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Mechanistic study of the photo-generation of hydrogen by decamethylruthenocene

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Abstract: Hydrogen evolution by decamethylruthenocene ($\text{Cp}^*_2\text{Ru}^{\text{II}}$) was studied in detail highlighting that metallocenes are capable of photo-reducing hydrogen without the need of an additional sensitizer. Electrochemical, gas chromatographic and spectroscopic (UV/vis, ^1H and ^{13}C NMR) measurements corroborated by density functional theory (DFT) calculations indicate that the production of hydrogen occurs by a two-step process. First, the decamethylruthenocene hydride ($[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$) is formed in the presence of an organic acid. Subsequently, $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ is reversibly reduced *via* a heterolytic reaction with one-photon excitation leading to a first release of hydrogen. Thereafter, the resultant decamethylruthenocenium ion ($[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$) is further reduced leading to a second release of hydrogen by deprotonation of a methyl group of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$. Experimental and computational data show the spontaneous conversion of $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ to $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ in the presence of protons. Calculations highlight that the first reduction is endergonic

($\Delta G^0 = 108 \text{ kJ}\cdot\text{mol}^{-1}$) and needs an input of energy by light for the reaction to occur. The hydricity of the methyl protons of $[\text{Cp}^*\text{Ru}^{\text{II}}]$ was also considered.

Introduction

One of the major issues facing the development of renewable energy strategies (solar and wind in particular) is the intermittent nature of the energy production *via* these routes (no electricity is produced when the sun does not shine and when there is no wind).^[1] Therefore, reliance on renewable energy requires energy storage. While batteries are able to cost effectively store the produced electricity for hour scale,^[2,3] different strategies are required for long-term energy storage. One proposed option is the storage of energy in the form of chemicals such as hydrogen (H_2) as a solar fuel to allow the stock-piling of clean energy produced in excess. The solar fuel may then be consumed on demand.^[4,5] H_2 has the advantage that it may be readily obtained in large amounts by “splitting” water.^[6,7] As a consequence, the development of efficient and sustainable methods to produce H_2 from water-splitting is the focus of intense research. Current approaches focus on the (photo)electrocatalytic production of H_2 at the surface of solid electrodes immersed in acidified aqueous or organic solutions utilizing highly engineered catalyst and photosensitizer combinations.^[8–10]

For photogeneration of hydrogen, various multicomponent artificial photosystems consisting of catalyst, photosensitizer, electron mediator or relay combinations,^[9,10] and often fueled by sacrificial electron donors (for example, triethylamine,^[11,12] triethanolamine,^[13] benzyl-dihydronicotinamide,^[14] and so forth) have been investigated in detail. Typically, the sacrificial donor irreversibly oxidizes upon charge transfer and provides protons and electrons to the catalyst, although some donors such as dimethyl-p-toluidine undergo dimerization to produce electrochemically active products.^[15,16] Also, there are some indications that ascorbate could function as a non-sacrificial donor.^[17] However, recyclability of these donors has never been demonstrated.

Our group developed an alternative strategy to photo-produce H_2 at electrified liquid-liquid interfaces with the use of a single molecule to achieve both proton reduction and photo-activation.^[18] Significantly, this approach overcomes problems encountered at solid electrode-liquid interfaces such as corrosion. The set-up consists of an organic electrolyte solution of low water miscibility, typically 1,2-dichloroethane (DCE) containing a dissolved lipophilic metallocene, that is in contact with an acidic aqueous electrolyte solution. Upon polarization of the liquid-liquid interface, either *via* the application of an external voltage or by dissolving a common ion in both phases, protons are pumped into the organic phase where they are reduced to H_2 .^[19–21] The reversible redox nature of the metallocene (electron donor (D)) is the key as it opens a new perspective in solar fuel generation as the oxidized electron donor (D^+) can be regenerated by a reduced electron acceptor species (A^-). The latter can be sourced from a second half-reaction, ideally, the light-driven oxygen evolution in

Figure 1. Batch water splitting. “A” is a recyclable electron acceptor that is reduced to oxidize water and “D” is a recyclable electron donor oxidized to reduce protons.

organic media^[22–26] and, in theory, both photo-systems will be “reset” by mixing the oil phases after photo-irradiation (*i.e.*, $D^+ + A^- \rightarrow D + A$). This concept has been termed “batch water-splitting” (Figure 1) and was discussed in more detail previously.^[27]

The key to success in a batch-water splitting arrangement is to ensure that D and A can (i) provide an efficient driving force for the photo-production of H_2 and O_2 , respectively, and (ii) be regenerated easily on mixing. In this regard, electron donors of higher (more positive) redox potentials are desirable, as weaker electron acceptors will be required to reset the photo-system. The use of metallocenes as a single molecule to replace the catalyst and sensitizer could offer an interesting alternative to state-of-the-art multi-component conventional systems.^[28]

Hydrogen production in a biphasic system by metallocenes was first established using decamethylferrocene ($[Cp^*_2Fe^{II}]$; $Cp^* = C_5Me_5$) without photo-activation.^[19] Thereafter, both osmocene ($[Cp_2Os^{II}]$, $Cp = C_5H_5$)^[29] and decamethylosmocene ($[Cp^*_2Os^{II}]$)^[20] have proved their capabilities to produce H_2 upon light irradiation. The hydrogen evolution rate can also be enhanced by functionalization of the liquid-liquid interface with solid catalysts.^[32–34] The formal redox potentials of metallocenes in DCE solvent are summarized in Figure 2. Some scattered works have also proposed the utilization of a single molecule to achieve the complex photocatalytic H_2 evolution process. For example, Cole-Hamilton^[35] reported H_2 photo-production from a platinum phosphine complex, while both Miller^[36] and Gray^[37] used iridium chloride complexes. Wang *et al.*^[38] reported an approach to photocatalytic H_2 evolution with diiron hydrides coupled to the reversible oxidation of ferrocenes to recycle the reaction. They stressed the importance of addressing the problem of using sacrificial electron donors and the role of metal hydrides in photochemical H_2 production. Furthermore, they also emphasize the lack of in-depth investigations on the photochemistry of metal hydrides.

We have previously described the photoproduction of hydrogen by $[Cp^*_2Ru^{II}]$ with the electrochemical recycling of the oxidized $[Cp^*_2Ru^{III}]^+$ product.^[18,28,39] Herein, we significantly advance our earlier work by investigating the photo-reduction of organic protons in a single organic phase. The multi-step photo-mechanism leading to H_2 evolution with $[Cp^*_2Ru^{II}]$ is fully elucidated using electrochemical, gas chromatographic (GC) and spectroscopic (UV/vis, 1H and ^{13}C NMR) experimental approaches, in corroboration with density functional theory (DFT) calculations. A comprehensive guide describing the influences of the nature of $[Cp^*_2Ru^{II}]$ itself (in comparison to similar experiments performed with $[Cp^*_2Os^{II}]$), the organic acid and the organic solvent on each step of the photo-generation of H_2 in acidified organic media is presented.

Results and Discussion

Electrochemical characterization of $[Cp^*_2Ru^{II}]$

Electrochemical characterization of $[Cp^*_2Ru^{II}]$ in DCE, a non-coordinating organic solvent^[40] favored for biphasic batch-water splitting applications, was performed to illustrate the electron donating ability of $[Cp^*_2Ru^{II}]$. Cyclic voltammograms (CVs) of $[Cp^*_2Ru^{II}]$ obtained at a glassy-carbon working electrode, with $TBAPF_6$ as the supporting electrolyte under anaerobic conditions (Figure 3, black CV), show a non-reversible Ru^{III}/Ru^{II} redox process with the formal redox potential for $[Cp^*_2Ru^{II}]$, $[E^{O'}_{[Cp^*_2Ru^{III}]/[Cp^*_2Ru^{II}]}]^{DCE}$, of 0.75 V *versus* the aqueous standard hydrogen electrode (SHE).^[31]

This result is in good agreement with our previous electrochemical characterization of $[Cp^*_2Ru^{II}]$ on an FTO electrode.^[28] Indeed, it has been shown that the oxidation

Figure 2. Formal redox potentials of various metallocenes and protons in DCE. The formal redox potentials of cobaltocene and ruthenocene were measured by cyclic voltammetry using a Pt electrode (25 μm in diameter), a silver wire as a quasi-reference electrode, and 5 mM bis(triphenylphosphoranyliden) ammonium tetrakis(pentafluorophenyl)borate (BATB) as supporting electrolyte, using ferrocene as an internal reference. The formal redox potentials of the other metallocenes were reported from literature data.^[20,28–31]

Figure 3. Cyclic voltammetry (CV) at 50 $\text{mV}\cdot\text{s}^{-1}$ of 0.5 mM $[\text{Cp}^*\text{Ru}^{\text{II}}]$ at a glassy carbon electrode immersed in a de-oxygenated solution of DCE containing 100 mM TBAPF_6 as supporting electrolyte. The large potential window (black line) shows the irreversible oxidation of Ru^{III} species to Ru^{IV} at 1.81 V leading to the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ reduction peak current on the reverse scan (i_{pc}) being significantly smaller than the oxidation peak current (i_{pa}) at 0.75 V. Limiting the potential window (red line) gives rise to $i_{\text{pa}} / i_{\text{pc}} = 1$ for $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ redox process. CVs were obtained under anaerobic conditions at ambient temperatures using silver and platinum wires as the reference and counter electrodes, respectively. CVs were calibrated *versus* the standard reduction potential of $[\text{Cp}^*\text{Ru}^{\text{II}}]$ in DCE on the SHE scale ($[E^\circ_{[\text{Cp}^*\text{2FeIII}]/[\text{Cp}^*\text{2FeII}]}]^{\text{DCE}} = 0.04 \text{ V vs. SHE}$).^[30]

proceeds by a reversible $1 e^-$ process in the presence of weakly coordinating solvent and anions.^[41–43] Further oxidation of the Ru^{III} species to Ru^{IV} at 1.81 V vs. SHE was irreversible. The reduction peak current on the reverse scan (i_{pc}) being significantly smaller than the oxidation peak current (i_{pa}) for the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ redox transition points to a chemical reaction coupled to the generation of the Ru^{IV} species. The reversible nature of the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ redox transition was confirmed by limiting the potential window to exclude the irreversible process at 1.81 V vs. SHE and observing that $i_{\text{pa}} / i_{\text{pc}} = 1$ under these experimental conditions (Figure 3, red CVs). Furthermore, two very small irreversible

reduction peaks were observed at potentials more negative than the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ redox potential and attributed to products of the overoxidized species, as these peaks were absent when the potential sweep was reversed before the oxidation of Ru^{III} (not shown).

Photo-generation of H_2 from acidified 1,2-dichloroethane using $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$

Considering that the formal redox potential for the reduction of protons to H_2 ($[E^{\text{O}'}_{\text{H}^+/\frac{1}{2}\text{H}_2}]^{\text{DCE}}$) is 0.55 V vs. SHE,^[44] $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ is thermodynamically not capable of evolving H_2 in the dark, as previously observed for $[\text{Cp}_2\text{Os}^{\text{II}}]$.^[20,29] Preliminary headspace GC analysis for the reaction between $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ and $[\text{H}(\text{OEt}_2)_2]\text{TB}$ under white light illumination, yielded considerable H_2 evolution after 2 hours (Figure 4A, red trace).^[28] The photo-production of H_2 under anaerobic conditions was confirmed by the absence of any measurable H_2 gas in a control experiment (in the dark, Figure 4A, black trace). Furthermore, no reaction takes place in the absence of $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$. Interestingly, monitoring the photo-production of H_2 as a function of illumination time (up to 4 hours) revealed that *ca.* 4 μmol of H_2 were evolved in the presence of an equimolar number of protons (Figure 4B). This represents a 200 % yield of H_2 based on the initial assumption that $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ would act as a 1 e^- donor, as previously observed, in the dark, for $[\text{Cp}_2^*\text{Fe}^{\text{II}}]$ in the presence of a suitable H_2 evolution catalyst.^[28,30,45–49] These initial GC experiments invited further in-depth mechanistic studies to fully elucidate the underlying factors leading to the $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ molecule seemingly acting as a 2 e^- donor.

Figure 4. Production of H_2 gas from solutions of $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ dissolved in DCE as a function of organic proton concentrations and light irradiation time. **(A)** Gas chromatograms of the headspace of a septum-sealed stirring solution of 4 μmol $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ and excess organic protons (16 μmol

[H(OEt₂)₂]TB; 4 equivalents) dissolved in DCE under anaerobic conditions with (red trace) and without (black trace) irradiation by a 500 W Xe lamp. **(B)** Summary of the quantities of H₂ gas evolved (μmol) in the presence of various equivalents of organic protons (0, 2, 4, 8, and 16 μmol [H(OEt₂)₂]TB) as a function of irradiation time by a 500 W Xe lamp. The horizontal lines represent the theoretical % yields assuming that [Cp*₂Ru^{II}] would act as a 1 e⁻ donor and react with organic protons in a stoichiometric 1:1 ratio.

Multi-step mechanism for the photo-generation of H₂ from acidified organic solutions containing [Cp*₂Ru^{II}]

A large body of work has emanated from the A. N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russian Federation) over the past 30 years on the organometallic chemistry of metallocenes, especially decamethylmetallocenes,^[50–57] including the UV photolysis of [Cp*₂Ru^{II}] in strong acidic solutions.^[58,59] The main focus of these previous studies was the synthesis and characterization of cationic derivatives of [Cp*₂Ru^{II}], especially with regard to the stabilization of up to three carbocationic sites (CH₂⁺) on the cyclopentadienyl rings by a single ruthenium metal atom^[54,55] and the reactivity of these cations towards strong nucleophiles.^[56,57] The proposed mechanism was divided into three steps: Ru^{IV} hydride formation in the dark (eq. (1)), generation of a transient Ru^{III} cationic intermediate (eq. (2)), and the breakdown of the latter to a cationic tuck-in Ru^{IV} species (eq. (3)) that contains a stabilized CH₂⁺ site.

The net reaction results in the generation of a single H₂ molecule per [Cp*₂Ru^{II}] in solution as one proton comes from the organic acid and another from a methyl-group on one of the cyclopentadienyl rings (eq. (4)).

While these earlier studies provided key clues to predict the behavior of photo-activated [Cp*₂Ru^{II}] in acidic organic media, we used alternative experimental characterization techniques, especially (spectro)electrochemistry and GC, and corroborate the present experimental findings with DFT calculations. Thus, we focus our attention on: (i) quantitative analytical determination of H₂ gas evolved (typically considered a by-product in previous studies), (ii) determining the possible factors that influence hydride formation (eq. (1)), from the Brønsted basicity of [Cp*₂Ru^{II}] to the choice of acid, and (iii) provide new mechanistic insights by kinetic investigations thanks to the stabilization of the transient [Cp*₂Ru^{III}]⁺ (eq. (2) and (3)).^[28]

Factors influencing hydride formation in the dark

The first step in the mechanism of H₂ evolution in acidified organic solutions with any metallocene, either light-activated or not, is the protonation of the metal center to form the cationic hydride in the dark,^[60] as described for [Cp*₂Ru^{II}] by eq. (1). The protonation reaction is followed by an internal electron transfer to form a hydride.^[61–63] The basicity of the metal has to be sufficient to allow the coordination to a proton, but at the same time, the formed bond should not be too strong as to hamper the elimination of H₂. Moreover, the Brønsted basicity of [Cp*₂Ru^{II}] is of particular importance for the design of catalytic H₂ evolution processes, as it provides thermodynamic information for rationally choosing the acid source. Thus, the strength of the organic acid is a crucial factor when designing experiments to accurately determine the maximum yields of H₂ gas evolved per [Cp*₂Ru^{II}] molecule present. Ideally, a strong organic acid that reacts in a 1:1 ratio with [Cp*₂Ru^{II}] to facilitate 100 % conversion to [Cp*₂Ru^{IV}(H)]⁺ was desirable in order to remove any ambiguity as to whether all of the [Cp*₂Ru^{II}] present is converted to [Cp*₂Ru^{IV}(H)]⁺ and preclude an underestimation of the maximum possible experimental yields of H₂ gas.

¹H NMR spectroscopy may be used to monitor the conversion of [Cp*₂Ru^{II}] to [Cp*₂Ru^{IV}(H)]⁺. ¹H NMR spectra were obtained in deuterated dichloromethane (DCM-d₂) using DCE (31.2 mM) as an internal standard, in the dark, at ambient temperatures and under anaerobic conditions. The similarities of the two solvents, DCM-d₂ and DCE, in terms of being non-coordinating, with similar dielectric constants are such that the trends seen by NMR in DCM-d₂ were expected to accurately reflect the processes that occur in DCE under otherwise identical experimental conditions. The ¹H NMR spectrum of pristine [Cp*₂Ru^{II}] obtained prior to the addition of organic acid shows a characteristic singlet at 1.62 ppm (Figure S3(A), Section 2, SI), in agreement with previous reports.^[28,58,60] The conversion of [Cp*₂Ru^{II}] to [Cp*₂Ru^{IV}(H)]⁺, was followed in a previous study by ¹H NMR.^[28] Briefly, the spectrum of [Cp*₂Ru^{IV}(H)]⁺ shows a singlet peak at –8.38 ppm corresponding to the metal bond hydride (Figure S3(B), Section 2, SI). In addition, the signal for the protons of the methyl groups on each cyclopentadienyl ring is shifted positively to 1.83 ppm. Herein, the ¹H NMR spectrum of [Cp*₂Ru^{IV}(H)]⁺ produced from [H(OEt₂)₂]TB was compared with the spectra generated by two other acids. Thus, spectra obtained *in situ* with either excess CF₃SO₃H (Figure S3(C), Section 2, SI) or CF₃CO₂H (Figure S3(D), Section 2, SI), are in close, but not perfect, agreement with those generated by [H(OEt₂)₂]TB. These slight discrepancies are related to the influence of the different organic counter-anions in solution.^[58,60]

Determining the extent of conversion of [Cp*₂Ru^{II}] to [Cp*₂Ru^{IV}(H)]⁺ was possible by monitoring the positive shift in the signal for the protons of the methyl groups on the cyclopentadienyl ring (Figure 5) and the appearance of the signal corresponding to the hydride (Figure S4, Section 2, SI) as a function of increasing concentrations of organic acid. In this manner, it was clearly demonstrated that [H(OEt₂)₂]TB and CF₃SO₃H (pK_a = –11.4 in DCE relative to picric acid)^[64,65] are sufficiently strong acids in DCE that one equivalent of acid was adequate to fully convert [Cp*₂Ru^{II}] into [Cp*₂Ru^{IV}(H)]⁺. Meanwhile, 10 equivalents of CF₃CO₂H were required to achieve full conversion (Figure 5).

Figure 5. Identifying strong organic acids capable of stoichiometrically protonating the relatively weak Brønsted base $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ to form the cationic hydride species. The efficiency of conversion of $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ (15 mM) to $[\text{Cp}_2^*\text{Ru}^{\text{IV}}(\text{H})]^+$, in terms of the number of equivalents of acid required to achieve 100 % conversion, was monitored by ^1H NMR spectroscopy of the hydrogen of the methyl groups in the presence of the organic acids (A) $\text{CF}_3\text{CO}_2\text{H}$, (B) $\text{CF}_3\text{SO}_3\text{H}$ and (C) $[\text{H}(\text{OEt}_2)_2]\text{TB}$. The raw NMR data as a function of increasing organic acid concentration is illustrated on the right and outlines the disappearance of the characteristic signal for the protons of the methyl groups on each cyclopentadienyl ring for $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ (blue circles; $\delta = 1.62$ ppm) and the concurrent appearance at more positive chemical shift values (orange inverted triangles; $\delta = 1.85$ ppm) of the equivalent protons for $[\text{Cp}_2^*\text{Ru}^{\text{IV}}(\text{H})]^+$. ^1H NMR spectra were obtained in deuterated dichloromethane ($\text{DCM}-d_2$) solvent using DCE (31.2 mM) as an internal standard, in the dark and under anaerobic conditions. The ^1H NMR spectra outlining the appearance of the signal corresponding to the hydridic proton (green square) at a characteristic negative value of -8.38 ppm for the experiments outlined here are presented in Figure S4, Section 2, SI.

To further aid the rational design of the HER involving $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$, the $\text{p}K_a$ of $[\text{Cp}_2^*\text{Ru}^{\text{IV}}(\text{H})]^+$ in DCE was investigated by measurement of the proton-transfer equilibria between $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ and $\text{CF}_3\text{SO}_3\text{H}$ in acetonitrile to limit the ion association impact. All the results and details are provided in Section 3, SI. The equilibrium constant for the protonation reaction was estimated to be smaller than 2×10^{-8} mol L^{-1} and the $\text{p}K_a$ value is higher than 7.69. Finally, the Gibbs free energy was estimated as being more negative than -43 kJ $\cdot\text{mol}^{-1}$ in DCE.

A ^1H NMR study of a mixture of $[\text{Cp}_2^*\text{Ru}^{\text{IV}}(\text{H})]^+$ with trityl cation (Ph_3C^+)^[66] was performed to assess the hydricity of the complex (Figures S8 and S9, Section 4, SI). The product of the reaction was the tuck-in complex $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$. We believe that the abstraction of the hydride leads to the very acidic and unstable $[\text{Cp}^*_2\text{Ru}]^{2+}$ which immediately converts to the tuck-in complex upon release

of a proton. The instability of $[\text{Cp}^*_2\text{Ru}]^{2+}$ would explain the irreversibility of the process observed by cyclic voltammetry at 1.81 V vs. SHE (Figure 3).

Additionally, to date, $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ has only been generated transiently *in situ*. $[\text{Cp}^*_2\text{Os}^{\text{IV}}(\text{H})]^+$ on the other hand is an isolable species.^[60] Photo-irradiation of pre-synthesized $[\text{Cp}^*_2\text{Os}^{\text{IV}}(\text{H})]^+$ in DCM-d2 led to high yields of the final product $[\text{Cp}^*\text{Os}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$.^[58]

Finally, $[\text{H}(\text{OEt}_2)_2]\text{TB}$ and $\text{CF}_3\text{SO}_3\text{H}$ are both sufficiently strong acids to generate $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ in a stoichiometric 1:1 fashion. However, in order to facilitate the batch-water splitting process, $[\text{H}(\text{OEt}_2)_2]\text{TB}$ was chosen as the organic acid for all subsequent mechanistic studies, in part due to its additional advantage of being a particularly poor nucleophile^[67] allowing the stabilization of the $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ intermediate species, for example, towards its electrochemical or chemical regeneration *via* the OER.^[28]

Kinetic analysis of the transient $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ species

Previously we have reported the *in situ* generation of cationic $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ species during irradiation of $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ in the UV or near-UV range in acidified organic solutions (eq. (2)).^[28] Indeed, we overcame the high instability and very short lifetime of the $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ intermediate by using weakly coordinating organic solvent (*e.g.* DCE) and supporting electrolyte anions (*e.g.* TB⁻). This allowed us to prevent the breakdown of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ to $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ and to determine the spectroscopic characteristics of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$; namely an absorbance band at 500 nm corresponding to a molar extinction coefficient of $960 \text{ M}^{-1}\cdot\text{cm}^{-1}$. Therefore, the clear identification of the UV/vis absorbance peak of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ in DCE provided an opportunity to study the formation of this intermediate *in situ* during irradiation of acidified DCE solutions of $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$. Details of the actual UV/vis spectra are shown in Figure S10, Section 5, SI. $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ and $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ do not absorb in the range of the absorption of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$.^[28] Therefore, the presence of these species did not interfere with our interpretation of the UV/vis data obtained.

In the absence of $[\text{H}(\text{OEt}_2)_2]\text{TB}$, and hence $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$, no significant changes of the UV/vis spectra were observed. With increased illumination time, some increase in the absorbance between 300 and 400 nm did occur, indicating that $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ may decompose to a certain extent with prolonged exposure to white light. When $[\text{H}(\text{OEt}_2)_2]\text{TB}$ was the limiting reagent (0.5 and 1 equivalent), under illumination, fast decomposition of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ occurred with the clear absorbance peak at 500 nm quickly giving way to a series of ill-defined absorbance bands. The latter suggests that the compound decomposes under light illumination and in the absence of protons. Finally, in the presence of an excess of $[\text{H}(\text{OEt}_2)_2]\text{TB}$ (2 and 4 equivalents), a clear initial increase of the absorbance at 500 nm was observed during the early stages of the reaction. After a certain period of time, approximately 50 min., the maximum absorbance was reached and the reaction proceeded accompanied by a gradual decrease of the band at 500 nm. Two isosbestic points were observed at 460 and 557 nm, and after 4 hours of illumination, a significant absorbance below 400 nm and a broad band at 450 nm were indicative of the presence of the final product of the reaction, identified as $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ *vide infra* (Figure S10, Section 5, SI; 2 and 4 equivalents).

The initial rates were used to determine the kinetics of the disappearance of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$, generated *in situ* in the dark in a de-oxygenated DCE solution containing excess $[\text{H}(\text{OEt}_2)_2]\text{TB}$ under anaerobic conditions, and on illumination with white light. To achieve this, the rate of change of the absorbance at $\lambda_{\text{max}} = 500 \text{ nm}$, corresponding to the concentration of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ generated by reaction of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ as described in eq. (2), was monitored with spectra taken every 10 s. Thus,

$$v = \frac{d\left(c_{[\text{Cp}_2^*\text{Ru}^{\text{III}}(\text{H})]^+}\right)}{dt} = k_{app} \left(c_{[\text{Cp}_2^*\text{Ru}^{\text{IV}}(\text{H})]^+}\right)^n \quad (5)$$

where k_{app} is the apparent rate constant of the reaction and n is reaction order.^[21]

Experiments were performed with various initial concentrations of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$, in the range of 1.4 to 2.8 mM, while keeping the $[\text{H}(\text{OEt}_2)_2]\text{TB}$ concentration in significant excess

Figure 6. Comparison of the experimentally observed kinetics of the disappearance of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ with the theoretical rate law for a first-order reaction with an apparent rate constant of $1.7 \times 10^{-4} \text{ s}^{-1}$ (dashed red lines). The disappearance of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ was determined by monitoring the appearance of the UV/vis absorbance peak corresponding to the reaction product $[\text{Cp}_2^*\text{Ru}^{\text{III}}]^+$ at $\lambda_{\text{max}} = 500 \text{ nm}$ upon commencing irradiation of the organic DCE solution with white light (see eq. (2)). The initial concentrations of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ present were 1.40 (black circles), 2.34 (blue triangles), 2.55 (green squares) and 2.81 (grey diamonds) mM. The organic acid $[\text{H}(\text{OEt}_2)_2]\text{TB}$ was present in excess at 42.20 mM in each experiment. Inset: Reaction order and rate constant determination with respect to $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ in the presence of excess protons: plot of $\ln(v)$ vs. $\ln(c_{[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+})$; the initial rate (v , $\text{mM} \cdot \text{s}^{-1}$) was determined for each starting concentration of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ as shown in Figure S11, Section 5, SI.

(42.2 mM), see Figure 6. First, the initial rate (v , $\text{mM} \cdot \text{s}^{-1}$) of the reaction described by eq. (2) was determined for each starting concentration of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ from the slopes of a plot of $c[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ versus time (Figure S11, Section 5, SI).

Next, the reaction order n and k_{app} were determined by plotting $\ln(v)$ vs $\ln([[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+])$, Figure 6 (inset). The slope indicated that the reaction was first order with respect to $c[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ and k_{app} was determined from the intercept (*i.e.*, $\ln(k_{app})$), as $1.7 \times 10^{-4} \text{ s}^{-1}$. This calculated value of k_{app} was used to determine the theoretical first order decrease in the concentration of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ as a function of illumination time (dashed red lines, Figure S11, Section 5, SI), with the integrated rate law for a first order reaction.

Finally, to highlight the excellent match between theory and experimental data for the initial rates of reaction, the experimental kinetic data was re-plotted on a logarithmic scale versus the theoretically derived data in Figure S12, Section 5, SI, thereby confirming that the assumed rate equations correspond with the experimental data. From the first order of the reaction, one can conclude that a bimolecular homolytic pathway (*i.e.* the equivalent

of a Tafel electrode reaction) where two $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ would react to release H_2 , as described in eq. (6), is excluded.

However, it can be envisaged that $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^{+,*}$ reacts with $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ to form 2 equivalents of $[\text{Cp}_2^*\text{Ru}^{\text{III}}]^+$ as described in eq. (7).

This reaction would also appear as first order due to the short-lived excited state and the low relative percentage of the complex in the excited state compared to the ground state. It would be in line with the studies of Miller and co-workers.^[61] They have established that a similar complex $[\text{Cp}^*\text{Ir}(\text{bpy})\text{H}]^+$ undergoes electron transfer with a ground state hydride to generate a transient pair of Ir(II) and Ir(IV) hydrides that react in a bimetallic fashion to release H_2 .

Otherwise, the equivalent of a Heyrovsky electrode reaction, consisting of a proton directly reacting with excited $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^{+,*}$ as described in eq. (8), is envisaged.

Both pathways are consistent with spectroscopic characterizations of the photoactivity of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$, corroborated with computed data, that excitation of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ is dominated by one main transition which induces an electronic enrichment on the hydride position after excitation.^[28]

We have concluded from the reaction of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ with trityl cation that $[\text{Cp}^*_2\text{Ru}^{\text{IV}}]^{2+}$ would quickly reorganize with the elimination of a proton to form the stable tuck-in complex $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ as described in eq. (9). The excess of $[\text{H}(\text{OEt}_2)_2]\text{TB}$ may slow down this reaction to allow for the formation of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ identified by UV/vis.

Reduction of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}]^{2+}$ to the $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ could be explained by a comproportionation reaction with $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ as shown in eq. (10).

However, as this reaction should also be inhibited by excess acid, it is questionable whether reaction (10) would be faster than reaction (9). Therefore, reaction 7 would be the most likely pathway.

Due to solubility constraints, it was not possible to add $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ in excess to determine the partial H^+ order. Nevertheless, the influence of the number of equivalents of $[\text{H}(\text{OEt}_2)_2]\text{TB}$ present relative to the initial concentration of $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ in solution on the observed absorbance at 500 nm as a function of illumination time is shown in Figure 7. As noted earlier, details of the actual UV/vis spectra are shown in Figure S10, Section 5, SI. Interestingly, although the maximum absorbance at 500 nm was reached after near identical periods of illumination time with both 2 and 4 equivalents of $[\text{H}(\text{OEt}_2)_2]\text{TB}$ present, the maximum magnitude of absorbance was greater for 2 equivalents which is in agreement with further reaction of the $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ to generate H_2 (*vide infra*). Additionally, the influence of the initial proton concentration was investigated by keeping the $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ concentration constant, as shown in Figure S13, Section 5, SI. Similarly, the initial rate of the reaction decreased as the H^+ concentration increased.

Figure 7. Plots of the absorbance at 500 nm versus time for UV/vis spectra taken during the generation and subsequent breakdown of the reaction intermediate $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ upon irradiating an acidified organic solution of $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ with white light. The influence of the number of equivalents of the strong organic acid $[\text{H}(\text{OEt}_2)_2]\text{TB}$ on the evolution of the UV/vis spectra was monitored for solutions of $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ (1.875 mM) in DCE subjected to white light illumination by a 500 W Xe lamp. UV/vis spectra were taken every minute under anaerobic conditions (Figure S10, Section 5, SI).

Further spectroscopic experiments were performed to study the HER by $[\text{Cp}^*_2\text{Ru}^{\text{II}}]$ at various light intensities (Figure S13, Section 5, SI). The quantities of H_2 and $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ produced show a linear dependence on the irradiation. These trends exclude the involvement of two-photon excitation processes in the H_2 elimination path described by eq. (6). Indeed, a quadratic dependence would have been observed for a two excitation process.^[68] As the experiments were performed outside the glove box, the cell was slightly contaminated by atmospheric O_2 (visible by GC). Thus, a higher quantity of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ (0.3 μmol) was observed due to the reduction of O_2 upon laser irradiation (O_2 reduction is thermodynamically more favourable than proton reduction) as observed previously.^[28,44] In Figure S14, Section 5, SI, 0.3 μmol of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ were subtracted and the result shows a perfect fitting between H_2 and $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ production.

Identification of the final photo-product as $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$

Briefly, the photo-irradiation of $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{H})]^+$ in acidified solutions (eq. (4)) was monitored by ^1H NMR spectroscopy, complementing the earlier GC experiments for this reaction where significant H_2 was detected (see Figure 4). The goal of these ^1H NMR experiments was to unambiguously identify the final form of the metallocene after photo-irradiation in acidified organic solutions. After 360 min. of illumination the signals characteristic of $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{H})]^+$ (Figure S3(B), Section 2, SI) disappeared, to be replaced by new ^1H NMR signals (Figure S15, Section 6, SI). After further purification by column chromatography (details in Section 1, SI), the formed product was unambiguously identified as $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ by ^1H and ^{13}C and DEPT-135 NMR analysis, in agreement with previous studies (Figures S16 and 17, Section 6, SI).^[58]

A UV/vis spectrum of $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ revealed a significant absorbance below 400 nm and a broad band at 450 nm (Figure S18, Section 6, SI). The latter is in agreement with the spectra shown in Figure S10, Section 5, SI, where solutions of $[\text{Cp}^*\text{Ru}^{\text{II}}]$ in the presence of excess $[\text{H}(\text{OEt}_2)_2]\text{TB}$ (2 and 4 equivalents) were illuminated, leading to the fast decomposition of $[\text{Cp}^*\text{Ru}^{\text{III}}]^+$ to $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$.

The second release of H_2 from the transient $[\text{Cp}^*\text{Ru}^{\text{III}}]^+$ species

The intermediate $[\text{Cp}^*\text{Ru}^{\text{III}}]^+$ species, previously unattainable due to its instability in the presence of slightly nucleophilic counter-anions, was synthesized by bulk electrolysis in DCE as described in our previous work.^[28] Solutions of $[\text{Cp}^*\text{Ru}^{\text{III}}]^+$ were subsequently illuminated in the presence of protons to investigate if H_2 could be produced from $[\text{Cp}^*\text{Ru}^{\text{III}}]^+$ as the initial form of the metallocene present. Indeed, H_2 was evolved and detected by GC with illumination in the presence of acid (Figure S19, Section 7, SI).

The major final product of the reaction is the tuck-in complex $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$. The mechanism involved is difficult to assess since $[\text{Cp}^*\text{Ru}^{\text{III}}]^+$ and $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ absorb at the same wavelength. One possible pathway is the formation of a Ru^{IV} /hydrogen complex $[\text{Cp}^*\text{Ru}^{\text{IV}}\text{H}]^+$ that can further evolve hydrogen via a photo-excited bimolecular pathway (eq. (11)).

The energy balance of the system

The proposed system is able to store 0.75 V per electron, as illustrated in Fig. 3 (formal potential of the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ species on the standard hydrogen scale). Illumination using photons at the wavelength of 243 nm (corresponding to *ca.* 5 eV of energy) results in a quantum yield of 25%, while photons of 365 nm (corresponding to *ca.* 3.4 eV) result in a quantum yield of *ca.* 5 %.^[28] Therefore, the energy efficiency of the system can be roughly estimated as *ca.* 4 % for 243 nm and 1.1 % for 365 nm. It is evident that utilization of higher wavelengths as well as improvement of the quantum yield is necessary to obtain a performance on par with the state-of-the-art solar hydrogen production systems.

DFT calculations

DFT calculations were performed to gain insights into the energetics of the different reaction steps (see Figure 8). It has to be stressed that the counter-anion TB^- was not taken into account in the computation, although it certainly has a strong influence on the reaction energies as it stabilizes the charged complexes. However, the size of the TB^- , as well as the steric hindrance of the metal

complex itself, prevent strong interactions between the metal and the counter-ion. For this reason, TB^- , which was not included in the computational model, should not qualitatively change the observed trends in reaction energies. Therefore, the computed results were in reasonable agreement with phenomena observed experimentally for the production of H_2 by $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$. For instance, in agreement with experimental observations, the formation of $[\text{Cp}_2^*\text{Ru}^{\text{IV}}(\text{H})]^+$ from $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ and $\text{CF}_3\text{SO}_3\text{H}$ is spontaneous in DCE at the PBE0-dDsC. The computed Gibbs energy of association was found to be $\Delta G_{\text{H}^+}^0, \text{DFT} = -70 \text{ kJ}\cdot\text{mol}^{-1}$, while the experimental estimation showing that the $\Delta G < -43 \text{ kJ}\cdot\text{mol}^{-1}$ are in relatively good agreement with the DFT prediction. Calculations also corroborate that the first step associated with H_2 release (eq. (2)), leading to $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$, is endergonic ($\Delta G^0 = 108 \text{ kJ}\cdot\text{mol}^{-1}$) in the ground state. It was found experimentally that the process only occurs if the reactants were excited by light, or in the presence of CF_3SO_3^- . While the explicit interactions between the conjugated base and $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ may play a crucial role in the second reaction, leading to the formation of the $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ species, these subtle effects were not accounted for computationally. Computational data show a pairing of spins energetically more favorable than the formation of unpaired electrons which is consistent with the formation of diamagnetic $[\text{Cp}_2^*\text{Ru}^{\text{IV}}\text{H}]^+$ and $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ complexes. However, results do not exclude the formation of diamagnetic metal $\cdots(\eta\text{-H})_2\cdots$ metal and metal $\cdots(\eta\text{-CH}_2)_2\cdots$ metal bond dimers including metals with opposite spin-momentum. The computed UV/vis spectrum of $[\text{Cp}^*_2\text{Ru}^{\text{III}}]^+$ shows a maximum absorbance peak around 420 nm at the $\omega\text{B97X-D/def2-TZVP}$ level but similar trends are obtained using other functionals, *e.g.*, PBE0/def2-TZVP (Figure S20, Section 8, SI). While the $\omega\text{B97X-D}$ absorption is commonly blue shifted as compared to experimental values, the large magnitude of the present shift (0.47 eV) once more suggests a strong interaction with the environment. This would be consistent with the metal to ligand electron transfer character of the transition. The difference may be explained by the strong influence of the counter ion which was not taken into account. The

Figure 8. (Top) Schematic representation of the computed Gibbs energy involved in the photo-production of H_2 by $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ in DCE. (Bottom) Density difference $\Delta\rho = \text{excited state} - \text{ground state}$ density of $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ for the main transition at 426 nm at the PBE0/TZP level; $\Delta\rho = -0.001$ (red), $\Delta\rho = +0.001$ (blue).

second H_2 release (eq. (3)) forming the final product $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ is thermoneutral ($-4 \text{ kJ}\cdot\text{mol}^{-1}$).

Conclusions

Herein, we investigate the mechanism of the photo-production of H_2 by $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ in the presence of protons. Two mechanisms coexist depending on the proton concentration. In the presence of sub-stoichiometric amounts of proton, the reaction of $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ with a proton from a methyl group of the cyclopentadienyl ring is favored, producing the tuck-in complex $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$. At higher acid concentrations, reaction of the photoactivated $[\text{Cp}^*_2\text{Ru}^{\text{IV}}(\text{H})]^+$ with external protons is favored, yielding the instable $[\text{Cp}^*_2\text{Ru}^{\text{IV}}]^{2+}$ which can either rearrange to form $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$ upon a proton release or be reduced generating the $[\text{Cp}_2^*\text{Ru}^{\text{III}}]^+$ intermediate. The hydrogen evolution process was monitored by gas chromatography, ^1H and ^{13}C NMR and UV/vis spectroscopies. Subsequent DFT computations corroborate the experimental results. The first photo-reaction is first order with respect to the concentration of $[\text{Cp}_2^*\text{Ru}^{\text{IV}}(\text{H})]^+$ ($k_{\text{app.}} = 1.7 \cdot 10^{-4} \text{ s}^{-1}$). Therefore, we exclude the occurrence of a homolytic bimolecular pathway as the results strongly indicate that a heterolytic reaction with one-photon excitation taking place.

The $[\text{Cp}_2^*\text{Ru}^{\text{III}}]^+$ intermediate is capable of further generating H_2 when illuminated, but only in the presence of protons. The final form of the metallocene was identified as $[\text{Cp}^*\text{Ru}^{\text{IV}}(\text{C}_5\text{Me}_4\text{CH}_2)]^+$.

Although DFT computations do not take into account the counter ion, the theoretical results are in good agreement with the experimental data. The protonation is also spontaneous ($\Delta G^0_{\text{H}^+} = -70$

$\text{kJ}\cdot\text{mol}^{-1}$, $\Delta G_{\text{H}^+, \text{Exp}}^0 < -43 \text{ kJ}\cdot\text{mol}^{-1}$) while the first oxidation step requires an input of energy to occur and the second is thermoneutral (108 and $-4 \text{ kJ}\cdot\text{mol}^{-1}$, respectively).

This study represents a step forward in the development of the batch water-splitting process as it overcomes the use of sacrificial electron donors, generates a stable oxidized product that can be easily reduced and therefore recycled, and can operate in biphasic conditions for water splitting. Thus, $[\text{Cp}_2^*\text{Ru}^{\text{II}}]$ coupled with an OER catalyst such as BiVO_4 ,^[22–24] already studied at soft interfaces, represents an attractive alternative to photo-produce H_2 fuel. Importantly, these investigations represent major progress in the general understanding of the photo-production of H_2 by metallocenes through resolution of the mechanism involved.

Experimental Section

Chemicals. All chemicals were used as received without further purification. All aqueous solutions were prepared with ultrapure water (Millipore Milli-Q, specific resistivity $18.2 \text{ M}\Omega\cdot\text{cm}$). The solvents used were 1,2-dichloroethane (DCE, $\geq 99.8 \%$, Fluka), deuterated dichloromethane (DCM-d_2 , 99.8+ atom % D, Merck), deuterated acetonitrile (MeCN-d_3 , 99.8+ atom % D, Merck), hydrochloric acid (HCl , 37 %, Merck) and sulfuric acid (H_2SO_4 , 98 %, Merck). Decamethylruthenocene ($\text{Cp}_2^*\text{Ru}^{\text{II}}$, 99 %) was supplied by ABCR and stored in a N_2 -filled glove-box until use. Ferrocenium hexafluorophosphate ($[\text{Cp}_2^*\text{Fe}^{\text{III}}]\text{PF}_6$, 97%), trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$, 98 %), trifluoroacetic acid ($\text{CF}_3\text{CO}_2\text{H}$, $\geq 99.0 \%$), tetrabutylammonium hexafluorophosphate (TBAPF_6 , $\geq 99.0 \%$) and dichloromethane (DCM , 99.9 %) were obtained from Sigma-Aldrich. Bis(triphenylphosphoranylidene)ammonium chloride (BACl , 98%) was purchased from Fluka. Lithium tetrakis-(pentafluorophenyl)borate ethyl etherate ($\text{Li}(\text{OEt}_2)_2\text{TB}$ purum) was purchased from Boulder Scientific. Bis(triphenyl-phosphoranylidene) ammonium tetrakis(penta-fluorophenyl)borate (BATB) was prepared by metathesis, as described previously.^[69]

Computational details. Geometries were optimized in the gas phase at the M06/def2-TZVP level,^[70–72] using an ultrafine grid for numerical integrations in Gaussian09.^[73] For Ru the LanL2DZ effective core potential^[74] was used. Single point energies were computed using the dispersion corrected hybrid PBE0-dDsC and a TZ2P basis set^[75–79] in the ADF package.^[80] Solvent effects were accounted for the frozen gas phase geometries using the COSMO-RS model^[81] (relative permittivity $\epsilon_r = 10.125$ for DCE). All spin multiplicities were computed to ensure lowest ground state electronic configuration. All the stationary points were verified by analytic computation of vibrational frequencies that were also used for the zero point energies and 298 K thermal contributions to the Gibbs free energy, using the usual rigid-rotator harmonic oscillator approximation. The low-lying excited state of $[\text{Cp}_2^*\text{Ru}^{\text{III}}]^+$ was obtained using the time dependent density functional theory (TDDFT) formalism^[82] at the $\omega\text{B97X-D/def2-TZVP}$ level^[83] and a LanL2DZ pseudopotential on Ru. Solvation effects on excitation energies were accounted using the SMD model^[84] for DCE in Gaussian09.

Additional experimental details are summarized in Section 1, SI.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: decamethylruthenocene • hydrogen evolution reaction • metallocenes • photoactivation • mechanism

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