

# Synthesis, characterization and crystal structure of rhenium(I) tricarbonyl diimine complexes coupled with their efficiency in producing hydrogen in a photocatalytic system



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## ABSTRACT

Herein, we present the synthesis and characterization of two complexes, namely  $[\text{ReBr}(\text{CO})_3\text{amphen}]$  (**1**) (amphen = 1,10-phenanthroline-5-amine) and  $[\text{ReBr}(\text{CO})_3\text{pq}]$  (**2**) (pq = 2-(2'-pyridyl)quinoxaline); complex **2** is reported for the first time. The X-ray crystal structure of **2** has been determined. Electrochemical and photophysical studies have been performed to study the effect of the variation of the diimine ligand on the redox and optical properties of this class of compounds. Both complexes were used as photosensitizers for hydrogen production in a homogeneous photocatalytic system also carrying  $[\text{Co}(\text{dmgH})_2]$  as a hydrogen reaction catalyst, triethanolamine as an irreversible reductive quencher and AcOH as proton source. Complex **1** produces  $\text{H}_2$  after only 2 h irradiation while complex **2** requires 24 h indicating that the differences in the electronic properties influence their photosensitizing ability.

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## 1. Introduction

It is well known that fossil fuel reserves are becoming exhausted at an alarming rate. The role of fossil fuels needs to be reviewed as they are non-renewable and they will run out at one point or another [1,2]. That gives us only one choice and that is to find an alternative source of energy. Scientists have turned to dihydrogen ( $\text{H}_2$ ) or methanol (MeOH) as renewable sources of energy and efforts are being made towards developing efficient storage for  $\text{H}_2$  [3,4]. Another facet of this challenge is the development of new active catalysts for the reduction of protons in aqueous solvent mixtures composed of abundant inexpensive metals, alternatives to the widely used Pt, which do not pollute the environment [5–7].

**Abbreviations:** AcOH, acetic acid; amphen, 1,10-phenanthroline-5-amine; bpy, 2,2'-bipyridine; CT, charge transfer; dmGH, dimethylglyoximate; dmGH<sub>2</sub>, dimethylglyoxime; DMF, *N,N'*-dimethylformamide; DMSO, dimethylsulfoxide; dpq, 2,3-di(2-pyridyl)quinoxaline; MeOH, methanol; MLCT, metal to ligand charge transfer; phen, 1-10-phenanthroline; PS, photosensitizer; ppq, [2,3- $\alpha$ :3',2'-c]dipyridophenazine; pq, 2-(2'-pyridyl)quinoxaline; py, pyridine; TR-IR, time-resolved infrared spectroscopy; TEOA, triethanolamine; TON, turnover number; WRC, water reduction catalyst.

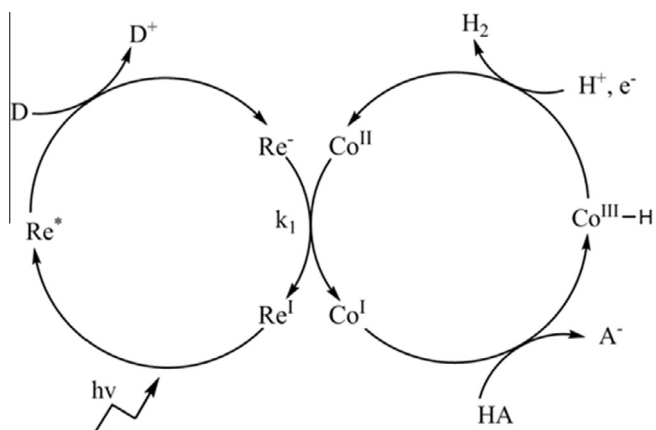
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In the past decade, the interest for reductive catalysts which in conjunction with photosensitizers such as  $[\text{Ru}(\text{bipy})_3]^{2+}$  or  $[\text{ReBr}(\text{CO})_3\text{bpy}]$  can reduce protons has been focused on complexes with cheap and abundant metal ions; among them an important class of compounds is cobaloximes [8–13] which appear to be both quite stable and active  $\text{H}_2$ -evolving catalysts. Among the aforementioned photosensitizers,  $[\text{Ru}(\text{bipy})_3]^{2+}$  is a well-known and widespread one, but it faces a drawback because of its long term stability, since after some hours of irradiation it decomposes [14]. On the other side, Re(I) compounds could play an important role as photosensitizers and the principle of such a system is given in Scheme 1 [15,16].

Actually, rhenium complexes with various oxidation numbers are being used widely in both fundamental and applied studies. Re(V) complexes have been studied as catalysts for oxygen transfer reactions [17] and show also biological activity [18]. At the same time, Re(I) complexes exhibit remarkable photophysical and photochemical properties [19–24] and they have found applications as anion sensors [25], DNA probes [26–28], photosensitizers in solar cells [29,30], luminescence probes and molecular parts in supramolecules [31,32].

Motivated by all these applications, but also by the studies of Probst et al. [4] and Fihri et al. [12], who investigated artificial photocatalytic systems using  $[\text{ReBr}(\text{CO})_3\text{bpy}]$  and  $[\text{ReBr}(\text{CO})_3\text{phen}]$  as



**Scheme 1.** General representation of the second-order pathway in  $\text{Co}^{\text{III}}\text{-H}$  to hydrogen.

photosensitizers and a cobaloxime complex as a catalyst, we decided to synthesize and characterize two Re(I) complexes, namely  $[\text{ReBr}(\text{CO})_3\text{amphen}]$  (**1**) and  $[\text{ReBr}(\text{CO})_3\text{pq}]$  (**2**), where amphen is 1,10-phenanthroline-5-amine and pq is 2-(2'-pyridyl) quinoxaline, in order to improve this class of photocatalytic systems. Actually, we designed two different light-harvesting units, substituting pq and amphen ligands on the  $\text{Re}(\text{CO})_3\text{Br}$  moiety for bpy and phen, respectively. Although these two ligands seem different in nature, they both carry N atoms on their substituents, which affects both the electronic and structural properties of the corresponding complexes. Moreover, a comparison among these four photosensitizers was undertaken. To the best of our knowledge complex **2** is being reported for the first time. Complexes **1** and **2** were used in a photocatalytic system as photosensitizers combined with  $\text{Co}(\text{dmgH}_2)$  as a catalyst, triethanolamine as a sacrificial electron donor and AcOH as a proton source for the reductive side of water splitting. This system was fully investigated and compared with the sensitizers used in the literature since it is well known that substituents on diimine ligands as well as a different coordinated halogen atom on the  $\text{Re}(\text{CO})_3\text{X}$  moiety affect the electronic properties of this class of compounds [33–35].

## 2. Experimental

### 2.1. Materials and reagents

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified prior to use by standard procedures [36]. The chemicals  $\text{ReBr}(\text{CO})_5$ ,  $\text{dmgH}_2$ ,  $[\text{Co}(\text{AcO})_2]\cdot 4\text{H}_2\text{O}$  and TEOA were purchased from Aldrich; they were of analytical grade and were used without further purification.

### 2.2. Physical measurements and instrumentation

Absorption spectra were recorded on a Varian Cary 300B spectrometer at  $25 \pm 0.2$  °C.  $^1\text{H}$  NMR spectra were recorded on a Varian Unity Plus 300 MHz spectrometer. Samples were run in a 5 mm probe with deuterated solvents as the internal lock and reference. FT-IR spectra were recorded on a type Class 1 Laser Product, SHIMADZU FT-IR (Fourier Transform Infrared spectrophotometer) using KBr pellets. Elemental analyses were conducted using a LECO-183 CHNS analyzer.

Cyclic voltammetry was carried out with a Bipotentiostat AFCBP1 from Pine Instrument Company and controlled with the AfterMath software. Experiments were performed using a glassy

carbon (50 mm diameter) disk and  $\text{Ag}/\text{AgCl}/\text{KCl}$  (sat.) as a working and reference electrode, respectively. A thin Pt gauge ( $8\text{ cm}^2$ , Sigma–Aldrich) was employed as a counter electrode. The working electrode was polished using successively 6, 3, 1  $\mu\text{m}$  alumina paste on a DP-Nap polishing cloth (Struers, Westlake, OH), washed with water, acetone and air-dried. The potential sweep rate varied between 50 and 400 mV/s. A 1 mM solution of  $[\text{ReBr}(\text{CO})_3\text{amphen}]$  or  $[\text{ReBr}(\text{CO})_3\text{pq}]$  in 0.5 M  $[\text{TBA}]\text{PF}_6$  in DMF under  $\text{N}_2$  was measured and all potentials are reported versus the ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) couple.

Excited-state emission quenching experiments were carried out with a RF-5301PC (spectrofluorophotometer) of Shimadzu, with a Xe lamp, 1000 W. A 0.5 mM solution of  $[\text{ReBr}(\text{CO})_3\text{amphen}]$  was prepared in DMF. One milliliter of this solution was used to prepare a solution of the desired Co complex,  $[\text{Co}(\text{dmgH}_2)_2]$ , thus  $[\text{Co}(\text{OAc})_2]\cdot 4\text{H}_2\text{O}$  equal to 0.03 M and 6 eq  $\text{dmgH}_2$  were mixed and the solution was degassed with Ar. Three milliliters of the  $[\text{ReBr}(\text{CO})_3\text{amphen}]$  solution was added to a quartz cuvette fitted with a septum and degassed with Ar. The effect of the Co complex on the emission of  $[\text{ReBr}(\text{CO})_3\text{amphen}]$  was monitored by collecting emission spectra between additions of aliquots of the  $\text{Co}/[\text{ReBr}(\text{CO})_3\text{amphen}]$  solution. The spectra were taken by excitation at 465 nm with scanning from 500 to 800 nm. Both emission and excitation slits were set to 5 nm. The same procedure was followed adding TEOA instead of cobaloxime.

Photochemical experiments: All manipulations were conducted under a pure argon atmosphere. Photocatalytic reactions were carried out with a solution of the photocatalysts **1** or **2**, 0.5 mM,  $[\text{Co}(\text{OAc})_2]\cdot 4\text{H}_2\text{O}$  1 mM, an excess of 6 eq of  $\text{dmgH}_2$  per cobalt acetate, AcOH 0.1 M, in the presence of TEOA 1 M, in DMF (30 mL). The solutions were irradiated in an irradiation apparatus at  $\lambda > 335$  nm using a 1000 W xenon (Xe) lamp purchased from Oriol, 68820, Universal Power Supply with an  $\text{H}_2\text{O}$  filter. The evolved  $\text{H}_2$  was analyzed by a BRUKER 30-GC (gas chromatographer) with a TCD detector operating at 150 °C and a CP-Molsieve 5A, PLOT fused silica column. The gas flow was set at 10 mL/min. The oven operated at 40 °C and the injector at 70 °C. The 50  $\mu\text{L}$  gas samples were injected using a Hamilton CO (1710 RN) gastight microliter syringe.

### 2.3. Crystal structure determination

Single red-brown crystals of **2** suitable for X-ray structure determination were grown by layering of n-hexane onto a concentrated dichloromethane solution of the complex. A summary of the data collection and structure refinement for  $[\text{ReBr}(\text{CO})_3\text{pq}]$  (**2**) is reported in Table 1. Single crystal data were collected with a Bruker Smart Breeze area detector diffractometer (Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073$  Å). Cell constants were obtained using 60  $\omega$ -frames of  $0.5^\circ$  width and scanned from three different zones of the reciprocal lattice. The intensity data were integrated from several series of exposure frames ( $0.3^\circ$  width) covering the sphere of reciprocal space [37]. The crystals were affected by twinning and an absorption correction was applied using the program TWINABS [38]. The structure was solved by direct methods [39] and refined on  $F^2$  with full-matrix least squares (SHELXL-2014) [40], using the Wingx software package [41]. Non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at their calculated positions. Graphical material was prepared with the MERCURY 3.5.1 program [42].

### 2.4. Synthesis of the Re(I) complexes

#### 2.4.1. $[\text{ReBr}(\text{CO})_3\text{amphen}]$ (**1**)

The complex  $[\text{ReBr}(\text{CO})_3\text{amphen}]$  (**1**) was synthesized according to the literature procedures [25,34]. Yield: 85.46%.  $^1\text{H}$  NMR

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