phosphaadamantane)$_4$Cl$_2$] in Organic Solvent and Water

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The interaction of the PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) ruthenium complex *trans*-[RuCl$_2$(PTA)$_4$] (*trans*-**1**) with visible light in chloroform and in water has been studied at room temperature. The complex *trans*-**1** isomerizes to the *cis* isomer in $CHCl_3$ with radiation of $\lambda > 416$ nm ($\Phi_{434\ nm}$ ($CHCl_3$) = 0.13 ± 0.01). The isomerization reaction is reversible as *cis*-**1** is transformed into *trans*-**1** with $\lambda = 367$ nm ($\Phi_{367\ nm}$ ($CHCl_3$) = 0.25 ± 0.02). Irradiation at $\lambda > 416$ nm of a solution of *trans*-**1** in water leads to the *cis*-isomer complex and to the aqua complex (OC-6-32)-[RuCl(H_2O)(PTA)$_4$]Cl (**2Cl**) by a photoisomerization and photoaquation reaction ($\Phi_{434\ nm}$ (D_2O) = 0.27 ± 0.02). The mole ratio of *cis*-**1** to **2Cl** is not dependent on the pH but on the concentration of the products in solution. Isomerization in water is not reversible even if only *cis*-**1** is present in solution. Synthesis and characterization of (OC-6-32)-[RuCl(H_2O)(PTA)$_4$](CF_3SO_3) (**2CF$_3$SO$_3$**) are also presented.

Introduction

Not many examples of photochemical syntheses employing water soluble complexes have been described so far which is quite surprising in view of the intense research activity centered on hydrosoluble metal complexes and the pressing need to develop more and more environmentally friendly technologies for the manufacture of fine chemicals.[1] Catalytic solar light synthesis in water at room temperature could provide a cheap and eco-benign method for synthesis. As is well-known, phosphines are among the best ligands to obtain metal complexes active in catalysis.[2] In spite of the extensive study of photochemical activity of complexes,[3] only one example of photochemically active metal complexes containing water soluble phosphines is known[4] although many examples of photoactive metal complexes containing phosphines have been identified. One of the first examples of photoisomerization of a ruthenium phosphine complex was *cis*-[Ru(dppm)$_2$Cl$_2$] (dppm = bis(diphenylphosphino)methane) which by 436 nm radiation was converted to the *trans*-[Ru(dppm)$_2$Cl$_2$] isomer.[5a] Shortly after, it was shown that *cis*-[Ru(dmpe)$_2$Cl$_2$] (dmpe = 1,2-bis(dimethylphosphino)ethane) is photoisomerized to the *trans* complex in ethanol,

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but photolysis in ethanol/water mixtures or in ethanol yielded *trans*-[Ru(dmpe)$_2$(H$_2$O)Cl]$^+$.[5b] Other examples of isomerization processes mediated by UV irradiation are the transformation of *trans*-[RuCl$_2$[K^2-*P,P*-(*S*)-peap}$_2$] ((*S*)-peap = (-)-*N,N*-bis(diphenylphosphanyl)-(*S*)-1-phenylethylamine) into the *cis*-isomer[6] and recently the isomerization of [RuCl$_2$(CO)-(PBu$_3$)$_2$].[7] There are many examples of photochemical release of H$_2$ such as from [RuH$_2$(dmpe)$_2$] and [RuH$_2$(CO){PhP-((CH$_2$)$_2$PPh$_2$)$_2$}] by 308 nm light.[8] Substitution reactions were also studied as in the replacement of a bipy by 2 NCCH$_3$ ligands in meso-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$) using 498 nm radiation to give rise to [Ru$_2$(dppcb)(bipy)$_2$(MeCN)$_4$](PF$_6$)$_4$ (dppcb = *cis*,*trans*,*cis*-1,2,3,4-*tetrakis*-(diphenylphosphino)cyclobutane; bipy = bipyridine).[9] The only example described until now of a photoactive complex containing a water soluble phosphine is [Ru(NH$_3$)$_4$(H$_2$O)(PTAH)]$^{3+}$ which was converted to the complex [Ru(NH$_3$)$_3$(H$_2$O)$_2$(PTAH)]$^{3+}$ through a photoaquation reaction by 330 and 370 nm irradiation in water solution (PTAH$^+$ = H-N-1,3,5-triaza-7-phosphaadamantane).[4]

We have published the synthesis of an entire family of water soluble ruthenium {CpRu(II)} organometallic complexes[10] including combinations of hydrosoluble and water-insoluble tertiary phosphine ligands, among them the PTA ligand (PTA = 1,3,5-triaza-7-phosphaadamantane). The systematic study of the possible photochemical activity of these complexes showed that they are not photoactive compounds under visible light.[10d] In spite of the negative results, we decided to assess the possible photoactive properties of the published water ruthenium soluble complexes containing water-soluble phosphines. In particular, we have paid attention to ruthenium complexes containing PTA as this is a stable and easily synthesized ligand, and its complexes show interesting properties in catalytic processes. Inorganic and organometallic complexes of PTA have found applications in coordination chemistry,[11] medicine,[12] aqueous/biphasic catalysis,[13] and as new polymeric materials.[14]

The earliest reports on the synthesis and catalytic activity of PTA complexes involved the ruthenium compound [RuCl$_2$(PTA)$_4$] which has been employed as a catalyst for the hydrogenation of aldehydes,[15] olefins,[15] and CO$_2$,[16] in aqueous or biphasic media. Recently, Mebi and Frost[17] have reported the isolation and solid-state characterization of *trans*-[RuCl$_2$(PTA)$_4$], and they conclude that the *cis*-[RuCl$_2$(PTA)$_4$] isomer is produced by thermal isomerization of the *trans* complex in CHCl$_3$. When the reaction was carried out in water the resulting *cis*-isomer was in equilibrium with an uncharacterized species which could be the result of the exchange of one of the ligands by a water molecule. In this paper, we show that the previously published results on [RuCl$_2$(PTA)$_4$] are erroneous and investigate systematically the photochemical activity of complexes containing water soluble phosphines with a view to photocatalysis. A reading of the literature, as currently available, leads to the conclusion that [RuCl$_2$(PTA)$_4$] and related ruthenium complexes containing PTA derivatives are not photoactive. We report the results obtained by the study of the interaction of the complex *trans*-[RuCl$_2$(PTA)$_4$] with visible light in chloroform and in water, revealing that its behavior is related to the photochemistry of [Ru(dppm)$_2$Cl$_2$] and [Ru(dmpe)$_2$Cl$_2$].

Experimental Section

General Procedures. All the reagents and chemicals were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. The solid complexes were

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collected on sintered glass-frits and washed as described. The ligand PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) was prepared as described in the literature.[18] D_2O and $CDCl_3$ for NMR measurements were acquired from Cortec-Euriso-top. $CDCl_3$ was dried over molecular sieves (0.4 nm). ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker DRX300 spectrometer operating at 300.13 MHz (^1H) and 121.49 MHz (^{31}P), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or were measured relative to external 85% H_3PO_4 with downfield values taken as positive (^{31}P). Infrared spectra were recorded on KBr discs using an IR-ATI Mattson Infinity Series. Elemental analysis (C, H, N, S) were performed on a Fisons Instruments EA 1108 elemental analyzer.

Photolysis. Irradiation of the NMR tubes by continuous visible light was carried out using a homemade photoreactor with a built-in standard 150 W halogen lamp (in Almeria)[19] or a Philips 125 W medium-pressure mercury arc (in York). Irradiation of bulk reactions by continuous visible light was performed with a standard 500 W halogen lamp at 10 cm from the reaction vessel. Irradiation at selected wavelengths was carried out with the mercury arc equipped with a water filter (5 cm) and appropriate band-pass or interference filters (Schott). A potassium ferrioxalate actinometer was used for quantum yield measurements.[20] Solutions for photolysis and dark reactions were prepared under Ar and transferred to a 1.0 cm path-length quartz cells. During the photolysis, the solution was stirred using a small magnetic bar stirrer inside the cell. The UV/vis spectra were recorded on an 8453E UV−visible spectrometer.

Synthesis of *trans*-[$RuCl_2(PTA)_4$] (*trans*-1). The complex *trans*-[$RuCl_2(PTA)_4$] (**1**) was synthesized by reaction of [$RuCl_2(PPh_3)_3$] (0.3 g, 0.31 mmol) and PTA (0.3 g, 1.91 mmol) in refluxing ethanol and in the dark. After 4 h the resulting yellow precipitate was filtered, washed with EtOH (2 × 2 mL) and Et_2O (2 × 2 mL), and vaccuum-dried. The $^{31}P\{^1H\}$ and ^1H NMR spectra of a D_2O solution of **1** are consistent with those reported by the literature.[15,17]

A crystalline sample of **1** was obtained from its CH_2Cl_2 solution by slow diffusion of dry Et_2O at −5 °C.

Yield powder: 243 mg, 98%

Synthesis of *cis*-[$RuCl_2(PTA)_4$] (*cis*-1). This complex can be obtained by two different procedures: (A) A vessel containing *trans*-**1** (0.2 g, 0.25 mmol) dissolved in 20 mL of $CHCl_3$ was irradiated with a 500 W halogen lamp. After 3 h the yellow solution was evaporated, and the resulting bright yellow powder vacuum-dried. The powder *cis*-**1** obtained by evaporation of the solvent can be recrystallized in CH_2Cl_2 by diffusion of Et_2O. (B) Complex *trans*-**1** (0.2 g, 0.25 mmol) and KCl (0.462 g, 6.25 mmol) were dissolved in 5 mL of H_2O and irradiated with a 500 W halogen lamp. After 1 h the resulting yellow solution was evaporated and extracted with $CHCl_3$ (3 × 3 mL), filtered through celite, and the solvent removed. The $^{31}P\{^1H\}$ and ^1H NMR spectra of a $CDCl_3$ solution of the compound were consistent with those reported in the literature for the *cis*-[$Ru(PTA)_4Cl_2$].[16]

Yield A: 0.156 g, 78%; Yield B: 0.164 g, 82%. UV−vis λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 334 (946), 369 (613).

Photoisomerization of *trans*-1 by Broadband Visible Light in $CHCl_3$. Into a 5 mm NMR tube was introduced *trans*-**1** (10 mg, 0.012 mmol) and 0.5 mL of $CDCl_3$. The solution was irradiated with a 150 W halogen lamp at 25 °C. The $^{31}P\{^1H\}$ NMR spectra were recorded after 15, 30, 45, 60, 120, and 240 min and 2 days. The NMR spectra showed that complex *trans*-**1** partially transforms into *cis*-[$RuCl_2(PTA)_4$] (*cis*-**1**). After 2 h the ratio of *trans*-**1** to *cis*-**1** was 30:70% remaining unaltered 2 days later. The proportions of *trans*-**1** and *cis*-**1** were not changed significantly at 35 and 45 °C. The $^{31}P\{^1H\}$ and ^1H NMR spectra of the $CDCl_3$ solution of *cis*-**1** were consistent with those reported by the literature.[17]

Photoisomerization of *trans*-1 in $CHCl_3$. The principal band of the UV/vis spectrum of a crystalline sample of *trans*-**1** dissolved in $CHCl_3$ is found at 453 nm. The absorption coefficient at that wavelength was determined using a concentration range from 2 × 10^{-4} to 1.5 × 10^{-3} M. Solutions of about 1 mM of *trans*-**1** in $CHCl_3$ were irradiated by visible light of wavelengths $\lambda > 400$ nm, > 416 nm, and >458 nm, and by an interference filter $\lambda = 434$ nm using a Philips 125 W medium-pressure mercury arc. The relative rate constants for the reaction under the different irradiation conditions were calculated assuming a first order reaction. The quantum yield was obtained at 434 nm.

$\varepsilon_{453\ nm}(CHCl_3) = 453$ dm^3 mol^{-1} cm^{-1}; $\lambda > 400$ nm: Not 1st order reaction; k (>458 nm) = 1.37 × 10^{-4} s^{-1}; k (>416 nm) = 5.81 × 10^{-4} s^{-1}; k (416 nm) = 2.71 × 10^{-4} s^{-1}; $\Phi_{434\ nm}(CHCl_3) = 0.13 \pm 0.01$.

Attempted Thermal Isomerization of *trans*-1 in $CHCl_3$. In dark conditions 10 mg of *trans*-**1** (0.012 mmol) was dissolved in 0.5 mL of $CDCl_3$ in a 5 mm NMR tube. The $^{31}P\{^1H\}$ NMR spectrum showed that in the dark the compound did not change after 1 month at 25 °C.

Isomerization of *trans*-1 in $CDCl_3$ with DMSO-d_6 under Irradiation and in the Dark. In a 5 mm NMR tube was dissolved 10 mg of *trans*-**1** (0.012 mmol) in 0.6 mL of $CDCl_3$ and 0.1 mL of DMSO-d_6, and then the solution was irradiated with $\lambda > 416$ nm at 25 °C. The $^{31}P\{^1H\}$ NMR spectrum showed that *cis*-**1** (90%) and a new complex (10%) were generated after about 1 h. The resulting solution was irradiated with $\lambda = 367$ nm. After about 1 h the starting complex was fully regenerated. The same process was repeated two more times without significant loss of starting complex.

A similar reaction was performed in the dark. No significant changes were observed in the solution by $^{31}P\{^1H\}$ NMR spectroscopy after 1 day at room temperature.

Photoisomerization of *cis*-1 in $CHCl_3$. A solution of *cis*-**1** (ca. 1 mM) was irradiated with 367 nm light at 25 °C. The *trans*formation of *cis*-**1** into *trans*-**1** was complete in 20 min. The rate constant was calculated from the data obtained by the UV/vis spectrum of the reaction.

k (367 nm) = 1.5 × 10^{-3} s^{-1}; $\Phi_{367\ nm}(CHCl_3) = 0.25 \pm 0.02$.

Photoisomerization and Photoaquation of *trans*-1 in D_2O. The study of the photoisomerization of *trans*-**1** in D_2O was made by a similar procedure to that previously used for the study of *trans*-**1** in $CHCl_3$. First, its UV−vis spectrum was obtained in water, and the absorption coefficient was evaluated using concentrations from 2.5 × 10^{-4} to 2.0 × 10^{-3} M at room temperature. A solution of *trans*-**1** in H_2O (1.5 mM) was irradiated at $\lambda > 416$ nm giving rise to a mixture of the compounds *cis*-**1** and (OC-6-32)-[$RuCl(H_2O)(PTA)_4$]Cl (**2Cl**).[21] After 30 min 100% of the starting complex was transformed leading to a *cis*-**1**/**2Cl** molar ratio of 5:95. The rate constants for the reaction under the radiation conditions were calculated at >416 and 434 nm. The quantum yield was determined by irradiation of a 2 mM solution of *trans*-**1** in H_2O at 434 nm.

$\varepsilon_{453\ nm}(H_2O) = 350$ dm^3 mol^{-1} cm^{-1}; k (434 nm) = 6.61 × 10^{-3} s^{-1}; k (>416 nm) = 1.26 × 10^{-3} s^{-1}; $\Phi_{434\ nm}(D_2O) = 0.27 \pm 0.02$.

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pH Influence on the Photoisomerization of *trans*-1 in D_2O. Solutions of *trans*-**1** in H_2O (1.5 mM and 0.012 mM) at pHs from 5 to 10 were irradiated by $\lambda > 416$ nm light. In all cases the resulting final compounds were *cis*-**1** and **2Cl** with a mole ratio similar to that obtained at neutral pH (*cis*-**1**/**2Cl** molar ratio = 5:95).

Influence of Concentration on the Photoisomerization of *trans*-1 in D_2O. Solutions of *trans*-**1** in H_2O (0.0015, 0.002, 0.004, 0.006, 0.012 M) were irradiated by $\lambda > 416$ nm light. The resulting **2Cl**/*cis*-**1** mole ratios were 200:1, 9:1, 4.1:1, 3.1:1, 1:1, respectively.

Photoisomerization of *trans*-1 in H_2O under Irradiation at >416 nm in Presence of KCl. A solution of *trans*-**1** in water (1.5 mM) was irradiated by $\lambda > 416$ nm light in the presence of 25 equiv of KCl. After about 30 min complex *trans*-**1** had disappeared and only complex *cis*-**1** was observed (UV−vis, $^{31}P\{^1H\}$ NMR) which remained the only complex present in solution after 4 h.

Photoisomerization of *cis*-1 in H_2O. A solution about 2 mM of *cis*-**1** in H_2O was irradiated with 367 nm light. No changes were observed even if 25 equiv of KCl were added to the solution.

Reactivity of *cis*-1 in D_2O in the Presence of KCl and $AgCF_3SO_3$. Into a 5 mm NMR tube was introduced *cis*-**1** (10 mg, 0.012 mmol) and D_2O (1 mL). The $^{31}P\{^1H\}$ NMR spectrum showed the presence in solution of *cis*-**1** and (OC-6-32)-$[RuCl(H_2O)(PTA)_4]^+$ (**2**) in molar ratio about 50:50. By addition of 10 equiv of KCl (8.87 mg) only the complex *cis*-**1** was observed after 25 min at room temperature.

In a similar experiment, 2 equiv of $AgCF_3SO_3$ was added to the solution of *cis*-**1** (10 mg, 0.012 mmol) in 0.5 mL of D_2O into a 5 mm NMR tube. The $^{31}P\{^1H\}$ NMR spectrum showed that only complex **2** was present in solution after 10 min at room temperature.

Synthesis of (OC-6-32)-$[RuCl(H_2O)(PTA)_4](CF_3SO_3)$ ($2CF_3SO_3$). A solution of $AgCF_3SO_3$ (0.07 g, 0.27 mmol) in 2 mL of H_2O was added to a solution of *cis*-**1** (0.2 g, 0.25 mmol) in 5 mL of H_2O. The white precipitate formed was filtered through celite, and the solution evaporated. The pale-yellow powder obtained was dissolved in 10 mL of $CHCl_3$, filtered, and the solvent removed.

Yield: 0.128 g, 55%; $S_{25\ °C,\ H2O}$ = 34 mg/mL. Elemental analysis for powder sample $C_{24}H_{48}N_{12}P_4ClRuH_2OCF_3SO_3$ (932.14 g mol^{-1}): found, C 31.78, H 5.70, N 17.75; S 3.17; calcd, C 32.18, H 5.41; N 18.03; S 3.43. UV−vis λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 316 (1603), 345 (1882). IR (KBr, cm^{-1}): ν(OH), 3444, 3262; δ(OH) 1634; ν(OSO) 1280, 1245. ^1H NMR (D_2O): δ(ppm) 3.91−4.27 (bm, P-CH_2, 6 H), 4.36−4.60 (bm, NCH_2N, 6 H). $^{31}P\{^1H\}$ NMR (D_2O, AM_2X pattern): δ(ppm) −16.50 (dt, δ_X, $^2J_{QM}$ = 30.0 Hz, $^2J_{XA}$ = 30.4 Hz, PTA-Ru-OH_2), −26.66 (dt, δ_A, $^2J_{AM}$ = 26.7 Hz, $^2J_{AX}$ = 30.4 Hz, PTA−Ru-Cl), −56.32 (dd, δ_M, $^2J_{MA}$ = 26.7 Hz, $^2J_{MX}$ = 30.0 Hz, *trans*-PTA). ^1H NMR ($CDCl_3$): δ(ppm) 4.21−4.27 (bm, P-CH_2, 6 H), 4.46−4.58 (bm, NCH_2N, 6 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, AM_2X pattern): δ(ppm), −16.03 (dt, δ_X, $^2J_{XM}$ = 30.7 Hz, $^2J_{XA}$ = 32.7 Hz, PTA-Ru-OH_2), −26.33 (dt, δ_A, $^2J_{AM}$ = 28.9 Hz, $^2J_{AX}$ = 32.7 Hz, PTA−Ru-Cl), −56.62 (dd, δ_M, $^2J_{MA}$ = 28.9 Hz, $^2J_{MX}$ = 30.7 Hz, *trans*-PTA).

Results and Discussion

Complex *trans*-**1** was synthesized from the starting complex $[RuCl_2(PPh_3)_3]$ by reaction with PTA in refluxing EtOH in the dark and recrystallized by slow diffusion of dry Et_2O into its CH_2Cl_2 solution. The synthesis of $[RuCl_2(PTA)_4]$ was previously described by Darensbourg and co-workers by a different procedure;[15] this complex was reported as *trans* and *cis* geometric isomers (Scheme 1). The complex *cis*-**1** was isolated from an aqueous solution of *trans*-**1**, which led them to the reasonable conclusion that the *cis* isomer is formed in the reaction. Nevertheless, they showed that the *cis* geometry is inconsistent with the observation of a single resonance at −47.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum in D_2O of the product of the synthesis. Recently Frost et al. isolated orange crystals of the *trans* isomer[17] from a dichloromethane solution of *trans*-**1** and concluded that the isolation of *cis* isomer from an aqueous solution of *trans*-**1** results from the thermal isomerization of the *trans* isomer.

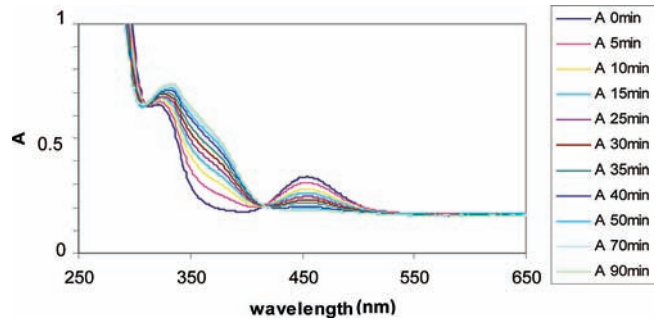
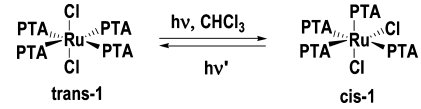


Figure 1. UV−vis spectrum of the isomerization of *trans*-**1** in $CHCl_3$ with $\lambda > 416$ nm.

Scheme 1. Photo-Isomerization of *trans*-**1** in $CHCl_3$



We found that the *trans*-**1** can be easily and quantitatively converted into the *cis*-**1** by visible light in $CHCl_3$, and in darkness at room temperature the transformation does not occur. That finding led us to research on the photochemical behavior of complex *trans*-**1**. We initially studied the photoisomerization from *trans*-**1** to its *cis*- isomer (Scheme 1) by irradiating a solution in $CHCl_3$ with a halogen lamp; we obtained an equilibrium with a maximum conversion into the product *cis*-**1** after 2 h (70%).

From these preliminary promising results we decided to investigate the photochemical properties of complex *trans*-**1** more thoroughly starting from its UV spectrum. The major absorption band in the UV spectrum for this compound in $CHCl_3$ is at 453 nm. The absorption coefficients at 453 nm in $CHCl_3$ were determined by using a crystalline sample of *trans*-**1**. The isomerization process was studied using 1 mM solutions of *trans*-**1** in $CHCl_3$ which were irradiated selectively by placing filters in front of a mercury-lamp. The reaction was fastest with light of $\lambda > 416$ nm (see, Experimental Section and Supporting Information, the rate constants are not corrected for the light output of the lamp). With irradiation at $\lambda > 416$ nm conversion was essentially complete.

The UV−vis spectrum of the reaction showed that the band at 453 nm, associated with *trans*-**1**, decreases while the band at 340 nm increases which is due to *cis*-**1** (Figure 1).

The quantum yield of the isomerization process of 1 mM solution of crystalline *trans*-**1** in $CHCl_3$ was evaluated with 434 nm narrow band irradiation as $\Phi_{434\ nm,\ CHCl3} = 0.13 \pm 0.01$ by using a potassium ferrioxalate actinometer.[20] The

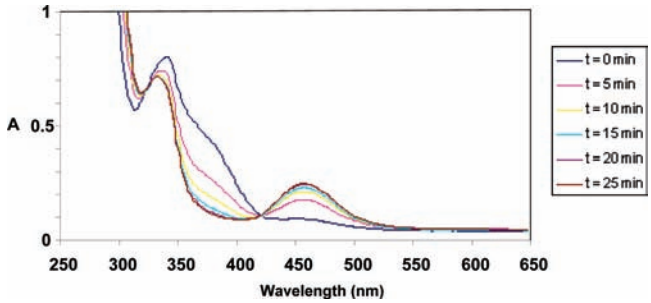


Figure 2. UV−vis spectrum of the isomerization of *cis*-**1** in $CHCl_3$ with $\lambda = 367$ nm.

Scheme 2. Photo-Isomerization-Aquation of *trans*-**1** in H_2O

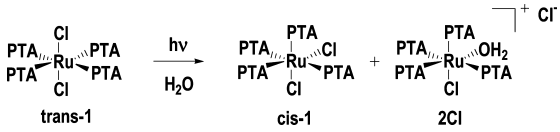


Table 1. Mole Ratio **2Cl**/*cis*-**1** Obtained by Irradiation of *trans*-**1** Solutions

[*trans*-**1**] (M)	mole ratio **2Cl**/*cis*-**1**
0.012	1:1
0.006	3.1:1
0.004	4.1:1
0.002	9:1
0.0015	200:1

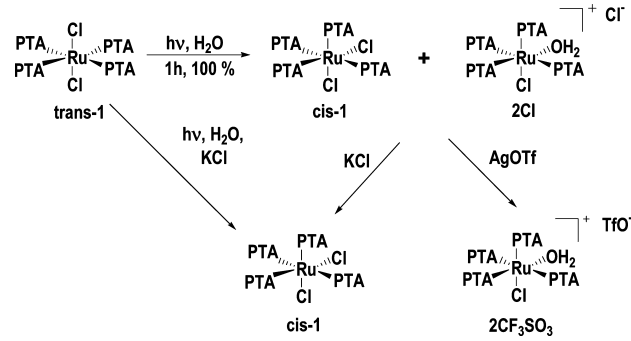
reversibility of the reaction was evaluated by irradiation at 367 nm of a solution containing *cis*-**1** that was obtained by irradiation of a 1 mM solution of *trans*-**1** with $\lambda > 416$ nm in $CHCl_3$ and a 1 mM solution of *cis*-**1** in $CHCl_3$. In both cases we observed complete return from *cis*-**1** to *trans*-**1** in about 20 min (Figure 2, Scheme 1). The calculated quantum yield for the reverse reaction is $\Phi_{367\ nm} = 0.25 \pm 0.02$. Since this quantum yield is larger than that for the forward reaction, complex *cis*-**1** is only obtained cleanly by visible light photoisomerization from *trans*-**1**. The synthesis of *cis*-**1** was easily achieved by 500 W halogen lamp irradiation of a solution of *trans*-**1** in $CHCl_3$. The powder *cis*-**1** obtained by evaporation of the solvent can be recrystallized in CH_2Cl_2 by diffusion of Et_2O.

Complex *trans*-**1** is more soluble in water than in $CHCl_3$.[17] The absorption coefficient for a solution of *trans*-**1** in water at $\lambda = 453$ nm is 350 $dm^3\ mol^{-1}\ cm^{-1}$, which is lower than that in $CHCl_3$ ($\varepsilon_{453\ nm}$ ($CHCl_3$) = 453 $dm^3\ mol^{-1}\ cm^{-1}$). When a 1.5 mM solution of *trans*-**1** was irradiated for 40 min with visible light (halogen lamp) we obtained the aqua-complex **2Cl** as the major product (95%) with a small amount (5%) of *cis*-**1** (Scheme 2).

The reaction was performed in dilute solution (1.5 mM) of *trans*-**1** in H_2O at different pH values (from 5 to 10). The mole ratio of products found in each case was the same (**3**/**2Cl** = 95:5). No dependence on pH was observed even in more concentrated solution of *trans*-**1** in water (0.012 M). However, a clear influence of the starting *trans*-**1** concentration was observed (Table 1).

If an excess of KCl was added to the product mixture, the transformation of **2Cl** into *cis*-**1** was observed independently of the starting *trans*-**1** concentration. Therefore, it is possible to obtain *cis*-**1** by irradiation of *trans*-**1** in aqueous solution

Scheme 3. Synthesis of *cis*-**1**, **2Cl**, and $\mathbf{2CF_3SO_3}$ in Water



in the presence of excess KCl (25 equiv) which is an additional procedure that could be used for its synthesis (Scheme 3).

We were able to obtain the pure aqua-complex $\mathbf{2CF_3SO_3}$ by addition of AgOTf to the product mixture obtained by visible light irradiation of *trans*-**1** in water (Scheme 3). The crude product obtained was extracted by $CHCl_3$ to give a pale yellow powder. Its elemental analysis and the IR spectrum support the exchange of a Cl by a H_2O molecule and the formation of a triflate salt. The ^1H NMR spectrum displays only broad signals in the region of the P−CH_2−N and N−CH_2−N groups in known PTA-Ru complexes.[22] More interesting is its $^{31}P\{^1H\}$ NMR spectrum which exhibits a AM_2X system constituted by a signal at −56.32 ppm that is in agreement with two Ru-coordinated-PTA ligands *trans* to each other (−57.64 ppm for *cis*-[$RuCl_2(PTA)_4$]), a signal at −26.66 ppm in the chemical region ascribable to Ru-coordinated-PTA *trans* to a Cl (−23.40 ppm for *cis*-[$RuCl_2(PTA)_4$]),[17] and a signal at −16.50 ppm that could be assigned to the Ru-coordinated-PTA *trans* to a H_2O molecule. That is in agreement with the assignment to $[Ru(H_2O)_2(PTA)_4]^{2+}$ in which the PTA *trans* to the H_2O resonates at −17.1 ppm.[23] There are few crystal structures authenticating examples of phosphine Ru complexes containing a coordinated water molecule[24] but none for a Ru PTA complex.

The photoisomerization and photoaquation of *trans*-**1** in water was studied under the same conditions as were employed to obtain the best results for its photoisomerization in $CHCl_3$. Complex *trans*-**1** was photoisomerized and photoaquated by irradiation with $\lambda > 416$ nm of its solution in water in 30 min. The quantum yield for loss of *trans*-**1** was obtained by using a 2 mM solution of *trans*-**1** in water and wavelength at 434 nm ($\Phi_{434\ nm,\ water} = 0.27 \pm 0.02$) which is larger than the quantum yield observed in $CHCl_3$ ($\Phi_{434\ nm}$ ($CHCl_3$) = 0.13 ± 0.01). Therefore the efficiency of the photoisomerization in water is greater than in $CHCl_3$ which

(22) Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* **2004**, *248*, 955–993, and references therein.
(23) Kovács, J.; Joó, F.; Bényei, A.; Laurenzy, G. *Dalton Trans.* **2004**, 2336–2340.
(24) (a) Venkateswaran, R.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2007**, *46*, 809. (b) Vertlib, V.; Figueira, J.; Mesquita, J.; Rodrigues, J.; Nattinen, K.; Rissanen, K. *Eur. J. Inorg. Chem.* **2007**, 1920. (c) Dinelli, L. R.; Batista, A. A.; Wohnrath, K.; de Araujo, M. P.; Queiroz, S. L.; Bonfadini, M. R.; Oliva, G.; Nascimento, O. R.; Cyr, P. W.; MacFarlane, K. S.; James, B. R. *Inorg. Chem.* **1999**, *38*, 5341. (d) Sun, Y.; Taylor, N. J.; Carty, A. J. *Inorg. Chem.* **1993**, *32*, 4457.

translates to a faster reaction rate in water (k (>416 nm) = 1.26×10^{-3} s^{-1}) than in $CHCl_3$ (k (>416 nm) = 5.81×10^{-4} s^{-1}). The photoreaction of *trans*-**1** was found to be irreversible under irradiation with light at 367 nm even if excess KCl (25 equiv) is present in the reaction and complex *cis*-**1** is the only product in solution.

The interesting results obtained for *trans*-**1** encouraged us to check the possible photoactivity of parent ruthenium complexes with PTA derivatives like the mPTA and dmPTA (mPTA = *N*-methyl-1,3,5-triaza-7-phosphaadamantane; dmPTA = *N*,*N*′-dimethyl-1,3,5-triaza-7-phosphaadamantane).[25] Studies are in progress to synthesize new ruthenium complexes containing water soluble phosphines and to study their potential use as photocatalysts for reactions such as isomerization and hydrogenation of olefins.

Mechanism. The possible mechanisms proposed for the isomerization of octahedral complexes could be either intramolecular or intermolecular processes.[26] The intermolecular mechanism could be associative or dissociative but an associative mechanism is very unlikely at a d^6 octahedral Ru. The dissociative mechanism includes the loss of a ligand giving a five coordinate unsaturated intermediate which is capable of reaction with the dissociated ligand to give the original or a new isomer. In an octahedral d^6 complex such as *trans*-**1**, the t_{2g} orbitals are fully occupied. Consequently, all ligand-field excited states must involve electronic population of an e_g orbital which has antibonding character with respect to metal−ligand σ bond.

Complex *trans*-**1** displays bands in its visible absorption spectra with absorption coefficients consistent with a d-d transition.[26] No exchange between the isomers of **1** is observed in $CHCl_3$ in the dark at room temperature while *trans*-**1** and *cis*-**1** can be fully interconverted by selective irradiation into their respective absorption bands in the visible and near UV. An intermolecular isomerization process requires that any other ligand in the reaction media could be incorporated into the coordination sphere of the complex, if the external ligand has a similar nucleophilicity to the dissociated ligand. Irradiation with $\lambda > 416$ nm of a solution of *trans*-**1** in 0.6 mL of $CDCl_3$ containing 0.1 mL of DMSO-d_6 led to the isomer *cis*-**1** (>90%) and to a new compound (<10%) (Figure 3). The $^{31}P\{^1H\}$ NMR signals for this new compound are in agreement with the exchange of a chloride by a DMSO-d_6 molecule. Subsequent irradiation with $\lambda =$ 367 nm of the resulting solution regenerates *trans*-**1** while *cis*-**1** and the other product disappear (Figure 3). This photoreaction cycle was repeated two more times with similar results and without apparent loss of starting complex. These results are consistent with two mechanisms for the major pathway: (a) a dissociative substitution mechanism, in which the five coordinate intermediate is an ion pair $\{(PTA)_4RuCl^+$-$Cl^-\}$ that would recombine to give isomerized product or starting material in the poor ion-solvating chloroform solvent,

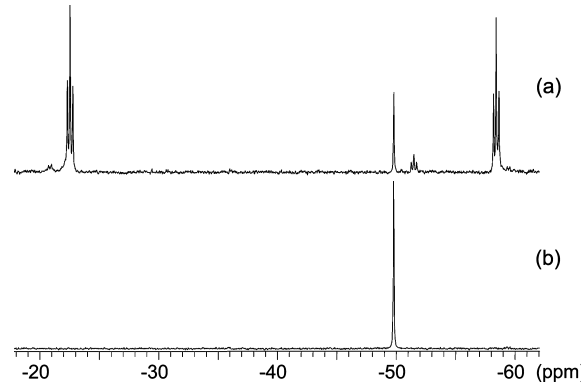
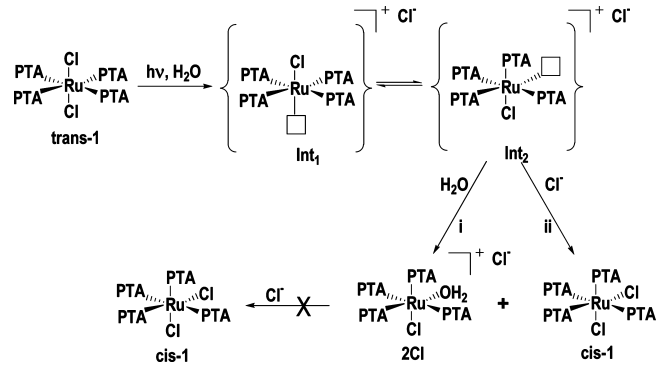


Figure 3. Irradiation of *trans*-**1** solution in $CDCl_3$ with DMSO-d_6 by (a) $\lambda > 416$ nm after 40 min; (b) $\lambda = 367$ nm after 1 h.

Scheme 4. Possible Dissociative Mechanism for Photoaquation and Photoisomerization of *trans*-**1** in Water



and (b) an intramolecular mechanism. The substitution process is a minor pathway.

As observed in $CHCl_3$, complex *trans*-**1** in water does not transform into *cis*-**1** in the dark at room temperature. However, in contrast with the reactivity observed in $CHCl_3$, irradiation of *trans*-**1** in aqueous solution by visible light generates *cis*-**1** together with the aqua ruthenium complex **2Cl** which is the main product. The product ratio is concentration dependent with lower concentrations of *trans*-**1** favoring **2Cl**. Isomerization from *trans*-**1** to *cis*-**1** by an intramolecular mechanism prior to the exchange of a Cl^- ligand by a water molecule is improbable. Complex *cis*-**1** does not show absorption bands in the wavelength region of $\lambda > 416$ nm which is the spectral region that induces the photoaquation and photoisomerization of the *trans*-**1** complex. Therefore, a simple dissociative mechanism for the photoreaction of *trans*-**1** is the most probable (Scheme 4). The initial five-coordinate intermediate **Int$_1$** formed by loss of Cl^- rearranges to a less crowded configuration **Int$_2$** in which the remaining coordinated Cl is *trans* to a PTA. This intermediate is able to react with the previously released Cl^- to give rise to *cis*-**1** or with water to produce complex **2Cl**. These considerations are consistent with the dissociative mechanism proposed in ref 4b. An additional possibility includes the reaction of the intermediate complex first with water leading to complex **2Cl** which can easily exchange a water molecule with a chloride ion. The concentration dependence must arise through the kinetics of reaction of the intermediate. The reaction of **Int$_2$** with H_2O (reaction i, Scheme 4) is first order in [**Int$_2$**]. The rate of the reaction of

(25) (a) Mena-Cruz, A.; Lorenzo-Luis, P.; Romerosa, A.; Saoud, M.; Serrano-Ruiz, M. *Inorg. Chem.* **2007**, *46*, 6120–6128. (b) Mena-Cruz, A.; Lorenzo-Luis, P.; Romerosa, A.; Serrano-Ruiz, M. *Inorg. Chem.* **2008**, *47*, 2246–2248.

(26) Adamson, A. W.; Fleischauer, P. D. *Concepts of Inorganic Photochemistry*; John Wiley & Sons: New York, 1975.

Int$_2$ with Cl^- depends on [**Int$_2$**][Cl^-], but this expression can be rearranged *in the initial condition* to [**Int$_2$**]^2, because [**Int$_2$**] = [Cl^-]. This argument assumes that **Int$_2$** exists as separated ions and not an ion pair which is reasonable considering that the solvent is water. Since reaction i is first order while reaction ii is initially second order, we observe a concentration dependence that favors *cis*-**1** at high concentration. This argument also indicates that the intramolecular isomerization of *cis*-**1** is negligible in water and disfavours the reaction of chloride with **2Cl** as the final step.

This mechanism is compatible with that proposed for the isomerization of *cis*- into *trans*-[Ru(dppm)Cl_2] in CH_2Cl_2, but there seems to have been no attempt to effect the reverse isomerization in this case.[5a] In contrast to our own work on the PTA complexes, the study of [Ru(dmpe)Cl_2] in ethanol shows photoisomerization of the *cis*- into the *trans*-isomer but no photoactivity for the *trans* isomer in this solvent.[5b] In water or water alcohol mixtures, the product of irradiating either isomer was [RuCl(dmpe)$_2$(H_2O)]$^+$, consistent with our observations. The authors suggest a dissociative mechanism with an equivalent rearrangement of the five-coordinate intermediate to that postulated in Scheme 4. Although there was no direct evidence for the existence of a five-coordinate, fragment along the isomerization reaction for photosubstitution reactions, our experimental data strongly suggests that this type of mechanism is still correct.

Conclusions

trans-[$RuCl_2$(PTA)$_4$] (*trans*-**1**) is isomerized into the *cis*-[$RuCl_2$(PTA)$_4$] (*cis*-**1**) by visible light in chloroform and in water at room temperature. The complex *cis*-**1** generated by photoisomerization of *trans*-**1** is obtained together with the aqua-complex (OC-6−32)-[RuCl(H_2O)(PTA)$_4$]Cl (**2Cl**) on irradiation in water. The molar ratio of reaction products is not dependent on the pH of the solution but on the concentration of the starting *trans*-**1** and the presence of Cl^- in the reaction. The photoisomerization in water is faster and more efficient than in $CHCl_3$. The complex *cis*-**1** isomerizes into *trans*-**1** with near UV light (λ = 367 nm) in $CHCl_3$ but not in water. Experimental results suggest that the mechanism of the photoprocesses in $CHCl_3$ is either dissociative or intramolecular. The photoreaction in water is mainly dissociative. This mechanism is compatible with that proposed for the isomerization of *cis*-[Ru(dppm)Cl_2][5a] and *cis*-[Ru(dmpe)Cl_2].[5b] Experimental data continue to strongly suggest that this type of mechanism is correct for ruthenium complexes containing phosphines. Ruthenium complexes containing aqua-soluble phosphines are worth considering for study in photochemical processes as reactions in water could be faster and more efficient than in organic solvents. The effects of the light in catalytic reactions mediated by complex [$RuCl_2$(PTA)$_4$] need to be evaluated and compared with published data.

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Supporting Information Available: Further details are given in Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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