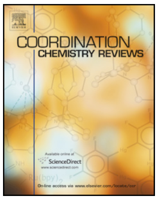
Coordination Chemistry Reviews 304–305 (2015) 73–87

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Transition metal complexes with N-heterocyclic carbene ligands: From organometallic hydrogenation reactions toward water splitting

Simon Kaufhold[1], Lydia Petermann[1], Robert Staehle[1], Sven Rau*

Institute of Inorganic Chemistry, Materials and Catalysis, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany

Contents

ARTICLE INFO

Article history:
Received 1 August 2014
Received in revised form 4 December 2014
Accepted 7 December 2014
Available online 13 December 2014

In Memoriam Karen J. Brewer.

Keywords:
Photocatalysis
N-heterocyclic carbenes
Ruthenium
Organometallic catalysis
Water splitting

ABSTRACT

N-Heterocyclic carbenes (NHCs) as a new class of ligands for the stabilization of catalytic metal complexes for catalytic water splitting are discussed. An overview over current applications of NHC stabilized metal catalysts in organometallic catalysis involving hydrogen in transfer hydrogenation, hydrogenation and acceptorless dehydrogenation is presented. A focus is placed on the role of the NHC ligand structure and utilized metal centers. The current status of NHC stabilized catalytic centers within the inter- and intramolecular photocatalytic hydrogen formation and water oxidation is reviewed. The very interesting photochemical properties of a new class of ruthenium complexes with NHC-carbene containing potential bridging ligands are discussed. These complexes can bind catalytic metal centers at the NHC sphere. The so formed photochemical devices are active photocatalysts for hydrogen evolution.

Abbreviations: A, acceptor; AD, acceptorless dehydrogenation; aNHC, abnormal *N*-heterocyclic carbene; AP, artificial photosynthesis; bip, 1-benzyl-1*H*-imidazo[4,5-*f*][1,10]phenanthroline; bbip, 1,3-dibenzyl-1*H*-imidazo[4,5-*f*][1,10]phenanthrolinium; CAN, cerium ammonium nitrate; cod, 1,5-cyclooctadiene; C_{ox}, oxidation center; C_{red}, reduction center; D, donor; DABCO, 1,4-diazabicyclo[2.2.2]octan; Et_2BzIm, 1,3-diethyl-1*H*-benzo[*d*]imidazol-3-ium; erNHC, expanded ring NHC; FTO, fluorine-doped tin oxide; ip, 1*H*-imidazo[4,5-*f*][1,10]phenanthroline; M, metal; MA, maleic anhydride; mmip, 1,3-dimethyl-1*H*-imidazo[4,5-*f*][1,10]phenanthrolinium; N,N′, 2,2′-bipyridine or 1,10-phenanthroline; NADPH, reduced nicotinamide adenine dinucleotide phosphate; NHC, *N*-heterocyclic carbene; P, photocenter; PMD, photochemical molecular device; tbbpy, 4,4′-di-*tert*-butyl-2,2′-bipyridine; TH, transfer hydrogentation; TON, turnover number; X, coordinated solvent.

* Corresponding author. Tel.: +49 731 5023900; fax: +49 731 5023039.
E-mail address: sven.rau@uni-ulm.de (S. Rau).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.ccr.2014.12.004

1. Introduction

It is widely agreed that climate change and shortage of fossil fuels are some of the major challenges for present and future generations alike. The carbon dioxide (CO_2) concentration in the atmosphere has been rising steadily since the beginning of the industrial revolution [1]. As a result the current CO_2 level is the highest in at least the past 800,000 years and a concomitant rise in average temperature and sea level has been witnessed [2–4]. Although resources of fossil fuels are expected to last something between decades and centuries the availability of cheap fossil energy will undeniably come to an end and thus alternative energy sources are necessary [5–7]. Of the alternative energy sources like geothermal, wind and hydro power, solar energy is the most outstanding due to the tremendous amount of energy the solar irradiation provides on the earth's surface [5]. However the great challenge of efficiently capturing and storing solar energy remains unsolved. One of the most promising approaches to tackle future energy supply problems as well as climate issues is capturing and converting solar energy into chemical energy by mimicking natural photosynthesis. In artificial photosynthesis (AP) water would be split into hydrogen (H_2) as the product of reduction – similar to NADPH in natural photosynthesis – and oxygen (O_2) as the product of oxidation. Among the different methods of AP the use of molecular assemblies in a homogenous system is a very promising approach. The principle setup of a homogeneous AP system is shown in Fig. 1. A photosensitizer P is brought into an electronically excited state by absorption of light. By charge separation an electron can be transported over an electron relay to the reduction center C_{red} where generation of H_2 from protons can take place. The oxidized photosensitizer is reduced by electrons shuttled from the oxidation center C_{ox} where water is split into O_2 and protons. The advantage of this system consisting of different building blocks is that each assembly can be modified and investigated separately and thus enables systematic optimization. This concept has been very successful in improving a wide range of organometallic catalytic reactions [8].

This overall water splitting in a single system is very challenging as it is composed of a 4-electron oxidation step and a 2-electron reduction step. Furthermore reactive intermediates can be formed during the reaction and might deactivate or damage the system especially in the case of the oxidation reaction [9–11]. Thus, it is helpful to simplify the operation by separating both half-reactions and investigate them discretely in order to gain deeper insight into the underlying processes. Although heterogeneous systems for catalytic overall water splitting are known, we will focus on concepts with separated half-reactions and molecular catalysts in this article.

To be able to carry out the reduction or oxidation separately it is necessary to add a sacrificial electron donor or acceptor to the system, respectively (Fig. 2).

One of the first molecular system for water reduction was reported by Lehn and Sauvage in the late 70ies using ruthenium and rhodium bipyridine complexes and colloidal platinum [12]. A few years later Meyer *et al.* introduced the “blue dimer” a binuclear ruthenium bipyridine complex for water oxidation [13].

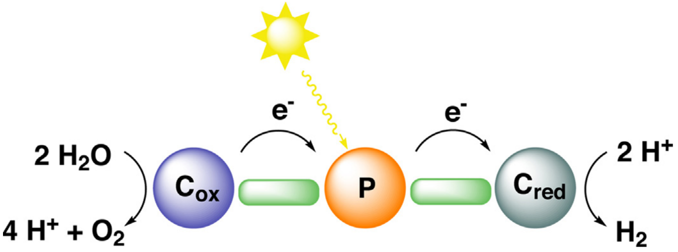


Fig. 1. General setup of an artificial photocatalytic system composed of oxidation catalyst C_{ox}, photosensitizer P and reduction catalyst C_{red}.

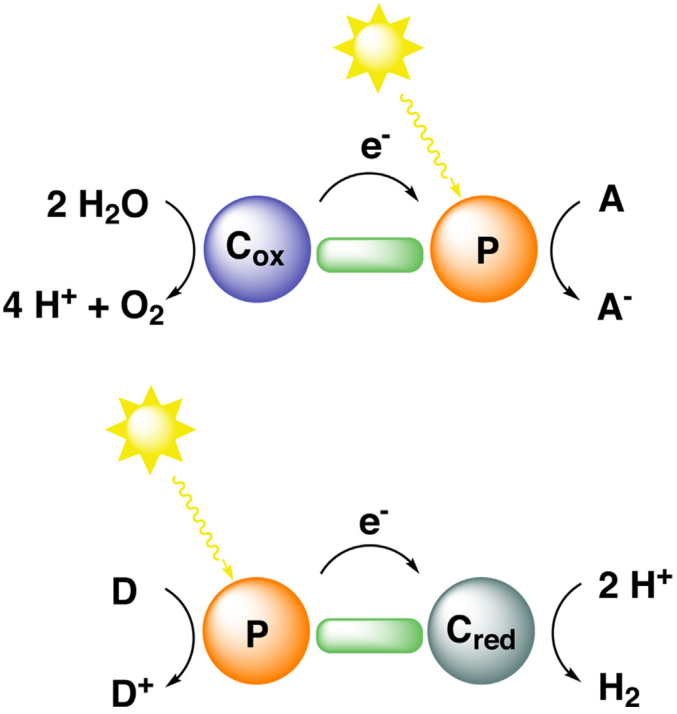


Fig. 2. Half-reactions for water oxidation and reduction.

Since then and especially in the past decade homogeneous photocatalytic water splitting has prospered significantly. This is due to deeper insight in underlying mechanisms as a result of more sophisticated spectroscopic and computational methods and the tunability of these systems by advanced synthetic approaches, as highlighted in several reviews [10,11,14–19].

All the early concepts feature intermolecular systems where each task (light absorption, electron mediation and catalytic turnover) are carried out by individual molecules and thus relying on collision processes for energy/electron transfer. Hence, efficiency is limited by diffusion and collision probability. More recently the concept of supramolecular catalysts – where the different moieties are linked to each other – found more and more favor [10,20–25]. An assembly like this can also be considered as a photochemical molecular device (PMD) where each part performs a certain task [26]. The complete device gives then insight into a structure and function correlation and underlying processes e.g. directional electron transfer. For better comparison of the individual catalytic systems the amount of product produced is correlated to the amount of catalyst used. This is usually reported in turnover numbers (TON = number of product molecules per catalyst molecule).

Apart from efficient photosensitizers and catalytic centers the bridging ligand plays an important role in the catalytic process [22,27]. Firstly it needs to be able to bind to the photocenter without altering the optical absorption behavior in order to sustain the function of the sensitizer. Secondly it has to be able to transfer electrons e.g. by an extended π-system and thirdly it has to bind and stabilize the catalytic center in different oxidation states to support the catalytic cycle [27]. The last aspect seems to be crucial as colloids are formed under catalytic conditions in some cases, indicating insufficient binding of the bridging ligand to the metal center in its reduced/oxidized state [22,28,29].

N-heterocyclic carbenes (NHCs) have become renowned ligands stabilizing high valence transition metal centers in complexes as