



PERSPECTIVE

Photochemical water splitting via transition metal complexes

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ABSTRACT

Photochemical water splitting by transition metal complexes provides a new approach to the production of hydrogen as a clean and sustainable energy carrier. Several selected systems are analyzed, and the two basic half reactions in the water splitting process which generates hydrogen and the compound of water oxidation (oxygen or hydrogen peroxide) are presented. Finally, a system designed for photochemical water splitting, based on the radical and organometallic chemistry of titanocene(III), is postulated.

1. Introduction

In 2019, the International Energy Agency (IEA) predicted that global energy demand will increase between 25 % and 30 % by 2040 [1], which within a social development context, dependent on oil, gas and carbon, would mean more CO₂ emissions, accelerating climate change. In order to avoid further environmental impact, this increase should come from clean energies only. Of these energies, green hydrogen (hydrogen made without the use of fossil resources) is a fuel that could help bring the world to net zero emissions, since the combination of hydrogen and oxygen is an energetically favorable reaction [2], which produces green energy, only emits water vapor and leaves no residue in the atmosphere. Furthermore, its impressive gravimetric energy density makes it a valuable compound for energy applications [3]. The most economically viable generation of green hydrogen relies on the electrolysis of water [4,5], where an electric current is passed through water to complete the water splitting reaction. The electricity used normally comes from renewable sources. However, in the last decade, the photochemical activation of water and splitting by transition metal complexes to produce O₂ and H₂ has become a promising way for the generation of clean energy. This process, unlike photochemical water splitting via transition metal oxides [6], although is currently at various early stages of research, offers long-term potential for environmentally friendly H₂ generation.

As future developments in photochemical water splitting catalyzed by transition metals will contribute to the improvement of a sustainable and environmentally compatible energy model, here we offer a personal perspective that critically analyzes selected recent approaches in the

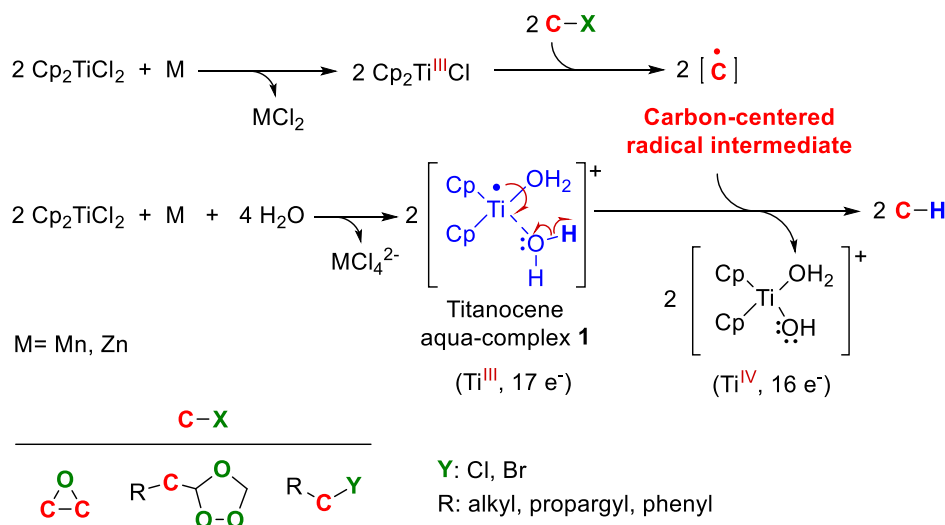
field of organometallic complexes that can split water photochemically into H₂ and an oxidized water equivalent, and also a brief comment on our own research, which may create opportunities that contribute to designing a new route for the production of green hydrogen from water. This article is not a comprehensive review of the field, and we apologize to all researchers whose papers are not included. We hope that this perspective will provide a useful guide for chemical engineers and chemists in developing systems that can promote light-driven water splitting in a fully closed catalytic cycle. This article is subdivided into two main sections: (1) selected photochemical water splitting using a transition-metal complex, and (2) a personal perspective on this field.

2. Selected organometallic complexes that photochemically split water

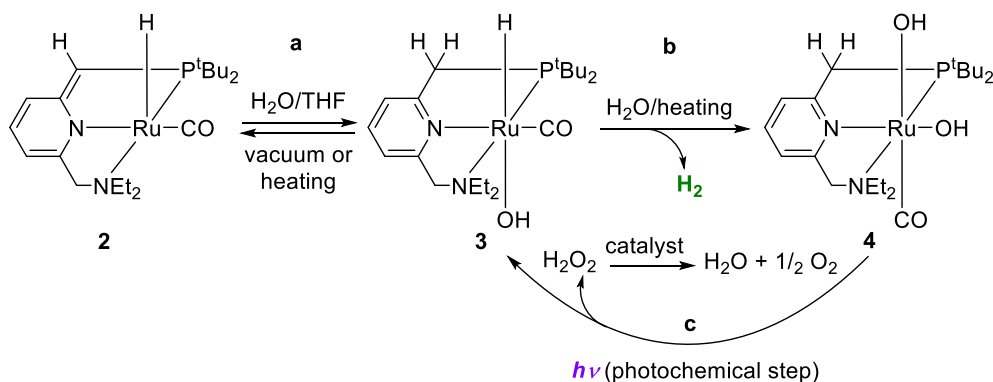
The direct cleavage of the O–H bond in the water molecule is energetically prohibitive (117.59 ± 0.07 kcal/mol) [7], as it is among the highest values for X–H bonds [8]. A possible solution to this problem is the activation of water by transition-metal complexes. This began to be considered a possibility as a result of the discovery of a decrease of almost 60 kcal/mol in the dissociation of the O–H bond of water when the titanocene(III) aqua-complex **1** is formed by the reaction between Cp₂TiCl and water [9–14] (Scheme 1). Active Cp₂TiCl is generated by the reduction of commercially available Cp₂TiCl₂ and Mn or Zn [15]. Initially, this Ti^{III}-aqua complex was used for the reduction of the carbon radicals formed in the reaction between Cp₂TiCl and functional groups having heteroatoms with free valence electrons [9–14] (Scheme 1). Although initially the aqua titanium(III) complex **1** was not used to

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Scheme 1. Proposed Cp₂TiCl aqua-complex 1 and reduction of carbon-centered radical intermediate.



Scheme 2. Photochemical water splitting via ruthenium transition metal complexes. (a) Reaction of water with the Ru(II) pincer complex 2. (b) Thermal activation of complex 3 with water, and H₂ generation. (c) Formation of O₂ after photolysis of 4.

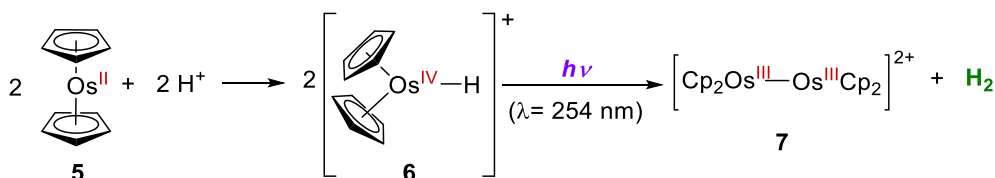
produce H₂ from water, subsequently several transition complexes with water-derived ligands were reported as possible platforms for investigating water-splitting processes in which a photochemical reaction was the key step. The main interest of these systems is that both half reactions of water nominally occur at a single site, and without the sacrifice of oxidants or reductants. In addition, water is used as an ideal donor in photochemical hydrogen production.

2.1. Ruthenium transition-metal complexes

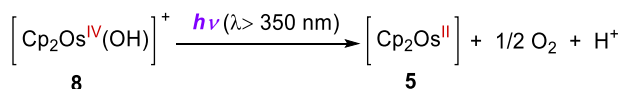
Milstein et al. reported one of the first of these water-splitting systems, applying a ruthenium pincer complex and light [16]. This system leads to the consecutive thermal H₂ and light-induced O₂ stoichiometric generation from water. The reaction of water with the dearomatized Ru(II) pincer hydride complex 2 gave the monomeric aromatic Ru(II) hydrido-hydroxo complex 3 with a quantitative yield (Scheme 2). This addition reaction does not change the oxidation state of ruthenium.

When the aromatic Ru(II) pincer complex 3 which has hydroxide and hydride ligands reacts with another H₂O molecule by heating, H₂ is released and the *cis*-dihydroxo complex 4 is formed (Scheme 2). Finally, in a photochemical step, the Ru(OH)₂ based complex 4 eliminates hydrogen peroxide (H₂O₂), which is rapidly and catalytically decomposed to form O₂ and water, thus regenerating the starting hydrido-hydroxo Ru(II) complex 3 (Scheme 2). A possible catalyst for the disproportionation of H₂O₂ could be complex 2.

Although at first sight, the combination of both separate stoichiometric reactions discussed before could give the idea that this system behaves as a dual catalyst, it is not actually yet catalytic. Other drawbacks of this system are that H₂O₂, rather than O₂, is the initial compound for water oxidation, and in addition, the formation of 4 requires heating, a fact that should be taken into account in the final energy balance. More recently, theoretical calculations have provided further details on the reaction mechanism of this system [17].



Scheme 3. Protonation of osmocene 5 and photochemical generation of H₂ from 6.

Scheme 4. Generation of O₂ by photooxidation of **8**.

2.2. Osmocene transition metal complexes

A second approach to the production of hydrogen using a photochemical system was reported in 2009 by Kunkely and Vogler [18]. They described a process based on two separate stoichiometric photoreduction/photooxidation reactions which can generate H₂ and O₂ from water using an osmocene complex.

Osmocene(II) (**5**) can be dissolved in H₂O only in the presence of acids. The reaction of **5** with acid leads to the formation of the osmocene (IV) **6**, which after irradiation with UV light produces H₂ and the dimer **7** (Scheme 3). Both photolysis compounds are generated in an approximate 1:1 ratio.

In a separate experiment, an aqueous solution of the hydroxo complex [Cp₂Os^{IV}(OH)]PF₆ (**8**) was irradiated with visible light giving as photoproducts osmocene(II) **5** and oxygen in the molar ratio 1:0.47 ± 5 % (Scheme 4). Later [19], this photooxidation was studied by theoretical calculations.

As shown in Scheme 4, O₂ is the initial product of photooxidation, avoiding the presence of other undesirable products such as H₂O₂. Again, by combining the separate stoichiometric photoreactions commented on here, the system appears to behave as a catalyzed process. However, it is not yet catalytic because both photoreactions are carried out separately. The disproportionation of the Os^{III} dimer **7** upon irradiation (λ = 366 nm) occurs in acid water solution (H₂SO₄, water) and gives osmocene(II) **5** and the light-stable aqua-complex [Cp₂Os^{IV}(H₂O)]²⁺. The main disadvantage of this system is the pH-dependent equilibrium between [Cp₂Os^{IV}(H₂O)]²⁺ and [Cp₂Os^{IV}(OH)]⁺ (**8**), which is the photoactive species. Furthermore, another disadvantage is that the photogeneration of oxygen and hydrogen happens at different wavelengths.

2.3. Titanocene transition metal complex

Another class of organometallic complexes that photochemically split H₂O into an oxidized water equivalent and H₂ was reported by Beweries et al. [20]. These authors reported a series of *ansa*-titanocene (III) triflate complexes for the elementary steps of the light-driven overall H₂O splitting. These complexes were selected because the *ansa*-cyclopentadienyl ligand remains coordinated to metal, avoiding the dissociation previously observed in the photolysis of a decamethyltitanocene(IV) dihydro complex [21].

In this system, as shown in Scheme 5, the first reaction was the solvation of the previously synthesized and isolated *ansa*-titanocene triflate **9**, where the triflate group was replaced by two water molecules, leading to the diaqua-complex **10**. In the presence of the radical scavenger (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO), the diaqua-

complex **10** loses one hydrogen atom, producing **11** and completing the reduction reaction of H₂O splitting. When the Ti^{IV} complex **11** was irradiated with UV-vis light in the presence of an excess of water, it abstracted one hydrogen atom from water to form the Ti^{III} complex **10** through a reduction reaction that also afforded a hydroxy radical, thus completing the catalytic cycle of H₂O splitting. Therefore, this *ansa*-titanocene(III/IV) system was capable of carrying out both H₂O reduction (by oxidation of a titanocene(III) species) and H₂O oxidation (by photoreduction of a titanocene(IV) species).

Later, a mechanistic understanding of H₂O splitting steps promoted by complex **9** was reported from a theoretical viewpoint [22].

The fact that this system needs TEMPO to accelerate the hydrogen abstraction process of **10** is perhaps its greatest drawback, since free hydrogen is not produced. Furthermore, OH radical is the initial compound produced in the water oxidation step, rather than oxygen.

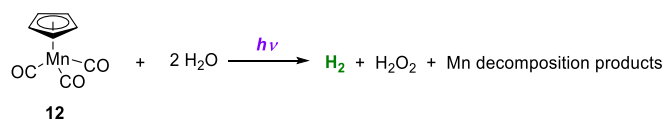
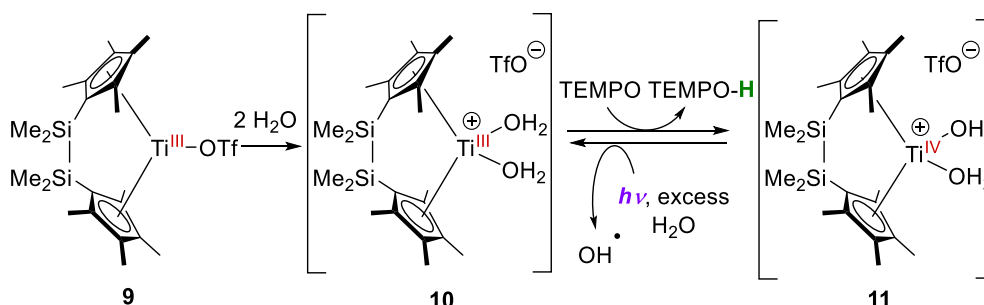
2.4. Organomanganese transition-metal complexes

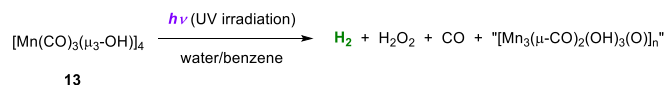
Photochemical water splitting was also carried out using an organomanganese transition metal complex [23–25]. Initially, Fan et al. reported the stoichiometric photoactivation of water by cyclopentadienyl manganese tricarbonyl CpMn(CO)₃ (**12**) to generate hydrogen and hydrogen peroxide [23]. Broad-band irradiation (300–800 nm) of CpMn(CO)₃ (**12**) in a water/hexane biphasic system gave hydrogen at 40–50 % yield and hydrogen peroxide (Scheme 6). Isotopic labeling experiments with D₂O have indeed shown that water is the hydrogen source. Although an important intermediate in this reaction is the water-coordinated complex CpMn(CO)₂(H₂O), which has been directly observed by time-resolved IR spectroscopy, more experimental evidence is necessary to ensure a correct mechanism for the system mentioned above.

The main drawbacks of this system are that it is not catalytic, produces hydrogen peroxide rather than oxygen as the initial product of water oxidation, and requires a more robust organometallic system.

Later, the same research group reported that the photolysis of another organomanganese transition metal complex (Mn₂(CO)₁₀) in an alkane/water biphasic system gave a better stoichiometric production of hydrogen, specifically 1.80 mol of hydrogen per mol of Mn₂(CO)₁₀ [24].

Finally, Lacy et al. [25] described that the photochemical water-splitting reaction with various solvated tricarbonyl organomanganese complexes such as **13** produced H₂, H₂O₂, and CO in higher yields than those previously reported with other organomanganese complexes, possibly because **13** and related complexes contain water-derived ligands prior to photolysis (Scheme 7).

Scheme 6. Photolysis of CpMn(CO)₃ (**12**) in a water/hexane biphasic system.Scheme 5. *ansa*-Titanocene process of water splitting.



Scheme 7. Photolysis of the Mn complex **13** in a water/benzene biphasic system.

Isotopic labeling experiments (organomanganese-**13** labelled with ^{18}O) suggested that water was the oxygen source, since label incorporation from ^{18}O -organomanganese (^{18}O -**13**) is not found in the oxidized product. Hydrogen production from **13** is the result of different reactions, one of which includes protons derived from the hydroxide ligands in complex **13**, establishing the reductive half reaction of H_2O splitting mediated by **13**. This system requires improvement to overcome its drawbacks, as that described by Fan [23].

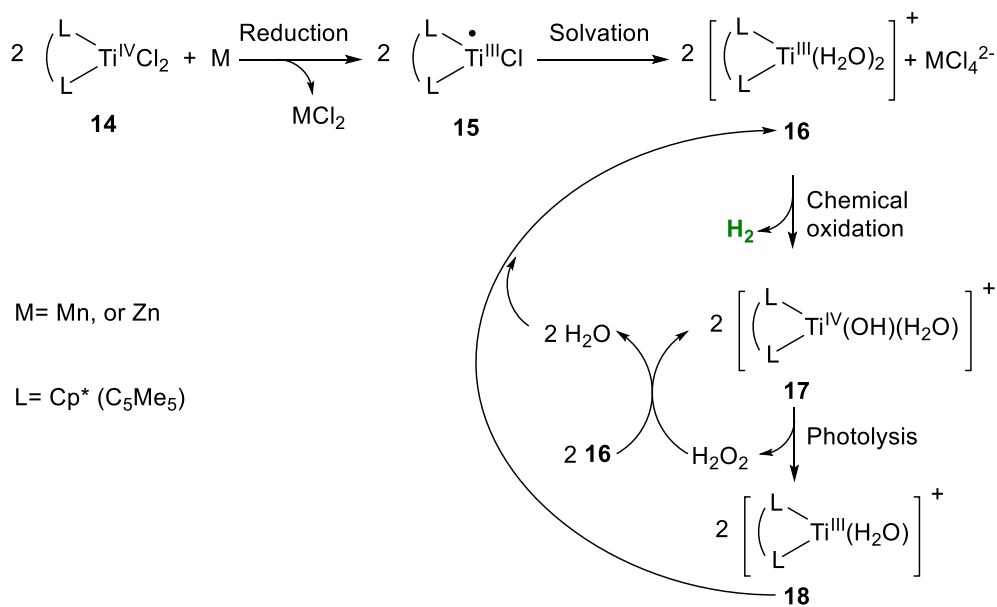
3. Conclusions and perspectives

The design of robust, catalytic, and efficient systems based on transition-metal complexes for photochemical water splitting is a promising methodology for the sustainable production of hydrogen. This article gives an overview of the most significant advances in the field of photochemical water splitting by transition metal complexes, which could provide a better understanding of the significant key steps of overall H_2O splitting driven by light. Several selected examples for photochemical systems based on transition metal complexes that can mimic both water oxidation and water reduction to produce an oxidized water equivalent and hydrogen have been presented. However, it is still a great challenge to design highly efficient catalytic systems for future scaled-up applications.

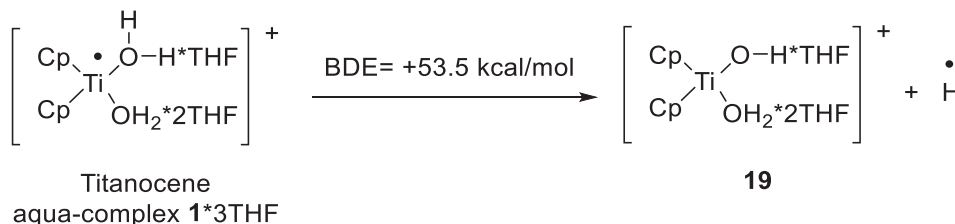
The ability of the H_2O molecule to act as a hydrogen atom transfer reagent can be explained in terms of the weakening of the OH-bond dissociation energy, by about 60 kcal/mol [11,12], due to the presence of titanocene(III) complex acting as a single electron transfer reagent [13]. For this reason, the corresponding titanocene(III) aqua-complex behaves as a hydrogen atom donor [11]. Here, we postulate that in situ formed titanocene(III) aqua-complex could be used as a possible platform for studying the water-splitting reaction. Unlike the titanocene(III) complexes used by Beweries [20] in photochemical water splitting, this aqua-complex can be freshly prepared by a simple and straightforward reduction of L_2TiCl_2 (L = Cp* (C₅Me₅) (**14**) with Zn or Mn in a THF-water solution.

This system requires two important premises for the generation of hydrogen through water splitting that must be considered. The first one is based on the preparation of a titanocene(III) aqua-complex where the reducing strength of the active catalyst is increased. This can be achieved by choosing more electron-rich Cp ligands such as Cp*. This aqua-complex with high redox potential would allow a single-electron transfer reaction between titanium and water under moderate temperature, giving hydrogen. The second premise requires the ligand to remain coordinated to the titanium during the photolysis process, which is possible using an *ansa*-cyclopentadienyl ligand as previously reported by Beweries et al. [20]. An excellent guide to the choice of low-titanocene(III) complexes for applications in chemistry has recently been reported by Gansäuer and Streuff et al. [26]. This system is shown in Scheme 8.

The reduction of titanocene(IV) complex **14** would give the active titanocene(III) intermediate **15**. The solvation of intermediate **15** would give the diaqua-complex **16**. In this intermediate, the water ligands would have a high propensity to act as a hydrogen-atom transfer system,



Scheme 8. Cycle of the diaqua-complex $[\text{Cp}_2^*\text{Ti}(\text{H}_2\text{O})_2]^+$ (**16**) for overall water splitting.



Scheme 9. Bond dissociation energy of **1***3THF by density functional theory (DFT) calculations.

since the in situ formed titanium(III) center has a high redox potential, encouraging a single electron-transfer between titanium and water, and therefore the oxidation of the Ti(III) center may be possible at low or moderate temperatures, and would allow the reduction reaction of water splitting to form hydrogen and the complex **17**. A theoretical study providing more details of the chemical oxidation of intermediate **1** (similar to **16**) was reported by Gansäuer et al. [12]. In this work the computed bond dissociation energy (BDE) of **1** coordinated to 3 molecules of THF to give the complex **19** was only +53.5 kcal/mol [12] (Scheme 9).

Based on the studies of photochemical activation of the Ti-O bond reported by Beweries et al. [20], we consider that the irradiation of **17** with UV-vis light would allow the second half reaction of overall water splitting, leading to the formation of intermediate **18** and hydrogen peroxide. Although H₂O₂, rather than O₂, is the initial compound for H₂O oxidation, this is not a problem when the propose titanocene(III) aqua-complex **16** is used, since the homolytic cleavage of the O-O bond catalyzed by titanocene(III) is well documented [27]. Due to the weakness of the O-O bond in hydrogen peroxide [27], its homolytic rupture mediated by **16** could generate complex **17** and water. Finally, the solvation of **18** would regenerate the diaqua-complex **16**, and therefore a sustainable and closed model cycle of overall water splitting would be possible. This catalytic cycle would represent an extraordinary contribution to the photochemical water splitting via transition metal complexes.

Experimental and theoretical studies of photochemical water splitting using a choice of titanocene derivatives and other metal complexes will be addressed in our lab, while there is still an urgent need to carry out continuous and extensive studies of photochemical water splitting using transition metal complexes to generate more efficient production of hydrogen from water.

Author Contributions

A.R.M.: design and coordination of the project, writing—original draft, and writing—review and. I.R.-G.: writing—review. All authors have read and agreed to the published version of the manuscript.

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CRediT authorship contribution statement

Antonio Rosales Martínez: Writing – review & editing, Writing – original draft, Project administration, Conceptualization. **Ignacio Rodríguez-García:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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