



## Review

## Rhenium complexes in homogeneous hydrogen evolution



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## ABSTRACT

This review is focused on the photocatalytic properties of the Re(I) compounds in the reduction of H<sup>+</sup> and their use in solar energy conversion. Different systems are discussed in terms of the photosensitizer – usually containing the core [ReX(CO)<sub>3</sub>diimine]<sup>+</sup> – and mechanistic details are provided. The effect of the axial ligand and coordination of solvent water or TEOA on hydrogen evolution rates is also discussed. Supramolecular systems that mimic enzymes by combining both the photosensitizer and the catalyst are also presented.

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**Abbreviations:** AcOH, acetic acid; AscH, ascorbic acid; BHAH, *N*-benzyl-1,4-dihydro-nicotinamide; bpy, 2,2'-bipyridine; CT, charge transfer; dmbpy, 4,4'-dimethyl-2,2'-bipyridine; dmgH, dimethylglyoximate; dmgH<sub>2</sub>, dimethylglyoxime; DMF, *N,N*-dimethylformamide; EDTA, ethylene-diamine-tetra-acetic acid; HES, higher excited states; HOMO, highest-occupied molecular orbital; ILCT, intra-ligand charge transfer; LF, ligand field; LLCT, ligand-to-ligand charge transfer; LUMO, lowest unoccupied molecular orbital; MLCT, metal-to-ligand charge transfer; MLLCT, metal-ligand-to-ligand charge transfer; MMLLCT, mixed-metal-ligand-to-ligand charge transfer; phen, 1,10-phenanthroline; PLS, photochemical ligand substitution; PS, photosensitizer; py, pyridine; SDS, sodium dodecyl sulfate; HBF<sub>4</sub>, tetrafluoroboric acid; THF, tetrahydrofuran; TR-IR, time-resolved infrared spectroscopy; TEOA, triethanolamine; TEA, triethylamine; TCPEP, tris-(2-carboxyethyl)phosphine; TOF, turnover frequency; TON, turnover number; WRC, water reduction catalyst.

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## 1. Introduction

The development of a secure, clean, and renewable energy source is a demand for our global future [1]. Sunlight can play an important role in this context since it can be converted into electricity through photovoltaic power plants or into chemical power via the synthesis of small molecules like MeOH, H<sub>2</sub>, etc. [2]. One of the various ways to produce H<sub>2</sub> is by bio-inspired photocatalysis, meaning that artificial chemical catalysts–photosensitizers – interact with light analog to the pigments in photosystem I and II and decompose water into H<sub>2</sub> and O<sub>2</sub>.

Recent years have seen a revival of artificial photosynthesis, mainly employing metal complexes as photosensitizers, noble metal catalysts to achieve proton reduction, tertiary amines as electron donor and methylviologen as electron acceptor and results are in accordance with previous investigations [3–10].

Although  $[\text{Ru}(\text{bpy})_3]^{2+}$  or derivatives were mainly used for studies of photocatalytic production of  $\text{H}_2$ , other metal complexes are also employed as photosensitizers [11–16]. Among them  $[\text{ReX}(\text{CO})_3\text{diimine}]$  (X = halogen or phosphine or pyridine-type ligand) type photosensitizers play a predominant role in last decade [17,18].

In fact, rhenium complexes with various oxidation numbers pose as appealing systems both for fundamental and applied studies. Thus, coordination chemistry of rhenium has been extensively developed in recent years due, to a large extent, to the fact that its complexes with diimine ligands display long lifetimes and also short-lived rhenium isotopes hold promise as  $\beta$ -emitters in radiotherapy [19–22]. The chemistry of oxorhenium complexes arouses particular interest among these compounds not only for their implication in various reactions of industrial and biological importance, including olefin epoxidation and catalysis by cytochrome P-450 [23,24] but also for their lipophilic character and the oxidation states of rhenium that is Re(I) to Re(VI) [21].

Re(V) complexes have been studied as catalysts for oxygen transfer reactions [25] and show biological activity [26]. On the other hand, Re(I) complexes show remarkable photophysical and photochemical properties [27–35] and among other applications have found use as anion sensors [36], DNA probes [37–39], photosensitizers in solar cells [40,41], luminescence probes [42,43] and molecular parts in supramolecules [44–46]. The unique properties of Re(I) tricarbonyl-diimine complexes are closely connected to the existence of energetically low-lying charge transfer excited states with a large electron density shift from the metal to the diimine ligand (MLCT state). The knowledge of the photochemistry of  $[\text{Re}(\text{CO})_3(\text{bpy})\text{X}]$ -type complexes is based on time resolved methods [47,48], DFT calculations [27,47,49], and structure–activity relations [50–52]. The photocatalytic conversion of the carbon dioxide to carbon monoxide catalyzed by  $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$  and the detailed mechanistic studies that followed [53–58] advanced the research of this class of compounds as photocatalysts for solar energy conversion. The latter is a very active research area where transition metal chemistry significantly contributes. Metal complexes allow tailoring of the required properties (redox potential, excited state energy, molecular geometry) in order for catalysis toward green fuels to occur. In this field, rhenium complexes act in two major ways: carbon dioxide reduction and photoinduced hydrogen production. This review is focused on hydrogen evolution using Re(I) complexes, so for  $\text{CO}_2$  reduction the reader is referenced to relevant reviews [59–61].

## 2. Photophysics and photochemistry of Re(I) complexes

Several excellent reviews can be found in the literature [17,18,62,63] where the photophysics and photochemistry of Re(I) complexes are covered in detail, so only the basic principles will be covered here.

Rhenium complexes of the type  $[\text{Re}(\text{CO})_3(\text{NN})\text{X}]$  (NN denotes diimine and X an axial ligand) have long been used as chromophores in solar energy conversion applications, due to their useful and well defined properties that include stability,  $^3\text{MLCT}$  excited states localized on the  $\text{Re}(\text{NN})$  moiety and emission at room temperature [64,65]. For the complex  $[\text{Re}(\text{bpy})(\text{CO})_3\text{X}]$  the HOMO has been assigned as mostly  $\text{Re}(\text{d})$  ( $\geq 50\%$ ) and  $\text{Cl}-\text{CO}$  ( $\sim 20\%$  each) in orbital composition, while the LUMO is mainly of diimine ( $\geq 80\%$ ) in orbital character [18], ultimately giving rise to a metal-ligand-to-ligand-charge-transfer (MLLCT) transition.

Regarding photochemically induced ligand exchange in rhenium (I) complexes used in photocatalysis, photochemical ligand substitution (PLS) reactions are highly depended on the axial and

diimine ligand as well as on the solvent [18,50,65–67]. It has also been indicated that the temperature-dependent nonradiative decomposition processes proceed via CO ligand dissociation and successive recombination of the produced compounds in rhenium(I) diimine complexes of the type  $[\text{Re}(\text{R}_2\text{bpy})(\text{CO})_3(\text{PR}'_3)]^+$ , suggesting an activated process proceeding from  $^3\text{MLCT}$  to  $^3\text{LF}$  states [68].

The photostability of  $\text{fac}-[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+$  (py: pyridine),  $\text{fac}-[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ , or related bipyridyl-substituted complexes seems to be the result of the weaker *trans*-labilizing ability of the py or chloride ligand compared to a phosphorus donor, and not to a larger activation energy being required to reach the  $^3\text{LF}$  state, when these complexes are illuminated with visible light [18,69]. In fact, this type of PLS reaction of  $\text{fac}-[\text{Re}(\text{diimine})(\text{CO})_3\text{Cl}]$  and  $\text{fac}-[\text{Re}(\text{diimine})(\text{CO})_3(\text{R-py})]^+$  (R-py = pyridine derivative) does not proceed by irradiation using  $\lambda > 330$  nm light [18,56,63]. Efficient PLS for  $\text{fac}-[\text{Re}(\text{R}_2\text{bpy})(\text{CO})_3(\text{PR}'_3)]^+$  yields substitution *trans* to the axial  $\text{PR}'_3$  group by CO loss ( $\text{R}_2\text{bpy}$  is 4,4'- $\text{R}_2$ -2,2'-bpy, where R = H,  $\text{CF}_3$ , OEt or Ph, and  $\text{PR}'_3$  is a tertiary phosphine or phosphite) and the biscarbonylrhenium(I) diimine complexes, *cis-trans*- $[\text{Re}(\text{R}_2\text{bpy})(\text{CO})_2(\text{PR}'_3)\text{L}]^{\text{m}+}$ , were produced with chloride, py or  $\text{CH}_3\text{CN}$  as the entering group [70]. The activation energies for photosubstitution lie between 0.40 and 0.60 eV, and photosubstitution yields were generally in the range of 0.1–0.55. Labeling ( $^{13}\text{C}$ ) studies demonstrated that the axial CO, which is *trans* to the phosphorus ligand, was indeed labilized, consistent with a dissociative mechanism and an associated excited-state kinetic *trans*-effect [68]. Ishitani et al. reported that the PLS reactions of  $\text{fac}-[\text{Re}(4,4'-\text{R}_2\text{bpy})(\text{CO})_3\text{Cl}]$  (R = H, MeO,  $\text{NH}_2$ ,  $\text{CF}_3$ ) are generated by high-energy (UV light) photoexcitation and yielded solvato complexes,  $\text{fac}-[\text{Re}(4,4'-\text{R}_2\text{bpy})(\text{CO})_2(\text{solvent})\text{Cl}]$  [56]. The PLS reaction rate was not affected by the presence of  $\text{O}_2$ , but the emission was efficiently quenched with a rate constant of  $3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and this result shows that the PLS reaction does not take place from the emissive state. Mechanistic studies, together with TR-IR measurements, obviously reveal that the PLS reaction does not proceed via the lowest  $^3\text{MLCT}$  state, but as an alternative it occurs via higher vibrational levels of the  $^1\text{MLCT}$  and/or higher electronic states, such as  $^1\pi \rightarrow \pi^*$ , and higher-lying  $\text{Re} \rightarrow \text{bpy}$  and  $\text{Re} \rightarrow \text{CO}$   $^1\text{MLCT}$  states. The TR-IR measurements have indicated that the CO ligand dissociates with subpicosecond rates after excitation, leading to vibrationally hot CO-loss photoproducts (with a very broad TR-IR band) after 1 ps of excitation and the relaxed photoproduct (with a distinct TR-IR band) forms during 50–100 ps after [18,56].

Photochemical isomerization of  $\text{fac}-[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  to the *mer*-isomer in a CO saturated THF solution proceeded by 313-nm irradiation instead of the ligand substitution reaction [71]. As previously mentioned for  $\text{fac}-[\text{Re}(4,4'-\text{R}_2\text{bpy})(\text{CO})_2(\text{solvent})\text{Cl}]$ , the PLS reaction of  $\text{fac}-[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  proceeds via higher vibrational levels [56]. The mechanism of the photochemical reactions of the aforementioned complex have been fully clarified by a combination of steady-state irradiation, TR-UV/Vis, TR-IP, and TR-EM experiments [72]. Thus, irradiation of  $\text{fac}-[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  using high energy light (270 nm) induces the formation of a higher singlet state ( $\tau \leq 30$  fs) which is rapidly converted to the corresponding triplet state ( $^3\text{HES}$ ) without the formation of  $^1\text{MLCT}$  [72]. This triplet state, in a THF solution, is converted to both  $^3\text{LF}$  and  $^3\text{MLCT}$  excited states ( $\tau = 200$  fs) with the former to be the reactive state for leading to the unsaturated  $[\text{Re}(\text{bpy})(\text{CO})_2\text{Cl}]$  and then to the corresponding THF complex  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{THF})\text{Cl}]$ .

Another example is the photoinduced alkylation of the bpy ligand in  $\text{fac}-[\text{Re}(\text{bpy})(\text{CO})_3\text{Br}]$  in the presence of triethylamine in DMF solution. The reaction was initiated by photochemical reduction of the Re(I) complex by TEA, and the ethyl group was only introduced at the 5-position of the bpy ligand [63,73].

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