Electrochemical Properties of a Rhodium(III) Mono-Terpyridyl Complex and Use as a Catalyst for Light-Driven Hydrogen Evolution in Water

Fakourou Camara 1,2, Thomas Gavaggio 1, Baptiste Dautreppe 1, Jérôme Chauvin 1, Jacques Pécaut 2, Dmitry Aldakov 2, Marie-Noëlle Collomb 1,* and Jérôme Fortage 1,*

1 DCM, CNRS, Université Grenoble Alpes, 38000 Grenoble, France
2 SyMMES, IRIG, CEA, CNRS, Université Grenoble Alpes, 38000 Grenoble, France
* Correspondence: marie-noelle.collomb@univ-grenoble-alpes.fr (M.-N.C.); jerome.fortage@univ-grenoble-alpes.fr (J.F.)

Abstract: Molecular hydrogen (H2) is considered one of the most promising fuels to decarbonize the industrial and transportation sectors, and its photocatalytic production from molecular catalysts is a field that is still abounding. The search for new molecular catalysts for H2 production with simple and easily synthesized ligands is still ongoing, and the terpyridine ligand with its particular electronic and coordination properties, is a good candidate to design new catalysts meeting these requirements. Herein, we have isolated the new mono-terpyridyl rhodium complex, [RhIII(tpy)(CH3CN)Cl2](CF3SO3) (Rh-tpy), and shown that it can act as a catalyst for the light-induced proton reduction into H2 in water in the presence of the [Ru(bpy)3]Cl2 (Ru) photosensitizer and ascorbate as sacrificial electron donor. Under photocatalytic conditions, in acetate buffer at pH 4.5 with 0.1 M of ascorbate and 530 μM of Ru, the Rh-tpy catalyst produces H2 with turnover number versus catalyst (TONcat) of 300 at a Rh concentration of 10 μM, and up to 1000 at a concentration of 1 μM. The photocatalytic performance of Ru/Rh-tpy/HA−/H2A has been also compared with that obtained with the bis-dimethyl-bipyridyl complex [RhIII(dmbpy)2Cl2]+ (Rh2) as a catalyst in the same experimental conditions. The investigation of the electrochemical properties of Rh-tpy in DMF solvent reveals that the two-electrons reduced state of the complex, the square-planar [RhI(tpy)Cl]4− (RhI-tpy), is quantitatively electrogenerated by bulk electrolysis. This complex is stable for hours under an inert atmosphere owing to the π-acceptor property of the terpyridine ligand that stabilizes the low oxidation states of the rhodium, making this catalyst less prone to degrade during photocatalysis. The π-acceptor property of terpyridine also confers to the Rh-tpy catalyst a moderately negative reduction potential (EPC(RhIII/RhI) = −0.83 V vs. SCE in DMF), making possible its reduction by the reduced state of Ru, [RuI(bpy)(bpy*)]+ (RuI−) (E1/2(RuII/Ru−) = −1.50 V vs. SCE) generated by a reductive quenching of the Ru excited state (*Ru) by ascorbate. A Stern–Volmer plot and transient absorption spectroscopy confirmed that the first step of the photocatalytic process is the reductive quenching of *Ru by ascorbate. The resulting reduced Ru species (Ru−) were then able to activate the RhIII-tpy H2-evolving catalyst by reduction generating RhI-tpy, which can react with a proton on a sub-nanosecond time scale to form a RhIII(H)-tpy hydride, the key intermediate for H2 evolution.

Keywords: rhodium complex; molecular electrochemistry; photocatalysis; hydrogen evolution; homogeneous catalysis

1. Introduction

Molecular hydrogen (H2) is considered as one of the best alternatives to fossil fuels to speed up the transition towards a carbon-neutral future [1]. However, 96% of hydrogen is produced from fossil fuels via a variety of processes, such as the steam reforming of methane, generating carbon dioxide at the same time. Therefore, to reach carbon...
neutrality, hydrogen should be cleanly produced using a renewable energy, such as sunlight, with water as a proton source. The pioneer work of Lehn and Sauvage demonstrated in the late 1970s that green hydrogen could be produced by the photo-induced reduction of protons via homogeneous photocatalytic systems [2,3]. These systems are usually composed of a sacrificial electron donor (SD) providing electrons to the system, a H₂-evolving catalyst (Cat), and a photosensitizer (PS) promoting the photo-induced electron transfers between the three compounds. For forty years, many photocatalytic systems have been investigated and numerous molecular catalysts have been employed, the latter being based on noble metal (Pd, Pt, Rh) or earth-abundant metal complexes (Co, Ni, Fe, Mo) [4,5]. Among the latter, the catalytic properties of rhodium complexes have been rarely explored in aqueous solutions (Rh₁–₁₀) [3,6–14] but more largely in hydro-organic solvent (Rh₁₁–₂₄) [10,15–33] (Scheme 1), although the use of water is a prerequisite for water-splitting applications [34]. Rhodium catalysts active in water for H₂ production have employed a small variety of ligands, such as bipyridyl (Rh₁–₃, Rh₈–₉) [3,8,9,11–13], cyclopentadienyl (Rh₃) [9], diphenylphosphinobenzene-sulphonate (Rh₄) [6,7], acetate (Rh₅–₉) [8,10], and diisocyanopropane (Rh₁₀) [8], under the form of mono- or bi-metallic complexes (Scheme 1a). The H₂-evolution with such rhodium catalysts generally proceeds via the transient formation of rhodium hydride species [34–36] generated upon their reduction in presence of protons. Among these Rh catalysts, only Rh₂, Rh₃, and Rh₄ exhibited turnover numbers per catalyst (TON_cat) superior to 100 in the presence of a ruthenium or iridium photosensitizer and ascorbate as SD in water, and TON_cat for the others catalysts do not exceed 10 [34]. In addition, when the Rh₂ bis-bipyridyl catalyst is covalently linked to two Ru photosensitizers, the performance of photocatalytic system SD/PS-Cat is clearly improved due to the faster kinetics of the electron transfer between PS and Cat [12]. In this context, exploring rhodium complexes with other polypyridyl ligands is important for identifying new efficient and robust H₂-evolving catalysts.

Herein, we report on the synthesis and structural characterization of a new rhodium monoterpyridyl complex, namely [Rh₃III(tpy)(CH₃CN)₂](CF₃SO₃)₂ (tpy = 2,2′;6,2′′-terpyridine) (denoted Rh-tpy, Scheme 2). We also investigated the electrochemical properties of this complex in organic solvent and the electrochemical generation and UV-visible spectroscopic characterization of the corresponding two-electron Rh¹ reduced species. The catalytic activity of Rh-tpy towards the light-driven H₂ production was tested in purely aqueous solution, in association with [Ru(bpy)₃]²⁺ (Ru) as photosensitizer and ascorbate (HA⁻) as sacrificial electron donor. In 2012, the group of Ogo investigated the capacity of the chemically synthesized rhodium(I) terpyridyl [Rh₁ᴵ(tpy)(CH₃CN)](CF₃SO₃) complex to form a rhodium(III) monohydride species in the presence of protons in CH₃CN, [Rh₁ᴵ(H)(tpy)(CH₃CN)₂](CF₃SO₃)₂, the latter being unstable and gradually transforming into a stable dinuclear Rh² complex [Rh₂ᴵ(tpy)₂(CH₃CN)₄](CF₃SO₃)₄, with the generation of H₂ by reductive elimination [37]. In this study, we demonstrate that the Rh-tpy can act as a H₂-evolving catalyst under photocatalytic conditions in acidic water (pH 4.0–4.5) with an efficiency competing with the benchmark rhodium(III) bis-dimethyl-bipyridyl complex [Rh₃ᴵᴵ(dmbpy)₂Cl₂]⁺ (Rh₂) (Scheme 1) for a low catalyst concentration of 1 µM, this latter being among the most efficient rhodium catalysts in water [11–13]. Finally, the first photo-induced steps involved in the H₂ production with the molecular Ru/Rh-tpy/HA⁻/H₂A system are investigated by means of time-resolved emission and absorption spectroscopies.
Scheme 1. Rhodium catalysts previously reported for light-driven H₂ production in water (a) and in hydro-organic solvent (b).

Rh5 : R = CH₃, L = H₂O  
Rh6 : R = CH₂OH, L = H₂O  
Rh7 : R = CF₃, L = acetone

Scheme 2. Structures of the photosensitizer (Ru), the H₂-evolving catalyst (Rh-tpy), and the sacrificial electron donor (HA⁻) used in this work.

Scheme 2. Structures of the photosensitizer (Ru), the H₂-evolving catalyst (Rh-tpy), and the sacrificial electron donor (HA⁻) used in this work.
2. Results and Discussion

2.1. Synthesis and Crystal Structure of the [Rh\textsuperscript{III}(tpy)(CH\textsubscript{3}CN)Cl\textsubscript{2}](CF\textsubscript{3}SO\textsubscript{3}) Complex

The synthesis of the \textbf{Rh-tpy} complex was inspired from that of the [Rh\textsuperscript{III}(tpy)(OH)(H\textsubscript{2}O)](NO\textsubscript{3})\textsubscript{2} complex isolated by Ogo (Scheme 3)\textsuperscript{[38]}\textsuperscript{[39]}. First, the [Rh\textsuperscript{III}(tpy)Cl\textsubscript{3}] complex is generated by reacting RhCl\textsubscript{3} • 3H\textsubscript{2}O with one equivalent of terpyridine in ethanol at 90 °C\textsuperscript{[39]}. Then, in order to solubilize the rhodium complex in water for the light-driven H\textsubscript{2} production experiments, a chloride ligand in axial position was exchanged by an acetonitrile molecule by reacting the tris-chloro complex with AgCF\textsubscript{3}SO\textsubscript{3} in acetonitrile at 90 °C, leading to the formation of the [Rh\textsuperscript{III}(tpy)(CH\textsubscript{3}CN)Cl\textsubscript{2}](CF\textsubscript{3}SO\textsubscript{3}) complex (\textbf{Rh-tpy}) with a yield of 50%. The water solubility of \textbf{Rh-tpy} is also favored by the presence of the triflate counter-anion.

![Scheme 3. Synthesis of the [Rh\textsuperscript{III}(tpy)Cl\textsubscript{3}] (a) and [Rh\textsuperscript{III}(tpy)(CH\textsubscript{3}CN)Cl\textsubscript{2}](CF\textsubscript{3}SO\textsubscript{3}) (b) (Rh-tpy) Complexes.](image)

Single crystals of \textbf{Rh-tpy} suitable for X-ray crystallography were obtained by diffusion of diethyl ether into an acetonitrile solution of the rhodium complex (Figure 1, Tables S1–S4). \textbf{Rh-tpy} crystallizes in the P\textsubscript{1} space group and displays a distorted octahedral geometry around the rhodium atom. The three nitrogen atoms of the terpyridine and one chloride ligand are in the equatorial plane, while the nitrogen atom of CH\textsubscript{3}CN and one chloride ligand are in an axial position. The terpyridine ligand is quasi-planar, with low torsion angles between the central pyridine of the terpyridine and the other two pyridines (3.90° between pyridines with N(1) and N(2) and 1.70° between pyridines with N(2) and N(3)). The nitrogen atoms of the terpyridine, the chloride atom, and the rhodium form a slightly distorted square plane, with N(1)-Rh-N(2) and N(2)-Rh-N(3) angles of 81.07(6)° and 81.00(6)°, respectively, which are slightly smaller than the ideal value of 90° for a perfect square plane geometry. This distortion is induced by the terpyridine, which imposes 5-atom rings comprising the rhodium, two nitrogen atoms (N(1)/N(2) or N(2)/N(3)), and two terpyridine carbon atoms. The distance between rhodium and the central pyridine nitrogen (N\textsubscript{central}) of the terpyridine (N(2)) is shorter (1.9386(14) Å) than that between rhodium and the two distal nitrogen (N\textsubscript{distal}) of the terpyridine (2.0258(14) and 2.0417(14) Å for Rh-N(1) and Rh-N(3), respectively). The rhodium atom is almost equidistant from the two chloride atoms (2.3530(5) vs. 2.3067(4) Å, respectively, for Rh-Cl(1) and Rh-Cl(2)) and the distance between the nitrogen of acetonitrile ligand and the rhodium atom (2.0220(14) Å for Rh-N(21)) is very similar to those between the rhodium and the terpyridine nitrogen atoms (Rh-N\textsubscript{tpy}). The distances and angles between the Rh center and the terpyridine ligand in \textbf{Rh-tpy} are very similar to those found in the [Rh\textsuperscript{III}(tpy)(OH)(OH\textsubscript{2})\textsubscript{2}](NO\textsubscript{3})\textsubscript{2} complex\textsuperscript{[38]}. Slightly shorter valence angles were found in the dinuclear [Rh\textsuperscript{II}(tpy)\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{4}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{4} complex where the two Rh centers are linked by a metal-metal bond, as a consequence of Rh\textsuperscript{III}-N\textsubscript{tpy} lengths being slightly longer than those of \textbf{Rh-tpy}. Regarding the low-valent [Rh\textsuperscript{I}(tpy)(CH\textsubscript{3}CN)](CF\textsubscript{3}SO\textsubscript{3}) complex, which adopts
a discrete structure of four $[\text{Rh}^\text{III}(\text{tpy})(\text{CH}_3\text{CN})]\text{Cl}_2^-$ units stacked via tpy-tpy interaction at the solid state, this complex displays slightly shorter valence angles and $\text{Rh}^\text{III}$-$\text{N}_{\text{tpy}}$ bond distances than those found in $\text{Rh-tpy}$ [37].

![Figure 1. ORTEP diagram of $[\text{Rh}^\text{III}(\text{tpy})(\text{CH}_3\text{CN})]\text{Cl}_2^-$ (Rh-tpy). Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles (º): $\text{Rh1}$-$\text{N1} = 2.0258(14)$ Å, $\text{Rh1}$-$\text{N2} = 1.9386(14)$ Å, $\text{Rh1}$-$\text{N3} = 2.0417(14)$ Å, $\text{Rh1}$-$\text{N21} = 2.0220(14)$ Å, $\text{Rh1}$-$\text{Cl1} = 2.3530(5)$ Å, $\text{Rh1}$-$\text{Cl2} = 2.3067(4)$ Å, $\text{N1}$-$\text{Rh1}$-$\text{N3} = 162.03(6)$º, $\text{N2}$-$\text{Rh1}$-$\text{N1} = 81.07(6)$º, $\text{N2}$-$\text{Rh1}$-$\text{N3} = 81.00(6)$º, $\text{N2}$-$\text{Rh1}$-$\text{N21} = 87.90(6)$º.](image)

2.2. Spectroelectrochemical Properties of the $[\text{Rh}^\text{III}(\text{tpy})(\text{CH}_3\text{CN})]\text{Cl}_2^-$ (Rh-tpy)

The redox properties of $\text{Rh-tpy}$ were investigated in DMF because of the wider electrochemical window of this solvent compared to water, facilitating the observation of the reduced state of the rhodium complex (Figure 2 and Table S5). By analogy with the previously reported electrochemical behavior of the rhodium bis-bipyridyl [11–13,36,40] and bis-terpyridyl [41] complexes in organic solvent, the irreversible redox process at $E_{p,a} = -1.13$ V vs. Ag/AgNO$_3$ observed on the cyclic voltammogram of $\text{Rh-tpy}$ is attributed to the two-electron reduction of the metal center ($\text{Rh}^\text{III}$ → $\text{Rh}^\text{II}$), while the poorly reversible process located at a lower potential ($E_{p,c} = -1.95$ V) is ascribed to the one-electron reduction of the terpyridine ligand (Figure 2A). The irreversibility of the $\text{Rh}^\text{III}$/Rh$^\text{I}$ system is the result of the release of the two axial ligands upon reduction to form a Rh$^\text{I}$ species with a square-planar geometry. On the reverse scan, the irreversible oxidation peak observed at $E_{p,c} = -0.70$ V, followed by another less defined at ca. $-0.3$ V, is related to the reoxidation of the metal center ($\text{Rh}^\text{I}$ → $\text{Rh}^\text{III}$) along with the recoordination of two exogeneous ligands, which can be the solvent (DMF), CH$_3$CN, and/or a chloride ion.

In order to further characterize and evaluate the stability of the reduced Rh$^\text{I}$ state of $\text{Rh-tpy}$, the initial species involved in the catalytic reduction of protons to H$_2$, an electrolysis was performed at $-1.25$ V. In accordance with the generation of a Rh$^\text{I}$ species, the exhaustive electrolysis required the exchange of two electrons per initial Rh$^\text{III}$ complex. The formation of this species was attested by the UV-Visible absorption spectrum (Figure 3) and cyclic voltammograms (Figure 2B) of the resulting electrolyzed solution. The initial pale yellow $\text{Rh-tpy}$ solution displays mainly intense absorption bands below 350 nm. After complete reduction, the deep blue solution obtained from Rh$^\text{I}$ exhibits two strong absorption bands at 279 and 327 nm, and four less intense absorption bands in the visible region at 384, 515, 607, and 665 nm (Figure 3). Very similar absorption spectra were reported by the group of Hartl in ethanol for the square-planar rhodium(I) terpyridyl halide complexes, $[\text{Rh}^\text{I}(\text{tpy})(X)]$ $\text{X} = \text{Cl}$ or Br, chemically synthesized from $[\text{Rh}(X)(\text{COD})]_2$ precursors ($X = \text{Cl}$ or Br; COD = cycloocta-1,5-diene) under inert atmosphere [42]. The similarity of
the absorption spectra strongly suggests the [Rh\textsuperscript{I}(tpy)Cl\textsuperscript{−}] structure for the electrogenerated Rh\textsuperscript{I} species as a result of the release of one CH\textsubscript{3}CN and one chloride ligand.

![Cyclic voltammograms](image)

**Figure 2.** Cyclic voltammograms at a glassy carbon electrode (Ø = 3 mm, v = 100 mV s\textsuperscript{−1}) of (A) 0.5 mM solution of Rh-tpy in DME, 0.1 M [Bu\textsubscript{4}N]ClO\textsubscript{4}, (B) after a two-electron exhaustive reduction at −1.25 V vs. Ag/Ag\textsubscript{NO\textsubscript{3}}, leading to the formation of the Rh(I) species, and (C) after a back exhaustive oxidation at 0 V.

Regarding the cyclic voltammograms of the Rh\textsuperscript{I} solution, the initial irreversible reduction peak (Rh\textsuperscript{III} → Rh\textsuperscript{I}) has fully disappeared and only the redox process centered on the tpy ligand is now present on the cyclic voltammogram, with an intensity similar to that of the initial solution of [Rh\textsuperscript{III}(tpy)(MeCN)Cl\textsubscript{2}]\textsuperscript{+} (Figure 2A,B), attesting to the stability of the Rh\textsuperscript{I} species under inert atmosphere. In addition, the irreversible oxidation peaks (Rh\textsuperscript{I} → Rh\textsuperscript{III}) observed by scanning from −1.1 to 0 V are accompanied, on the reverse scan, by the appearance of a Rh\textsuperscript{III} → Rh\textsuperscript{I} reduction peak in accordance with the regeneration of a Rh\textsuperscript{III} species. Besides, the UV-vis. spectrum and the cyclic voltammograms of the electrolyzed solution do not show any changes after several hours when the latter is stored under inert atmosphere free of oxygen (glove box), showing the excellent stability of the Rh\textsuperscript{I} terpyridyl complex. By contrast, under similar experimental conditions, solutions of [Rh\textsuperscript{I}(Rbpy)\textsubscript{2}]\textsuperscript{+} electrogenerated from rhodium(III) bis-bipyridyl complexes [Rh\textsuperscript{III}(Rbpy)\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{+} (R = dimethyl or ditertio-butyl) are less stable and start to decompose after 1.5 h [36]. This is likely due to the higher π-acceptor capacity of terpyridine compared to that of bipyridine, which discharges the excess of electron density of Rh\textsuperscript{I} to the ligand, thus stabilizing the low oxidation states of the metal [42]. The rigid and planar geometry of the tpy ligand can also contribute to the stability of the square planar Rh\textsuperscript{I} species. A back exhaustive electrolysis at $E = 0$ V restores a Rh\textsuperscript{III} complex. However, the two-electron reduction of the metal center (Rh\textsuperscript{III} → Rh\textsuperscript{I}) is now located at a slightly more
negative potential ($E_{p_a} = -1.27 \text{ V vs. } \text{Ag/AgNO}_3$) compared to the initial solution of \textbf{Rh-tpy}, suggesting a slightly different coordination sphere for the Rh$^{III}$ center, which might be the substitution of the initial CH$_3$CN axial ligand by DMF. Indeed, the two chloride ligands remain coordinated to the Rh$^{III}$ center, as judged by the absence of the characteristic electroactivity of free chlorides (irreversible oxidation peak at ca. 0.7 V vs. Ag/AgNO$_3$) in the positive potential region from \textbf{Rh-tpy} [36].

This electrochemical study shows that the activation of the \textbf{Rh-tpy} complex for photoinduced H$_2$ production is possible using Ru as photosensitizer. Indeed, \textbf{Rh-tpy} can be reduced either by the reduced [Ru$^{II}$(bpy)]($\text{bpy}^+\text{-})$] (denoted Ru$^-$) or by the excited states of Ru (denoted *Ru$^{II}$), since both reactions are favored from a thermodynamic point of view. Considering the reduction potential of \textbf{Rh-tpy} ($E_{p_c}$ (Rh$^{III}$/Rh$^I$) = $-1.13 \text{ V vs. } \text{Ag/AgNO}_3$ ($-0.83 \text{ V vs. SCE}$)) in DMF, and the redox potential of Ru at reduced Ru$^-$ and excited *Ru$^{II}$ states in water ($E_{1/2}$ (Ru$^{II}$/Ru$^-$) = $-1.50 \text{ V and } E_{1/2}$ (Ru$^{II}$/*Ru$^{II}$) = $-1.07 \text{ V vs. SCE}$ [3], see Table S5), the driving forces ($\Delta G_0$) are clearly exergonic with values of $-0.67$ and $-0.24 \text{ eV}$, respectively. Photophysical experiments (see below) allowed for deciphering the photocatalytic mechanism occurring with the system Ru/$\text{Rh-tpy}$/HA$^-$/H$_2$A.

2.3. \textit{Photocatalytic Hydrogen Production}

The catalytic activity of \textbf{Rh-tpy} for the light-driven production of H$_2$ was evaluated in the presence of the Ru photosensitizer and ascorbate as a sacrificial electron donor in deaerated aqueous solutions (5 mM) at 298 K under visible light irradiation (400–700 nm). The light-driven evolution of H$_2$ was determined by gas chromatography in the course of the photocatalysis, and these data were used to calculate the TON (turnover number) and initial TOF values (turnover frequency) per molecule of catalyst (respectively denoted as TON$_{\text{Cat}}$ and TOF$_{\text{Cat}}$), which characterize the performance of the photocatalytic system (Table S7).

The catalytic activity of \textbf{Rh-tpy} was first investigated in a HA$^-$/H$_2$A buffer (total concentration 1.1 M, see Table S6) at pH 4.0 with 530 $\mu$M of PS, similar to our previous experiments with Rh$_2$ [11,12] and cobalt catalysts [43–47]. In these conditions, the Ru/$\text{Rh-tpy}$/HA$^-$/H$_2$A system displays 220 TON$_{\text{Cat}}$ after 22 h of irradiation with a catalyst concentration of 10 $\mu$M (Figure 4). However, the stability of the photocatalytic system did not exceed 7–8 h and about 90% of the total amount of H$_2$ was achieved after 6 h. The UV-vis absorption spectrum of the photocatalytic solution recorded at the end of the photocatalysis
indicates the complete transformation of the Ru PS into the bis-bipyridyl Ru(II) derivative, [Ru(bpy)2(X)2]n+, with the disappearance of the initial absorption band at 450 nm of Ru and the appearance of a new shoulder at 473 nm with a lower intensity (Figure 5A). This is due to the well-known poor stability of the reduced state Ru− in acidic water, generated upon the reductive quenching of *Ru by HA− (see below), which easily undergoes a ligand substitution by solvent molecules and/or anions such as ascorbate [48,49]. In view of slowing down the degradation of Ru and thus improving the stability of the photocatalytic system, a lower HA−/H2A concentration of 0.1 M was used. To keep the pH constant during the photocatalytic experiment, the aqueous solution was buffered with an acetate buffer (1 M) at pH 4.0. Such conditions have been already employed for several photocatalytic systems for H2 production involving cobalt catalysts [48,50–53]. In acetate buffer containing 0.1 M of HA−/H2A at pH 4.0, the Ru/Rh-tpy photocatalytic system is clearly more stable, since the H2 production is still effective after 22 h of irradiation. At this stage, the TONCat value has reached 380, which is almost twice as high as the TONCat value obtained in 1.1 M HA−/H2A buffer, and the Ru PS is less degraded at the end of photocatalysis (Figure 5B). However, when the concentration of the sacrificial electron donor is divided by 10, the initial TOFcat value is lower than that obtained in 1.1 M HA−/H2A (38 vs. 95 TOFcat, respectively, see Table S7). The pH was further optimized using the acetate buffer with 0.1 M HA−/H2A medium. The highest TONCat value of 423 was obtained at pH 4.5 after 22 h of irradiation. A further increase of the pH to 4.8 leads to a decrease of the TONCat value (Figure 4). Basically, the pH at which photocatalysis is optimal is governed by a delicate balance between the reactivity of the catalyst (generation of the Rh2+ hydride species) and the efficiency of the photoinduced electron transfer process (concentration of both protonated and non-protonated form of the SD) [34,54]. More acidic conditions make the protonation of the catalyst, i.e., the H2-evolution catalysis, faster, but the generation of the reductant Ru− is slowed down because the concentration of the ascorbate electron donor is smaller. In other words, in less acidic conditions, the higher concentration of ascorbate makes the quenching or regeneration of PS more efficient, but the low concentration in protons decreases the H2-evolving activity of the catalyst.

![Figure 4](image-url)

**Figure 4.** Photocatalytic hydrogen production (TONcat) as a function of time under 400–700 nm irradiation from a deaerated aqueous solution (5 mL) of Ru (530 µM) and Rh-tpy (10 µM) containing an acetate buffer (1 M) and NaHA/H2A (0.1 M) at different pHs (4.0; 4.5; 4.8) (solid trace) or only a buffer of NaHA/H2A (1.1 M) at pH 4.0 (dotted trace).
In order to rule out the formation of Rh\textsuperscript{0} colloids from Rh-tpy during the photocatalysis, an experiment was carried out with 530 µM of Ru, 10 µM of Rh-tpy in acetate buffer (0.1 M) containing HA\textsuperscript{−} /H\textsubscript{2}A (0.1 M) at pH 4.5, in the presence of an excess of mercury (Figure 6). Rh\textsuperscript{0} colloids are known to catalyze the reduction of protons to H\textsubscript{2} and can be deactivated by generating an amalgam with mercury [55,56]. The absence of effect on the photocatalytic behavior of the Ru/Rh-tpy/HA\textsuperscript{−} /H\textsubscript{2}A system due to the Hg addition confirms that no colloidal rhodium is formed during photocatalysis and the molecular Rh-tpy catalyst is involved in the H\textsubscript{2} evolution.
In order to rule out the formation of Rh$_0$ colloids from Rh-tpy, the amount of H$_2$ stemming from Ru, are thus of 300, 558, and 1012 at 10, 5, and 1 µM, respectively (Table S7).

UV-vis absorption spectra recorded at the end of the photocatalysis show that the Ru PS is partially transformed in Ru-bis-bipyridine species and that this transformation is more pronounced as the concentration of the catalyst is low (Figure 8) [53]. The degradation of the PS is most probably the main limiting factor for the H$_2$ production after 22 h [54].

The photocatalytic performance of Ru/Rh-tpy/HA$^-$/H$_2$A has also been compared with that obtained with Rh$_2$ as catalyst in the same experimental conditions (Table S7). In combination with a molecular photosensitizer, the Rh$_2$ complex is among the most efficient H$_2$ evolving catalysts based on rhodium that operate in water [11,12,15,34]. At pH 4.5 in 1 M acetate buffer containing 0.1 M of HA$^-$/H$_2$A, the Rh$_2$ catalyst appears significantly more active than Rh-tpy for the higher catalyst concentration of 10 µM, with corrected TON$_{Cat}^*$ of 1140 vs. 300 for Rh-tpy. However, in contrast to what was observed for Rh-tpy and, in a previous reported study for Rh$_2$ in the 1.1 M HA$^-$/H$_2$A buffer [11], if the catalyst concentration is decreased, the TON$_{Cat}^*$ also decreases to about 780 at 5 µM and 770 at 1 µM (Figure 7). Thus, Rh-tpy is clearly less efficient than Rh$_2$ at the higher catalyst concentrations of 10 and 5 µM (TON$_{Cat}^*$ of 300 and 558 for Rh-tpy vs. 1140 and
778 for Rh2), but challenges Rh2 in more diluted conditions (for 1 µM, TONCat* of 1012 for Rh-tpy vs. 772 for Rh2). In fact, the higher stability of the RhI species for Rh-tpy compared to that of Rh2, as revealed in organic solvent, could explain the photocatalytic performance of Ru/Rh-tpy/HA−/H2A competing with that of Ru/Rh2/HA−/H2A at very low concentrations of catalyst. Therefore, the use of tridentate tpy ligand compared to bidentate bpy ligands leads to a less active but potentially more stable H2-evolving catalyst. However, the instability of Ru PS does not allow for comparing the long-term stability of Rh-tpy and Rh2 catalysts. A more stable PS in water such as the triazatriangulenium TATA+ organic dye should be employed, but the reduction potential of this PS, which is less negative than that of Ru [53], will not allow for an efficient reduction of the Rh catalysts.

Figure 7. Photocatalytic hydrogen production as a function of time under 400–700 nm irradiation from a deaerated 1 M acetate aqueous buffer (5 mL) at pH 4.5 containing NaHA/H2A (0.1 M), in the presence of Ru (530 µM) and Rh-tpy at 10, 5, and 1 µM: (A) TONCat and (B) nH2 and VH2.
300 400 500 600 700 800
0.0
0.2
0.4
0.6
0.8
1.0 Absorbance
Wavelength / nm
 initial solution
after 22 h of irradiation with 
with [Rh-tpy] = 10 µM
 with [Rh-tpy] = 5 µM
 with [Rh-tpy] = 1 µM
[Ru] = 530 µM 0.1 M HA−/H2A at pH 4.5
1 M acetate

Figure 8. UV-vis absorption spectra of Ru (530 µM) in acetate buffer (1 M) at pH 4.5 and NaHA/H2A (0.1 M), initial solution and after about 22 h of irradiation with Rh-tpy at various concentrations (10, 5, and 1 µM). Optical path = 1 mm.

We also summarized the performances of the various three-components photocatalytic systems for H2 production in homogeneous solution in Tables S8 and S9, involving a rhodium complex (Rh1–24, Scheme 1) as a H2-evolving catalyst previously reported in view to compare the efficiency of these systems with those of Rh2 and Rh-tpy as catalysts. Tables S8 and S9 summarize the performances in hydro-organic (Rh11–24, Scheme 1b) and in purely aqueous (Rh1–10, Scheme 1a) solution, respectively. The structures of the various photosensitizers employed in these photocatalytic systems are gathered in Scheme S1. In aqueous organic media, PSs mainly rely on heteroleptic cyclometaled iridium(III) complexes of the type [Ir(C^N)2(N^N)]+ (C^N = phenylpyridine ligand and N^N = bipyridine ligand) with various substituents, although there are a few examples employing copper. In purely aqueous solution, most of the systems rely on Ru. Reliable comparison of the efficiency of the different systems is not obvious, since in addition to the fact that the experimental conditions are carried out in different experimental set-up, TON_Cat values are strongly dependent on the PS and Cat concentrations, the PS/Cat ratio, the nature of the solvent and of sacrificial electron donor, and the long-term stability of the PS.

Among the Rh catalysts employed in water (Rh1–10, Scheme 1a), only Rh2, Rh3, and Rh4 exhibited turnover numbers per catalyst (TON_Cat) higher than 100 in the presence of a ruthenium or iridium photosensitizer and ascorbate as SD [11]; TON_Cat for the others catalysts, Rh5–10, do not exceed 10 [3,8] (Table S9). However, these later systems used significantly higher catalyst concentration ranging from 50 µM to 1.56 mM, and the catalyst concentration is generally higher than that of the PS, resulting in lower TON_Cat. Concerning the Wilkinson catalyst Rh4, although up to 2000 TONS_Cat were reported [6,7], further studies by our group have shown that this catalyst is much less efficient than Rh2 [11].

Significantly higher TON_Cat were obtained in hydro-organic media. The highest TON_Cat in such media, from 2362 up to 9886, were obtained by the group of Kataoka with the Rh5, Rh15–16 and Rh11 catalysts in association with Ir1, Ir2, and Ir7 as PSs in THF/H2O [28,29] (Table S8). In these examples, the concentration ranges are similar to our studies, i.e., 500 µM for the PS and 5 µM for the catalyst. Interestingly, in the other studies combining Ir3–5 (100 µM) and Rh1 or Rh11–14 (100 µM) of Bernhard [15], Ir1 (50 µM) and Rh8–9 or Rh17 (50 µM) of Wang [10] and Ir2 (926 µM) and Rh18–21 (926 µM) of Kozlova [32,33], for which the Ir/Cat ratio is close to 1/1, TONS_Cat are comprised between 15 and 150, and reach 380 in one case.
These examples show that even with quite similar families of catalysts (for instance, Rh5–9 [8] and Rh5, Rh15–16 [28,29]) and PS, the TONCat values can be very different depending on the experimental conditions. The most relevant comparisons are therefore those made under similar experimental conditions. We can thus compare the efficiency of our systems with rhodium with those of the cobalt(III) tetraazamacrocyclic [CoIII(CR14)Cl2]+ (Co) complex, which is one of the most efficient H2-evolving catalyst in acidic water [43,45,47,53]. The catalytic performances of this complex have been recorded under similar experimental conditions with 500 µM Ru and 0.1 M of HA−/H2A in 1 M acetate buffer at pH 4.5 for catalyst concentrations of 10 and 5 µM (Table S7) [53]. TONCat* of 1086 and 1822 were obtained for Co compared to 300 and 558 for Rh-tpy for 10 and 5 µM, respectively. At both catalysts’ concentrations, Rh-tpy is thus much less efficient than Co, with more than three times less hydrogen produced.

2.4. Mechanistic Insight for the Ru/Rh-tpy/HA−/H2A System from Photophysical Measurements

The light-driven H2 production with the Ru/Rh-tpy/HA−/H2A three-component system is initiated by the generation of the excited state of the Ru, *RuII, under light absorption (Scheme 4). *Ru could be then quenched by an electron transfer to the sacrificial electron donor (HA−) to generate the reduced form of PS, Ru−, and the oxidized form of ascorbate (HA*) (reductive quenching). Ru− is able, in turn, to reduce the catalyst (RhIII-tpy to RhI-tpy), reforming the ground state Ru. HA* can lose a proton to form A•+, which can disproportionate generating the dehydroascorbic acid (DHA) [34,64,65], a very good electron acceptor able to withdraw electrons from Ru− and/or RhI-tpy. Therefore, a back electron transfer takes place from Ru− to HA* or DHA (BET process) to restore RuII and HA−, or from RhI-tpy to HA* or DHA (BETC process) to regenerate RhIII-tpy.

![Scheme 4. Proposed catalytic mechanism for the light-driven H2 production with the system Ru/Rh-tpy/HA−/H2A. For reasons of simplicity, only the pathway showing the heterolytic mechanism from RhIII(H)-tpy is shown. *RuII represents the triplet excited state of RuII, and Ru−, its one-electron reduced state.](image)

The *Ru can also be quenched by the catalyst leading to the oxidized form of the PS, RuIII, and the reduced state of catalyst, RhI-tpy (oxidative quenching), this process being unfavorable (see below).

Photophysical measurements allow us to identify which one of these two mechanisms is the most favorable. By using a Stern–Volmer plot, a rate constant (kQ1) of 1.0 × 107 M−1 s−1 was determined by the Schmehl’s group for the reductive quenching of the *RuII luminescence by HA− in an aqueous acetate buffered at pH 4.5. In the same medium, we determined a rate constant of 6.87 × 108 M−1 s−1 for the oxidative quenching
(kQ\textsubscript{0}) of \textsuperscript{\ast}Ru by Rh-tpy (Figure 9), which is about 70 times higher than that of the reductive quenching of \textsuperscript{\ast}Ru by HA\textsuperscript{−}. Although the oxidative quenching is kinetically more favored than the reductive quenching, the reductive pathway dominates over the oxidative one with pseudo-first-order kinetics of $1.0 \times 10^6$ s\textsuperscript{−1} and 0.069–3.4 $\times 10^4$ s\textsuperscript{−1}, respectively, considering that the HA\textsuperscript{−} concentration (0.1 M) is much higher than that of Rh-tpy (1–10 \mu M) under photocatalytic conditions. Noteworthily, the rate constant of the oxidative quenching of \textsuperscript{\ast}Ru by Rh\textsuperscript{III}-tpy is very similar to that previously determined by our group between \textsuperscript{\ast}Ru and Rh2 (3.2 $\times 10^8$ M\textsuperscript{−1} s\textsuperscript{−1}) [11]. This similarity of rate constants could be correlated to their akin driving forces $\Delta G_0$ of $-0.24$ eV for \textsuperscript{\ast}Ru/Rh-tpy and $-0.28$ eV for \textsuperscript{\ast}Ru/Rh2, considering the reduction potentials (Rh\textsuperscript{III}/Rh\textsuperscript{I}) of Rh-tpy and Rh2, and the oxidation potential of \textsuperscript{\ast}Ru (see Table S5).

Nanosecond flash photolysis experiments have also been performed to characterize the photoinduced electron transfer process occurring in the system Ru/Rh-tpy/HA\textsuperscript{−}/H\textsubscript{2}A at pH 4.5. In the absence of Rh-tpy, the transient absorption spectra recorded after excitation at 455 nm (Figure S1) show the formation of the Ru\textsuperscript{−} species with positive absorption bands at 360 and 510 nm [66]. The formation of Ru\textsuperscript{−} occurs from an electron transfer between \textsuperscript{\ast}Ru and HA\textsuperscript{−} [9,11]. Ru\textsuperscript{−} growth follows a pseudo first-order kinetics with an estimated rate constant of $4.3 \times 10^6$ s\textsuperscript{−1} ($\tau = 235$ ns, Figure S2). The decay of the transient absorption trace at 510 nm, due to the back electron transfer (BET) between Ru\textsuperscript{−} and the oxidized forms of ascorbate (HA\textsuperscript{•}) and DHA), can be fitted according to a second order kinetics law (Figure S3). The rate constant (k\textsubscript{BET}) is estimated to be $7.4 \times 10^9$ M\textsuperscript{−1} s\textsuperscript{−1}.

In the presence of Rh-tpy, flash photolysis experiments also show the formation of the Ru\textsuperscript{−} species, evidenced by an increase of absorption at 360 and 510 nm (Figure 10). The growth of the signal occurs in a similar time scale ($\tau = 215$ ns, corresponding to a constant at $4.6 \times 10^6$ s\textsuperscript{−1}, Figure S4) to that observed without Rh-tpy (Figure S2). This confirms that the photocatalytic cycle is initiated by a reductive quenching of \textsuperscript{\ast}Ru by HA\textsuperscript{−} and that the presence of Rh-tpy does not interfere with this first electron transfer process. However, the decay of the transient absorption trace at 510 nm is accelerated in the presence of Rh-tpy (Figure 11). This is a consequence of an electron transfer process between the transient Ru\textsuperscript{−} and Rh\textsuperscript{III}-tpy leading to the initial Ru\textsuperscript{II} and Rh\textsuperscript{I}-tpy, which efficiently competes with the BET process between Ru\textsuperscript{−} and the oxidized ascorbate (e.g., HA\textsuperscript{•} and DHA).

![Figure 9](image-url) - Stern–Volmer plot performed in a deaerated aqueous solution of acetate buffer (1 M) at pH 4.5 for the oxidative quenching of Ru (10 \mu M) at an excited state by Rh-tpy by varying its concentration (0; 0.06; 0.08; 0.1; 0.15; 0.2; 0.3 mM). The lifetime of \textsuperscript{\ast}Ru without catalyst ($\tau_0$) was determined to be 620 ns in water at pH 4.5.
This has allowed us to determine the real rates of the ET and BET processes (νET and νBET) at 5.45 × 10⁻⁵ and 3.81 × 10⁻⁴ M s⁻¹, respectively (see ESI for the calculation details).

In the presence of Rh-tpy, the decay of the transient Ru⁻ species is best fitted by a pseudo-first-order kinetics law, leading to a rate constant for the ET process of 2.4 × 10⁴ s⁻¹ (Figure S5). Considering the concentration of the catalyst in solution (200 µM), this would correspond to a bimolecular rate constant (kET) of 1.2 × 10⁸ M⁻¹ s⁻¹, which is 62 times lower than the kBET value (7.4 × 10⁸ M⁻¹ s⁻¹). The difference between these two kinetics should contradict the faster decay of Ru⁻ in presence of RhIII-tpy observed in the transient absorption trace in Figure 11. Nevertheless, we have estimated the initial concentration of Ru⁻ (2.27 × 10⁻⁷ M), calculated from the concentration of *RuIII* (9.1 × 10⁻⁷ M) just after the excitation pulse (∆A@450 nm = –0.01 and ∆ε = –11,000 M⁻¹ cm⁻¹) and considering a quantum yield of 25% for the Ru⁻ formation from reaction between *Ru* and HA [45].

Figure 10. Transient absorption spectra recorded at different times after flash laser excitation (λ = 455 nm) of a deaerated aqueous solution of acetate buffer (1 M) at pH 4.5 containing Ru (100 µM), NaHA/H₂A (0.1 M), and Rh-tpy (200 µM) (path length = 1 cm).

Figure 11. Transient absorption traces on the microsecond time scale recorded at 510 nm after laser excitation at 455 nm of a deaerated aqueous solution of acetate buffer (1 M) at pH 4.5 containing: (a) Ru (100 µM) and NaHA/H₂A (0.1 M), (b) Ru (100 µM), NaHA/H₂A (0.1 M), and Rh-tpy (200 µM).
In other words, under our experimental conditions, the ET process dominates over the BET process with a $v_{ET}/v_{BET}$ ratio of 14.3. Finally, although the two-electron reduced catalyst ($\text{Rh}^\text{III}$(tpy)) exhibits a large absorption band between 550 and 700 nm (Figure 3), its typical spectroscopic signature is not observed in the transient absorption spectra. This is attributed to the fast reactivity of the $\text{Rh}^\text{III}$(tpy) species (i.e., $[\text{Rh}^\text{III}(\text{tpy})\text{X}^\text{II}](\text{H})$, X = Cl$^-$ or H$_2$O with n = 0 or 1, respectively) with protons, below the nanosecond time-scale, to form a $\text{Rh}^\text{III}$(H)(tpy) hydride species (i.e., $[\text{Rh}^\text{III}(\text{H})(\text{H}_2\text{O})\text{X}^\text{II}](\text{H})$, X = Cl$^-$ or H$_2$O with n = 1 or 2, respectively), the key intermediate to reduce protons into H$_2$. Indeed, from this species, different pathways can lead to the production of H$_2$ via homolytic (reaction with another $\text{Rh}^\text{III}$(H)(tpy) species to generate H$_2$ and two Rh(II) species) or heterolytic (reaction with a proton to form H$_2$ and a Rh(III) species) route (Scheme 4). $\text{Rh}^\text{III}$(H)(tpy) could be also further reduced by $\text{Ru}^-$ to a Rh(II) hydride species, $\text{Rh}^\text{II}$(H)(tpy), from which H$_2$ can be released via similar homolytic and heterolytic pathways, generating Rh(I) and Rh(II) species, respectively. The group of Ogo has shown that in CH$_3$CN, the hydride complex $[\text{Rh}^\text{III}(\text{H})(\text{tpy})(\text{CH}_3\text{CN})_2]^{2-}$ can slowly generate H$_2$ via reductive elimination leading to the Rh(II) dimer species (homolytic route) [37]. However, we cannot rule out that in acidic water, other pathways can proceed in parallel to this homolytic mechanism. For instance, according to theoretical calculations, we have shown that, for the Rh2 catalyst in acidic water, H$_2$ is preferentially released through a heterolytic mechanism from the $\text{Rh}^\text{III}$(H) species and that both homo- and heterolytic mechanisms are thermodynamically favorable to generate H$_2$ via the $\text{Rh}^\text{II}$(H) species [13]. Furthermore, although the formation of the $\text{Rh}^\text{III}$(H)(tpy) hydride species is very fast, the catalysis of proton reduction generally remains the rate-determining step of the photocatalytic mechanism, occurring within three-component systems for photocatalytic evolution of H$_2$ in homogeneous media [44,54].

3. Materials and Methods

3.1. Synthesis of $[\text{Rh}^\text{III}$(tpy)Cl$_3$]

$\text{RhCl}_3$$ \cdot $3H$_2$O (150 mg, 0.55 mmol) and 2, 2′,6′, 2′′-terpyridine (129 mg, 0.55 mmol) were dissolved in absolute ethanol (24 mL). After stirring at 90 °C for 12 h, a yellow precipitate appeared to correspond to $[\text{Rh}^\text{III}$(tpy)Cl$_3$], which was filtered off from the hot reaction mixture and washed with diethyl ether (188 mg, yield, 77%). $^1$H NMR (DMSO-d$_6$, 400 MHz, δ (ppm): 9.28 (d; J = 5.2 Hz; 2H); 8.81 (d; J = 8 Hz; 2H); 8.77 (d; J = 7.6 Hz; 2H); 8.54 (t; J = 8 Hz; 1H); 8.38 (t; J = 7.6 Hz; 2H); 7.95 (t; J = 6.4 Hz; 2H). IR (cm$^{-1}$): 3069, 2932, 2324, 1598, 1570, 1472, 1447, 1397, 1312, 1321, 1252, 1184, 1157, 1136, 1048, 1026, 751, 668, 655. ESI-MS, positive mode m/z (%): 405.87 (59) [M − Cl]$^+$, 463.83 (81) [M + Na]$^+$.

3.2. Synthesis of $[\text{Rh}^\text{III}$(tpy)(CH$_3$CN)Cl$_2$](CF$_3$SO$_3$)$_2$ (Rh-tpy)

[Rh$^\text{III}$(tpy)Cl$_3$] (116 mg, 0.26 mmol) was added to an acetonitrile solution (232 mL) of AgCF$_3$SO$_3$ (209 mg, 0.81 mmol). After stirring at 90 °C for 20 h, the white precipitate of AgCl formed was filtered off from the hot reaction mixture. The resulting pale yellow filtrate was concentrated until 30 mL, yielding a yellow precipitate of $[\text{Rh}^\text{III}$(tpy)(CH$_3$CN)Cl$_2$](CF$_3$SO$_3$)$_2$, which was filtered off and washed with diethyl ether to give a pale yellow powder. $[\text{Rh}^\text{III}$(tpy)(CH$_3$CN)Cl$_2$](CF$_3$SO$_3$)$_2$ was recrystallized by slow diffusion of diethyl ether into an acetonitrile solution of complex (80 mg, yield, 51%). $^1$H NMR (D$_2$O, 400 MHz, δ (ppm): 9.06 (d; J = 5.6 Hz; 2H); 8.66 (d; J = 7.6 Hz; 2H); 8.59 (d; J = 7 Hz; 1H); 8.46 (t; J = 8 Hz; 2H); 8.02 (t; J = 7.6 Hz; 2H); 2.94 (s, 3H). IR: 3088, 2930, 2324, 1604, 1575, 1479, 1452, 1403, 1320, 1258, 1223, 1123, 1139, 1030, 773, 635. ESI-MS, positive mode m/z (%): 446.95 (100) [M − CF$_3$SO$_3$]$^+$, 405.93 (26) [M − CF$_3$SO$_3$−CH$_3$CN]$^+$. 

4. Conclusions

We demonstrated, for the first time, that the terpyridyl rhodium complex, $[\text{Rh}^\text{III}$(tpy)(CH$_3$CN)Cl$_2$](CF$_3$SO$_3$)$_2$ (Rh-tpy), is able to catalyze the light-induced proton reduction into H$_2$ in aqueous solution in the presence of the [Ru$^\text{II}$(bpy)$_3$]Cl$_2$ (Ru) photosensitizer and ascorbate as sacrificial electron donors. Under photocatalytic conditions, TON$_{\text{Cat}}$ values of
300 and up to 1000 were obtained for H₂ production for a Rh-tpy catalyst concentration at 10 and 1 µM, respectively, after subtraction of the amount of H₂ stemming from the Ru only. The photocatalytic performance of Ru/Rh-tpy/HA⁻/H₂A has also been compared with that obtained with Rh2 as a catalyst in the same experimental conditions. It appears that Rh-tpy is clearly less efficient than Rh2 at the higher catalyst concentrations of 10 and 5 µM (TONcat* of 300 and 558 for Rh-tpy vs 1140 and 778 for Rh2), but challenges Rh2 in more diluted conditions (for 1 µM, TONcat* of 1012 for Rh-tpy vs. 772 for Rh2). Therefore, the use of tridentate tpy ligand compared to bidentate bpy ligands leads to a less active but potentially more stable H₂-evolving catalyst. However, Rh-tpy, is much less efficient than the cobalt(III) tetraazaamacrocyclic [CoIII(CR14)Cl₂]⁺ (Co) complex, one of the most efficient H₂-evolving catalysts in acidic water, since with this catalyst, TONcat* of 1086 and 1822 were reached at 10 and 5 µM, respectively.

The electrochemical study in DMF reveals that the reduced state of the rhodium catalyst, identified as [RhI(tpy)Cl] (RhI-tpy) from its UV-visible signature, is stable for several hours under an inert atmosphere owing to the π-acceptor property of the terpyridine ligand that stabilizes the low oxidation states of the rhodium. A good stability of the low-valent form of the rhodium catalyst makes it less prone to degradation in the course of photocatalysis. The π-acceptor property of terpyridine also confers moderately negative reduction potential to the Rh-tpy catalyst (about −0.8 V vs. SCE), making its reduction by the reduced state of Ru effective (E1/2(RuII/RuI) = −1.50 V vs. SCE). A Stern–Volmer plot and transient absorption spectroscopy have shown that the first step of the photocatalytic process is a reductive quenching of the Ru excited state by ascorbate. The resulting Ru− species is then able to reduce the RhIII-tpy catalyst generating RhI-tpy, which reacts with a proton on a sub-nanosecond time scale to form a RhIII(H)-tpy hydride, the key intermediate for H₂ evolution. The search for new molecular catalysts for H₂ production with simple and easily synthesized ligands is still ongoing, and the terpyridine ligand, with its particular electronic and coordination properties, is a good candidate for designing new catalysts to meet these requirements.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27196614/s1, Materials and general experimental details. Additional data and experimental details for X-ray structure determination, electrochemistry, UV-Vis absorption spectroscopy, 1H NMR, mass spectrum, photocatalytic hydrogen production, photophysics, nanosecond transient absorption spectroscopy (Figures S1–S8 and Tables S1–S7). CCDC 2173038 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44-1223-336033.

Author Contributions: Conceptualization, M.-N.C. and J.F.; methodology, M.-N.C., J.F., F.C. and D.A.; validation, F.C., M.-N.C. and J.F.; formal analysis, F.C. and J.F.; investigation, F.C., T.G., B.D., J.C. and J.P.; resources, M.-N.C. and J.F.; data curation, F.C. and J.F.; writing—original draft preparation, M.-N.C. and J.F.; writing—review and editing, M.-N.C.; visualization, M.-N.C.; supervision, M.-N.C. and J.F.; project administration, M.-N.C. and J.F.; funding acquisition, M.-N.C. and J.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work has been partially supported by the French National Research Agency through the project TATADyes (ANR-20-CE05-0041) for the Master1 grant of T.G., Labex ARCANDE and CBH-EUR-GS (ANR-17-EURE-0003) and by “Université Grenoble Alpes” for the PhD grants of F.C. and B.D.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.
Acknowledgments: We are grateful to the CNRS, the Université Grenoble Alpes and the French National Research Agency through the project TATADyes (ANR-20-CE05-0041), Labex ARCANE and CBH-EUR-GS (ANR-17-EURE-0003) for their financial supports. This work was also supported by ICMG Chemistry Nanobio Platform (FR2067). F.C. and B.D. thank the “Université Grenoble Alpes” for their PhD grant, and T.G. thanks the French National Research Agency (TATADyes; ANR-20-CE05-0041) for his Master1 grant.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds [RhIII(tpy)Cl3] and [RhIII(tpy)(CH3CN)Cl2](CF3SO3) are available from the authors.

References
1. Armaroli, N.; Balzani, V. The Hydrogen Issue. ChemSusChem 2011, 4, 21–36. [CrossRef] [PubMed]
2. Lehnn, J.; Sauvage, J.P. Chemical Storage of Light energy—Catalytic Generation of Hydrogen by Visible-Light or Sunlight Irradiation of Neutral Aqueous Solution. Nat. J. Chem. 1977, 1, 449–451. [CrossRef]
3. Kirch, M.; Lehnn, J.; Sauvage, J.P. Hydrogen Generation by Visible-Light Irradiation of Aqueous-Solutions of Metal-Complexes—Approach to the Photo-Chemical Conversion and Storage of Solar-Energy. Helv. Chim. Acta 1979, 62, 1345–1384. [CrossRef]
4. Eckenhoff, W.T.; Eisenberg, R. Molecular systems for light driven hydrogen production. Dalton Trans. 2012, 41, 13004–13021. [CrossRef]
5. Dalle, K.E.; Warnan, J.; Leung, J.I.; Reuillard, B.; Karmel, I.S.; Reisner, E. Electro- and Solar-Driven Fuel Synthesis with First Row Transition Metal Complexes. Chem. Rev. 2019, 119, 2752–2875. [CrossRef]
6. Oishi, S. A Water-Soluble Wilkinson Complex as a Homogeneous Catalyst for the Photochemical Reduction of Water. J. Mol. Catal. 1987, 39, 225–232. [CrossRef]
7. Bauer, R.; Werner, H.A.F. Investigations on a Homogeneous Wilkinson Catalyst for the Water Photolysis. Int. J. Hydrogen Energy 1994, 19, 497–499. [CrossRef]
8. Tanaka, S.; Masaoaka, S.; Yamauchi, K.; Annaka, M.; Sakai, K. Photochemical and thermal hydrogen production from water catalyzed by carboxylate-bridged dirhodium(II) complexes. Dalton Trans. 2010, 19, 11218–11226. [CrossRef]
9. Fukuzumi, S.; Kobayashi, T.; Suenobu, T. Photocatalytic Production of Hydrogen by Disproportionation of One-Electron-Reduced Rhodium and Iridium–Ruthenium Complexes in Water. Angew. Chem. Int. Ed. 2011, 50, 728–731. [CrossRef]
10. Xie, J.; Li, C.; Hou, Y.; Zhang, B.; Wang, X. Large Improvement in the Catalytic Activity Due to Small Changes in the Diimine Ligands: New Mechanistic Insight into the Dirhodium(II,II) Complex-Based Photocatalytic H2 Production. Inorg. Chem. 2012, 51, 6376–6384. [CrossRef]
11. Wang, J.; White, T.A.; Arachchige, S.M.; Brewer, K.J. A new structural motif for photoinitiated electron collection: Ru,Rh bearing an Osmium(II) Bis(terpyridyl) Moiety as a Light-Harvesting Unit: Application to Photocatalytic Production of Dihydrogen. Dalton Trans. 2015, 44, 10497–10509. [CrossRef]
12. Stoll, T.; Gennari, M.; Ferrero, L.; Fortage, J.; Chauvin, J.; Odobel, F.; Rebarz, M.; Poizat, O.; Sliwa, M.; Deronzier, A.; et al. [RhIII(bpy)2Cl2] as a Highly Efficient Catalyst for Visible-Light-Driven Hydrogen Production in Pure Water: Comparison with Other Rhodium Catalysts. Chem.-Eur. J. 2013, 19, 782–792. [CrossRef]
13. Stoll, T.; Gennari, M.; Fortage, J.; DeBardelaben, C.E.; Rebarz, M.; Sliwa, M.; Poizat, O.; Odobel, F.; Deronzier, A.; Collomb, M.-N. An Efficient RuII–RhIII–RuII Polypyrrolidyl Photocatalyst for Visible-Light-Driven Hydrogen Production in Aqueous Solution. Angew. Chem. Int. Ed. 2014, 53, 1654–1658. [CrossRef]
14. Kayanuma, M.; Stoll, T.; Daniel, C.; Odobel, F.; Fortage, J.; Deronzier, A.; Collomb, M.-N. A computational mechanistic investigation of hydrogen production in water using the [RhIII(bpy)2Cl2]1+[RuII(bpy)3]2+/ascorbic acid photocatalytic system. Phys. Chem. Chem. Phys. 2015, 17, 10497–10509. [CrossRef]
15. Canterbury, T.R.; Arachchige, S.M.; Brewer, K.J.; Moore, R.B. A new hydrophilic supramolecular photocatalyst for the production of H2 in aerobic aqueous solutions. Chem. Commun. 2016, 52, 8663–8666. [CrossRef]
16. Clime, E.D.; Adamson, S.E.; Bernhard, S. Homogeneous Catalytic System for Photoinduced Hydrogen Production Utilizing Iridium and Rhodium Complexes. Inorg. Chem. 2008, 47, 10378–10388. [CrossRef]
17. Miyake, Y.; Nakajima, K.; Sasaki, K.; Saito, R.; Nakanishi, H.; Nishibayashi, Y. Design and Synthesis of Diphosphine Ligands Bearing an Osmium(II) Bis(terpyridyl) Moiety as a Light-Harvesting Unit: Application to Photocatalytic Production of Dihydrogen. Organometalics 2009, 28, 5240–5243. [CrossRef]
18. White, T.A.; Higgins, S.L.H.; Arachchige, S.M.; Brewer, K.J. Efficient Photocatalytic Hydrogen Production in a Single-Component System Using Ru,Rh,Ru Supramolecules Containing 4,7-Diphenyl-1,10-Phenanthroline. Angew. Chem. Int. Ed. 2011, 50, 12209–12213. [CrossRef]
19. White, T.A.; Whitaker, B.N.; Brewer, K.J. Discovering the Balance of Steric and Electronic Factors Needed To Provide a New Structural Motif for Photocatalytic Hydrogen Production from Water. J. Am. Chem. Soc. 2011, 133, 15332–15334. [CrossRef]
20. Peuntinger, K.; Pilz, T.D.; Staehe, R.; Schaub, M.; Kaufhold, S.; Petermann, L.; Wunderlin, M.; Görls, H.; Heinemann, F.W.; Li, J.; et al. Carbone based photochemical molecular assemblies for solar driven hydrogen generation. *Dalton Trans.* **2014**, *43*, 13683–13695. [CrossRef]

21. Zhou, R.; Manbeck, G.F.; Wimer, D.G.; Brewer, K.J. A new Ru^IV/Rh^III bimetallic with a single Rh–Cl bond as a supramolecular photocatalyst for proton reduction. *Chem. Commun.* **2015**, *51*, 12966–12969. [CrossRef] [PubMed]

22. Wagner, A.T.; Zhou, R.; Quinn, K.S.; White, T.A.; Wang, J.; Brewer, K.J. Tuning the Photophysical Properties of Ru(II) Monometallic and Ru(II),Rh(III) Bimetallic Supramolecular Complexes by Selective Ligand Deuteration. *J. Phys. Chem. A* **2015**, *119*, 6781–6790. [CrossRef] [PubMed]

23. Mengele, A.K.; Kaufhold, S.; Streb, C.; Rau, S. Generation of a stable supramolecular hydrogen evolving photocatalyst by alteration of the catalytic center. *Dalton Trans.* **2016**, *45*, 6662–6668. [CrossRef] [PubMed]

24. Kagalwala, D.N.; Chirdon, D.N.; Mills, I.N.; Budwal, N.; Bernhard, S. Light-Driven Hydrogen Generation from Microemulsions Using Metallosurfactant Catalysts and Oxalic Acid. *Inorg. Chem.* **2017**, *56*, 10162–10171. [CrossRef] [PubMed]

25. Manbeck, G.F.; Fujita, E.; Brewer, K.J. Tetra- and Heptametallic Ru(II),Rh(III) Supramolecular Hydrogen Production Photocatalysts. *J. Am. Chem. Soc.* **2017**, *139*, 7843–7854. [CrossRef] [PubMed]

26. McCullough, B.J.; Neyhouse, B.J.; Schrage, B.R.; Reed, D.T.; Osinski, A.J.; Ziegler, C.J.; White, T.A. Visible-Light-Driven Photosystems Using Heteroleptic Cu(I) Photosensitizers and Rh(III) Catalysts To Produce H_2. *Inorg. Chem.* **2018**, *57*, 2865–2875. [CrossRef] [PubMed]

27. Saeedi, S.; Xue, C.; McCullough, B.J.; Roe, S.E.; Neyhouse, B.J.; White, T.A. Probing the Diphosphine Ligand’s Impact within Heteroleptic, Visible-Light-Absorbing Cu(I) Photosensitizers for Solar Fuels Production. *ACS Appl. Energy Mater.* **2019**, *2*, 131–143. [CrossRef]

28. Kataoka, Y.; Yano, N.; Handa, M.; Kawamoto, T. Intrinsic hydrogen evolution capability and a theoretically supported reaction mechanism of a paddlewheel-type dirhodium complex. *Dalton Trans.* **2019**, *48*, 7302–7312. [CrossRef]

29. Vasilchenko, D.B.; Tkachev, S.V.; Baidina, I.; Korolkov, I.; Berdyugin, S.; Kozlova, E.A.; Kozlov, D.V. Preparation of a rhodium(iii) cis-diaquacomplex by protic acid induced oxalate-release from mer-[Rh(C_2O_4)Cl(py)]. *New J. Chem.* **2018**, *42*, 19637–19643. [CrossRef]

30. Vasilchenko, D.B.; Tkachev, S.V.; Kurenkova, A.Y.; Kozlova, E.A.; Kozlov, D.V. Photocatalytic hydrogen evolution by iridium(iii) hydride species. *Dalton Trans.* **2016**, *45*, 2959–2967. [CrossRef]

31. Stoll, T.; Castillo, C.E.; Kayanuma, M.; Sandroni, M.; Daniel, C.; Odobel, F.; Fortage, J.; Collomb, M.-N. Photo-induced redox catalysts for proton reduction to hydrogen with homogeneous molecular systems using rhodium-based catalysts. *Coord. Chem. Rev.* **2015**, *304–305*, 20–37. [CrossRef]

32. Bakac, A. Aqueous rhodium(III) hydrides and mononuclear rhodium(II) complexes. *Dalton Trans.* **2006**, *13*, 1589–1596. [CrossRef]

33. Castillo, C.E.; Stoll, T.; Sandroni, M.; Gueret, R.; Fortage, J.; Kayanuma, M.; Daniel, C.; Odobel, F.; Deronzier, A.; Collomb, M.-N. Electrochemical Generation and Spectroscopic Characterization of the Key Rhodium(III) Hydride Intermediates of Rhodium Poly(bipyridyl) H_2-Evolving Catalysts. *Inorg. Chem.* **2018**, *57*, 11225–11239. [CrossRef]

34. Inoki, D.; Matsumoto, T.; Nakai, H.; Ogo, S. Experimental Study of Reductive Elimination of H_2 from Rhodium Hydride Species. *Organometallics* **2012**, *31*, 2996–3001. [CrossRef]

35. Paul, P.; Spey, S.; Adams, H.; Thomas, J.A. Synthesis and structure of rhodium complexes containing extended terpyridyl ligands. *Inorg. Chim. Acta* **2004**, *357*, 2827–2832. [CrossRef]

36. de Pater, B.C.; Frühauf, H.-W.; Vrieze, K.; de Gelder, R.; Evert, J.B.; McCormack, D.; Lutz, M.; Anthony, L.S.; Hartl, F. Strongly Nucleophilic Rh^I Centre in Square-Planar Complexes with Terdentate (κ_3) 2,2′,6′,2″-Terpyridine Ligands: Crystallographic, Electrochemical and Density Functional Theoretical Studies. *Eur. J. Inorg. Chem.* **2004**, *2004*, 1675–1686. [CrossRef]
43. Varma, S.; Castillo, C.E.; Stoll, T.; Fortage, J.; Blackman, A.G.; Molton, F.; Deronzier, A.; Collomb, M.-N. Efficient photocatalytic hydrogen production in water using a cobalt(III) tetraaza-macrocyclic catalyst: Electrochemical generation of the low-valent Co(I) species and its reactivity toward proton reduction. Phys. Chem. Chem. Phys. 2015, 17, 15744–15752. [CrossRef]

44. Gimbert-Surinach, C.; Albero, J.; Stoll, T.; Fortage, J.; Collomb, M.-N.; Deronzier, A.; Palomares, E.; Llobet, A. Efficient and Limiting Reactions in Aqueous Light-Induced Hydrogen Evolution Systems using Molecular Catalysts and Quantum Dots. J. Am. Chem. Soc. 2014, 136, 7655–7661. [CrossRef] [PubMed]

45. Gueret, R.; Castillo, C.E.; Rebarz, M.; Thomas, F.; Hargrove, A.-A.; Pécaut, J.; Sliwa, M.; Fortage, J.; Collomb, M.-N. Cobalt(III) tetraaza-macrocyclic complexes as efficient catalyst for photoinduced hydrogen production in water: Theoretical investigation of the electronic structure of the reduced species and mechanistic insight. J. Photochem. Photobiol. B Biol. 2015, 132, 82–94. [CrossRef] [PubMed]

46. Lo, W.K.C.; Castillo, C.E.; Gueret, R.; Fortage, J.; Rebarz, M.; Sliwa, M.; Thomas, F.; McAdam, C.J.; Jameson, G.B.; McMorran, D.A.; et al. Synthesis, Characterization, and Photocatalytic H2-Evolving Activity of a Family of [Co(N4Py)(X)]11 Complexes in Aqueous Solution. Inorg. Chem. 2016, 55, 4564–4581. [CrossRef] [PubMed]

47. Gueret, R.; Castillo, C.E.; Rebarz, M.; Thomas, F.; Sliwa, M.; Chauvin, J.; Daubrepppe, B.; Pécaut, J.; Fortage, J.; Collomb, M.-N. Cobalt(II) Pentaaaza-Macroyclic Schiff Base Complex as Catalyst for Light-Driven Hydrogen Evolution in Water: Electrochemical Generation and Theoretical Investigation of the One-Electron Reduced Species. Inorg. Chem. 2019, 58, 9043–9056. [CrossRef] [PubMed]

48. Singh, W.M.; Baine, T.; Kudo, S.; Tian, S.L.; Ma, X.A.N.; Zhou, H.Y.; DeYonker, N.J.; Pham, T.C.; Bollinger, J.C.; Baker, D.L.; et al. Electrolytic and Photocatalytic Hydrogen Production in Aqueous Solution by a Molecular Cobalt Complex. Angew. Chem. Int. Ed. 2012, 51, 5941–5944. [CrossRef]

49. Khnayzer, R.S.; Thi, V.S.; Nippe, M.; King, A.E.; Jurss, J.W.; El Roz, K.A.; Long, J.R.; Chang, C.J.; Castellano, F.N. Towards a comprehensive understanding of visible-light photogeneration of hydrogen from water using cobalt(II) polypyridyl catalysts. Energy Environ. Sci. 2014, 7, 1477–1488. [CrossRef]

50. Singh, W.M.; Mirmohades, M.; Jane, R.T.; White, T.A.; Hammerstrom, L.; Thapper, A.; Lomoth, R.; Ott, S. Voltammetric and Spectroscopic Characterization of Early Intermediates in the Co(II)-Polypyridyl-Catalyzed Reduction of Water. Chem. Commun. 2013, 49, 8638–8640. [CrossRef]

51. Natali, M.; Badetti, E.; Deponti, E.; Gamberoni, M.; Scaramuzzo, F.A.; Sartorel, A.; Zonta, C. Photoinduced hydrogen evolution with new tetradeinate cobalt(II) complexes based on the TPMA ligand. Dalton Trans. 2016, 45, 14764–14773. [CrossRef]

52. Lucarini, F.; Pastore, M.; Vasilyevskyi, S.; Varisco, M.; Solari, E.; Crochet, A.; Fromm, K.M.; Zobi, F.; Ruggi, A. Heptacoordinate CoII Complex as a New Architecture for Photochemical Hydrogen Production. Chem. Eur. J. 2017, 23, 6768–6771. [CrossRef]

53. Gueret, R.; Poulard, L.; Oshinowo, M.; Chauvin, J.; Dahmane, M.; Dupeyre, G.; Lainé, P.P.; Fortage, J.; Collomb, M.-N. Challenging the [Ru(bpy)3]2+ Photosensitizer with a Triazatriangulenium Robust Organic Dye for Visible-Light-Driven Hydrogen Production in Water. ACS Catal. 2018, 8, 3792–3802. [CrossRef]

54. Costentin, C.; Camara, F.; Fortage, J.; Collomb, M.-N. Photoinduced Catalysis of Redox Reactions. Turnover Numbers, Turnover Frequency, and Limiting Processes: Kinetic Analysis and Application to Light-Driven Hydrogen Production. ACS Catal. 2022, 12, 6246–6254. [CrossRef]

55. Amouyal, E.; Koffi, P. Photochemical Production of Hydrogen from Water. J. Photochem. 1985, 29, 227–242. [CrossRef]

56. Weddle, K.S.; Aiken, J.D.; Finke, R.G. Rh(0) nanoclusters in benzene hydrogenation catalysis: Kinetic and mechanistic evidence for homo- and heterogeneous photocatalytic water reduction. Dalton Trans. 2013, 42, 334–337. [CrossRef]

57. Sandroni, M.; Gueret, R.; Wegner, K.D.; Reiss, P.; Fortage, J.; Aldakov, D.; Collomb, M.-N. Cadmium-Free CuInS2/ZnS Quantum Dots as Efficient and Robust Photosensitizers in combination with a Molecular Catalyst for Visible-Light-Driven Hydrogen Production in Water. Energy Environ. Sci. 2018, 11, 1752–1761. [CrossRef]

58. Bachmann, C.; Guttenstag, M.; Spingler, B.; Alberto, R. 3d Element Complexes of Pentadentate Bipyridine-Pyridine-Based Ligand Scaffolds: Structures and Photocatalytic Activity. Inorg. Chem. 2013, 52, 6055–6061. [CrossRef]

59. Weddel, K.S.; Aiken, J.D.; Finke, R.G. Rh(0) nanoclusters in benzene hydrogenation catalysis: Kinetic and mechanistic evidence that a putative (C4Hg2)2NCH3]+ [RhCl]+ ion-Pair catalyst is actually a distribution of Cl− and [(C4Hg2)2NCH3]1+ stabilized Rh(0) nanoclusters. J. Am. Chem. Soc. 1998, 120, 5653–5666. [CrossRef]

60. Sandroni, M.; Gueret, R.; Wegner, K.D.; Reiss, P.; Fortage, J.; Aldakov, D.; Collomb, M.-N. Cadmium-Free CuInS2/ZnS Quantum Dots as Efficient and Robust Photosensitizers in combination with a Molecular Catalyst for Visible Light-Driven H2 Production in Water. Energy Environ. Sci. 2018, 11, 1752–1761. [CrossRef]

61. Bachmann, C.; Guttenstag, M.; Spingler, B.; Alberto, R. 3d Element Complexes of Pentadentate Bipyridine-Pyridine-Based Ligand Scaffolds: Structures and Photocatalytic Activity. Inorg. Chem. 2013, 52, 6055–6061. [CrossRef]

62. Tong, L.; Zong, R.; Thummel, R.P. Visible Light-Driven Hydrogen Evolution from Water Catalyzed by A Molecular Cobalt Complex. J. Am. Chem. Soc. 2014, 136, 4881–4884. [CrossRef]

63. Vennampalli, M.; Liang, G.; Katta, L.; Webster, C.E.; Zhao, X. Electronic Effects on a Mononuclear Co Complex with a Pentadentate Ligand for Catalytic H2 Evolution. Inorg. Chem. 2014, 53, 10094–10100. [CrossRef]

64. Bachmann, C.; Probst, B.; Guttenstag, M.; Alberto, R. Ascorbate as an electron relay between an irreversible electron donor and Ru(II) or Re(I) photosensitizers. Chem. Commun. 2014, 50, 6737–6739. [CrossRef] [PubMed]
65. Guttentag, M.; Rodenberg, A.; Kopelet, R.; Probst, B.; Buchwalder, C.; Brandstätter, M.; Hamm, P.; Alberto, R. Photocatalytic H₂ Production with a Rhenium/Cobalt System in Water under Acidic Conditions. *Eur. J. Inorg. Chem.* 2012, 2012, 59–64. [CrossRef]

66. Mulazzani, Q.G.; Emmi, S.; Fuochi, P.G.; Hoffman, M.Z.; Venturi, M. On the nature of tris(2,2′-bipyridine)ruthenium(1+) ion in aqueous solution. *J. Am. Chem. Soc.* 1978, 100, 981–983. [CrossRef]