**Photochemistry**

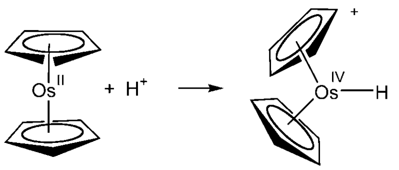
DOI: 10.1002/anie.200804712

# Water Splitting by Light with Osmocene as Photocatalyst**

*Horst Kunkely and Arnd Vogler**

Photochemical water splitting can be viewed as the simplest version of artificial photosynthesis.[1–3] Solid semiconductors as well as metal complexes in homogenous solution have been examined as photocatalysts. In the case of molecular complexes, a photoredox system must be identified that participates in the generation of $H_2$[4] and $O_2$[5] by multielectron-transfer processes. Consecutive one-electron transfer reactions, as take place in biological environments, are possible in principle but rather difficult to realize in a practical manner. In particular, the intermediate formation of reactive radicals is a serious complication. As a consequence, it has been suggested that mononuclear and binuclear transition-metal complexes be introduced that participate in simultaneous multielectron transfer. This background motivated our present study, which deals with a cyclic system based on the photoredox properties of osmocene ($[Cp_2Os^{II}]$, $Cp^- = C_5H_5^-$). The photoreduction of protons and the photooxidation of hydroxide ions take place in separate experiments. In this context, a previous investigation of molybdocene as a potential photocatalyst deserves special attention.[6]

Osmocene dissolves in water only in the presence of acids. The protonation of osmocene leads to the formation of a well-known hydride complex [Eq. (1)]:[7]



(1)

Generally, osmocene is not light-sensitive, but it undergoes photolysis in acidic ($H_2SO_4$ or $HBF_4$) aqueous solutions. Irradiation with UV light ($\lambda_{irr} = 254$ nm) is accompanied by characteristic spectral changes (Figure 1) that unambiguously indicate the formation of $[Cp_2Os^{III}\text{–}Os^{III}Cp_2]^{2+}$[8] ($\lambda_{max} = 605$ ($\varepsilon = 400$), 465 (1230), 317 (11900), 220 nm (sh, 9400 $\text{M}^{-1}\,\text{cm}^{-1}$)). Simultaneously, hydrogen is released. Both photolysis products are formed approximately in a 1:1 ratio ($[Cp_2Os^{III}\text{–}Os^{III}Cp_2]^{2+}/H_2 = 1.06 \pm 5\,\%$). This photoreaction can thus be described by the simple stoichiometric Equation (2):

$$2\,[Cp_2Os^{IV}(H^-)]^+ \xrightarrow{h\nu} [Cp_2Os^{III}-Os^{III}Cp_2]^{2+} + H_2 \quad (2)$$

Product formation could take place through the intermediate formation of a radical pair [Eq. (3)]:

$$\begin{aligned}[Cp_2Os^{IV}(H^-)]^+ &\rightarrow [Cp_2Os^{III}]^+ + \text{H atom}\\ &\xrightarrow{2\times} [Cp_2Os^{III}-Os^{III}Cp_2]^{2+} + H_2\end{aligned} \quad (3)$$

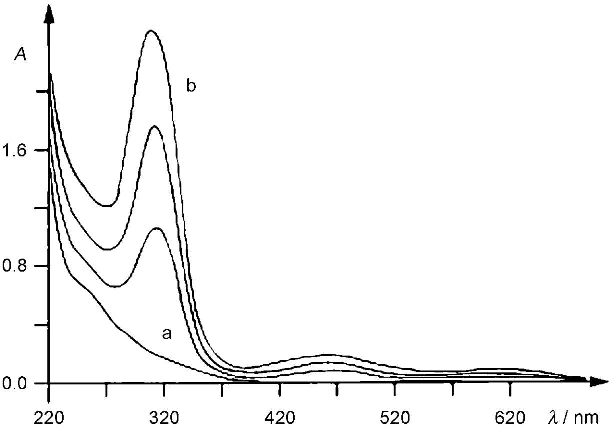


***Figure 1.*** Spectral changes during the photolysis of $2.37\times10^{-4}$ M osmocene in 5 M $H_2SO_4$ after 0 min (a), 20, 40, and 80 min (b) irradiation times with $\lambda_{irr} = 254$ nm 1 cm cell.

However, this reaction path can be excluded, as $[Cp_2Os^{III}]^+$ radicals disproportionate immediately under these conditions [Eq. (4)]:[8]

$$2\,[Cp_2Os^{III}]^+ \rightarrow [Cp_2Os^{IV}]^{2+} + [Cp_2Os^{II}] \quad (4)$$

Accordingly, we suggest that the photolysis is preceded by a reversible dimerization of the hydride complex, which subsequently undergoes reductive elimination without the formation of radicals:

$$\begin{aligned}2\,[Cp_2Os^{IV}(H^-)]^+ &\rightleftharpoons [Cp_2Os^{IV}H\cdots HOs^{IV}Cp_2]^{2+}\\ &\xrightarrow{h\nu} [Cp_2Os^{III}-Os^{III}Cp_2]^{2+} + H_2\end{aligned} \quad (5)$$

This special type of hydrogen bonding has also been considered to occur in other cases.[9] As this bonding is certainly rather weak, the monomer is expected to prevail in the equilibrium. The apparent quantum yield for the formation of $[Cp_2Os^{III}\text{–}Os^{III}Cp_2]^{2+}$ amounts to $\phi = 10^{-3}$ ($\lambda_{irr} = 254$ nm). However, it must be taken into account that the photoactive dimeric hydride complex is probably present only in small concentrations, while the monomer absorbs most of the light. A comparable photolysis has been described earlier but without discussion of the mechanism: $2\,[HIr^{I}(PF_3)_4] \rightarrow H_2 + [(PF_3)_4Ir^{0}\text{–}Ir^{0}(PF_3)_4]$.[10]

In coordinating solvents (L) such as $CH_3CN$, the $Os^{III}$ dimer is well known to undergo slow disproportionation [Eq. (6)]:[8]

---

[*] Dr. H. Kunkely, Prof. Dr. A. Vogler
Institut für Anorganische Chemie, 93040 Regensburg (Germany)
E-mail: arnd.vogler@chemie.uni-regensburg.de

[**] We are grateful for financial support by DFG (grant Vo 211/18-1).

$$[Cp_2Os^{III}{-}Os^{III}Cp_2]^{2+} + L \rightarrow [Cp_2Os^{II}] + [Cp_2Os^{IV}L]^{2+} \qquad (6)$$

This reaction also proceeds photochemically, as indicated by the concomitant spectral changes, which are identical in both cases. When the irradiation is carried out in acidic solution ($H_2SO_4$, $L = H_2O$), comparable spectral variations are observed (Figure 2). Since the photolysis products are apparently stable under these conditions and interfering inner-filter effects are absent, the photolysis ($\lambda_{irr} = 366$ nm) can be performed to completion. The $Os^{III}$ dimer disappears with $\phi = 8\times10^{-3}$ at $\lambda_{irr} = 436$ nm. Disproportionations of this kind, which take place as a consequence of the photochemical splitting of a metal–metal bond, are an important reaction type in organometallic chemistry.[11,12]

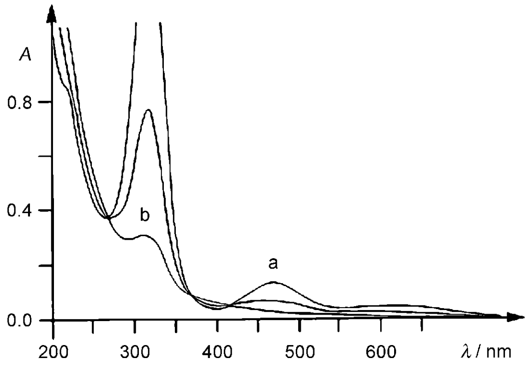


***Figure 2.*** Spectral changes during the photolysis of $1.06\times10^{-4}$ M $[Cp_2Os^{III}{-}Os^{III}Cp_2](PF_6)_2$ in 5 M $H_2SO_4$ after 0 min (a), 20, 40, and 80 min (b) irradiation times with $\lambda_{irr} = 366$ nm, 1 cm cell.

The stoichiometry of Equation (6) has been confirmed experimentally. Osmocene was extracted from the acidic solution with *n*-hexane and identified spectroscopically,[13] and its concentration was determined quantitatively. Comparison of the spectra of the extracted solutions of the photolyzed samples and those kept in the dark (not photolyzed) yielded a molar ratio of 1:0.96 ± 5 %. The concentration of complex $[Cp_2Os^{IV}(H_2O)]^{2+}$ was determined via its substitution product $[Cp_2Os^{IV}I]^+$ ($\lambda_{max} = 416$ nm, $\varepsilon = 1040\,M^{-1}cm^{-1}$ and $\lambda_{max} = 316$ nm, $\varepsilon = 1030\,M^{-1}cm^{-1}$), which is formed upon addition of iodide to the solution remaining after extraction. The molar ratio of osmocene to $[Cp_2Os^{IV}I]^+$ amounts to 1:0.97 ± 5 %. The substitution of L by $X^-$ is generally used for the synthesis of $[Cp_2Os^{IV}X]^+$ complexes from $[Cp_2Os^{IV}L]^{2+}$.[8]

When the photolysis of $[Cp_2Os^{IV}H]^+$ is performed with white light instead of UV light, the spectral variations do not follow a simple pattern, because the primary photolysis of the hydride complex and the secondary photolysis of the $Os^{III}$ dimer are superimposed. The combined photolyses with white light proceed according to Equation (7):

$$[Cp_2Os^{II}] + 2\,H^+ + H_2O \rightarrow H_2 + [Cp_2Os^{IV}(H_2O)]^{2+} \qquad (7)$$

The aqua complex ($L = H_2O$) is apparently light-stable and does not undergo any further photolysis.

Various salts with the cation $[Cp_2Os^{IV}L]^{n+}$ (L = halide or coordinating organic solvent) have been prepared and characterized by Taube and co-workers.[8] The reddish brown hydroxo complex $[Cp_2Os^{IV}(OH)]PF_6$ described by Fischer and Grubert is also a compound of this type.[14] Aqueous solutions of this salt are acidic and light-sensitive. They are bleached upon irradiation with visible light ($\lambda_{irr} >$ 350 nm, Figure 3). As photoproducts, only osmocene and oxygen could be detected. From the spectral changes, it can be deduced that the hydroxo complex is converted to osmocene nearly quantitatively. Furthermore, osmocene and oxygen are formed in the molar ratio 1:0.47 ± 5 %. These observations are consistent with Equation (8):

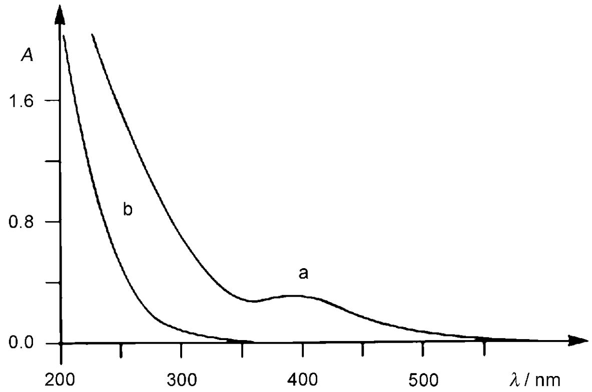


***Figure 3.*** Spectral changes during the photolysis of $5.25\times10^{-4}$ M $[Cp_2Os^{VI}(OH)]PF_6$ in $H_2O$ after 0 min (a) and 40 min (b) irradiation times with $\lambda_{irr} > 350$ nm, 1 cm cell.

$$[Cp_2Os^{IV}(OH)]^+ \xrightarrow{h\nu} [Cp_2Os^{II}] + 1/2\,O_2 + H^+ \qquad (8)$$

The quantum yield for the disappearance of $[Cp_2Os^{IV}(OH)]^+$ amounts to $\phi = 2\times10^{-3}$ ($\lambda_{irr} = 405$ nm). In the solid state this complex apparently also undergoes this decomposition thermally, but only at 185 °C.[14] In the photolysis, oxygen is generated in the singlet state, at least partially. When the photolysis is carried out in acetonitrile in the presence of diphenylacetylene, benzil was formed and identified by its characteristic luminescence at $\lambda_{max} = 507$ nm. The addition of $^1O_2$ to diphenylacetylene has been previously used for the detection of singlet oxygen.[15]

We suggest that the photolysis of the hydroxo complex consists of the following consecutive steps [Eqs. (9)–(11)]:

$$[Cp_2Os^{IV}(OH)]^+ \rightleftharpoons [Cp_2Os^{IV}{=}O] + H^+ \qquad (9)$$

$$2\,[Cp_2Os^{IV}{=}O] \rightleftharpoons [Cp_2OsO_2OsCp_2] \qquad (10)$$

$$[Cp_2OsO_2OsCp_2] \xrightarrow{h\nu} 2\,[Cp_2Os^{II}] + O_2 \qquad (11)$$

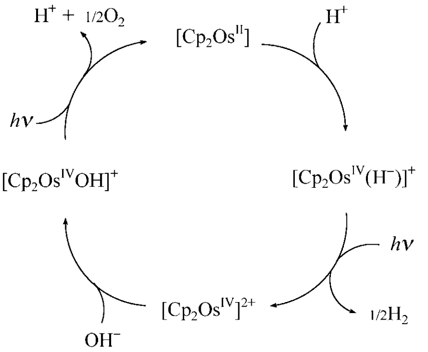
The electronic structure of the fragment $[OsO_2Os]^{4+}$ is not clear. However, we assume that this binuclear cation exists as peroxo complex, $[Cp_2Os^{III}(O_2{}^{2-})Os^{III}Cp_2]$. Binuclear peroxo complexes of this type frequently photolyze under elimination of oxygen in general and $^1O_2$ in particular.[16]

Recently, we studied such a photoredox reaction[17] which proceeds in analogy to the photolysis of the binuclear osmium complex [Eq. (12)]:

$$[\text{(porphyrin)Fe}^{\text{III}}(O_2^{2-})\text{Fe}^{\text{III}}\text{(porphyrin)}] \xrightarrow{h\nu/\text{LMCT}} 2\,[\text{(porphyrin)Fe}^{\text{II}}] + O_2\ (^1O_2) \quad (12)$$

In this context it is of interest that the complex $[Cp_2Os^{III}\text{-}(S_2^{2-})Os^{III}Cp_2]^{2+}$ is apparently not stable but thermally decomposes to osmocene and sulfur.[18] In any case, product formation is certainly facilitated by the high stability of osmocene.

In summary, photochemical water splitting can be described in a simplified version by the cyclic process shown in Scheme 1. It is apparent from this scheme that the reductive and oxidative part of the water splitting by osmocene shows interesting analogies to photosystem I and II of natural photosynthesis which also take place as separate processes.



*Scheme 1.*

In the future, further details of photochemical water splitting will be studied. In particular, the pH-dependent equilibria with participation of $[Cp_2Os^{IV}L]^{n+}$ ($L = H_2O, OH^-, O^{2-}$) certainly play an important role. However, complications by other processes are expected. In particular, oligomerization with formation of hydroxo and oxo bridges as well as bridging by Cp rings may interfere.[8]

## Experimental Section

Osmocene is commercially available (Strem Chemicals). The compounds $[Cp_2Os^{III}\text{–}Os^{III}Cp_2](PF_6)_2$[8] and $[Cp_2Os^{IV}(OH)]PF_6$[14] were prepared according to published procedures. The photolyses were performed in aqueous solutions saturated by argon. Light sources were a low-pressure mercury lamp (Hanau, 6 W, $\lambda_{irr} = 254$ nm) and a high-pressure mercury lamp (Osram HBO 200 W/2). The detection of $H_2$ and $O_2$ was achieved by indirect procedures which, however, are considered to be reliable under our experimental conditions. The gas exchange between the photolysis cell and an analysis cell takes place via a gas bridge by convection and diffusion only. Hydrogen reduces aqueous $PdCl_2$ to elemental palladium,[19] which is formed as a black-brown colloid.[20] Oxygen quenches the luminescence of $Tl^+$ ($\lambda_{max} = 464$ nm) in aqueous potassium chloride ($2.0 \times 10^{-4}$ M TlCl, 4 M KCl).[21] The emission quantum yield of $\phi = 0.88$[21] is reduced to 0.1 upon saturation by air.[22] In our system, the emission quantum yield was reduced to 0.65 after photolyzing aqueous $[Cp_2Os^{IV}(OH)]^+$. The quantitative determination of the amount of $H_2$ and $O_2$ produced was carried out by measuring the volume of the released gas in an acidic ($H_2SO_4$) solution of $[Cp_2Os]$ ($\lambda_{irr} = 254$ nm) and an aqueous solution of $[Cp_2Os^{IV}(OH)]PF_6$ ($\lambda_{irr} > 350$ nm), respectively, after the photolyses were driven to completion. Photolysis was carried out in argon-saturated solutions in a 3 cm quartz cell that was connected to a constant-pressure gas burette.[19]

Received: September 26, 2008
Published online: January 27, 2009

**Keywords:** coordination chemistry · osmium · photocatalysis · photochemistry · water splitting

[1] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729–15735.
[2] A. J. Bard, M. A. Fox, *Acc. Chem. Res.* **1995**, *28*, 141–145.
[3] *Inorg. Chem.* **2005**, *44*, 6799–6892 (Forum on Solar and Renewable Energy).
[4] A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022–4047.
[5] *Inorg. Chem.* **2008**, *47*, 1697–1699 (Forum on Making Oxygen).
[6] G. T. Baxley, A. A. Avey, T. M. Aukett, D. R. Tyler, *Inorg. Chim. Acta* **2000**, *300–302*, 102–112.
[7] E. S. Shubina, A. N. Krylov, A. Z. Kreindlin, M. I. Rybinskaya, L. M. Epstein, *J. Organomet. Chem.* **1994**, *465*, 259–262.
[8] M. W. Droege, W. D. Harman, H. Taube, *Inorg. Chem.* **1987**, *26*, 1309–1315.
[9] R. H. Crabtree, O. Eisenstein, G. Sini, E. Peris, *J. Organomet. Chem.* **1998**, *567*, 7–11.
[10] T. Kruck, G. Sylvester, I.-P. Kunau, *Angew. Chem.* **1971**, *83*, 725; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 725.
[11] A. E. Stiegmann, D. R. Tyler, *Acc. Chem. Res.* **1984**, *17*, 61–66.
[12] A. E. Stiegmann, D. R. Tyler, *Coord. Chem. Rev.* **1985**, *63*, 217–240.
[13] H. Kunkely, A. Vogler, *Transition Met. Chem.* **2000**, *25*, 234–236.
[14] E. O. Fischer, H. Grubert, *Chem. Ber.* **1959**, *92*, 2302–2309.
[15] H. Sugimoto, D. T. Sawyer, *J. Am. Chem. Soc.* **1984**, *106*, 4283–4285.
[16] A. Vogler, H. Kunkely, *Coord. Chem. Rev.* **2006**, *250*, 1622–1626.
[17] H. Kunkely, A. Vogler, *Inorg. Chim. Acta* **2005**, *358*, 4086–4088.
[18] M. W. Droege, H. Taube, *Inorg. Chem.* **1987**, *26*, 3316–3318.
[19] A. Vogler, H. Kunkely, *Inorg. Chem.* **1984**, *23*, 1360–1363.
[20] A. Vogler, C. Quett, H. Kunkely, *Ber. Bunsen-Ges.* **1988**, *92*, 1486–1492.
[21] P. J. Mayne, G. F. Kirkbright, *J. Inorg. Nucl. Chem.* **1975**, *37*, 1527–1529 .
[22] A. Vogler, H. Nikol, *Pure Appl. Chem.* **1992**, *64*, 1311–1317.