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Review

# Cobalt complexes as artificial hydrogenases for the reductive side of water splitting ☆

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## ABSTRACT

The generation of $H_2$ from protons and electrons by complexes of cobalt has an extensive history. During the past decade, interest in this subject has increased as a result of developments in hydrogen generation that are driven electrochemically or photochemically. This article reviews the subject of hydrogen generation using Co complexes as catalysts and discusses the mechanistic implications of the systems studied for making $H_2$. This article is part of a Special Issue entitled: Metals in Bioenergetics and Biomimetics Systems.

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## 1. Introduction

### 1.1. Background

In nature, photosynthesis plays the essential role of converting solar energy into stored chemical energy in the form of fuels and oxygen that sustains life on Earth. Through photosynthesis in plants and photosynthetic bacteria, $CO_2$ and water ($H_2O$) are converted into carbohydrates and oxygen via a series of photochemical and thermally-driven electron transfer reactions and dark catalytic reactions [1–3]. There are two related photosystems in photosynthesis [2,4] (Fig. 1, Z-scheme): Photosystem I (P700) and Photosystem II (P680). When Photosystem I is excited by sunlight, an electron transfer (ET) process is induced to reduce a series of electron acceptors, such as, phylloquinone and ferredoxin, ultimately reducing the cofactor $NADP^+$ (nicotinamide adenine dinucleotide phosphate) to NADPH (biological hydrogen) and Photosystem I is oxidized. NADPH is both the electron source and a partial proton source for $CO_2$ transformation into carbohydrates in the Calvin cycle [5]. Oxidized Photosystem I is regenerated by obtaining electrons from Photosystem II through several electron relays, such as, plastoquinone, cytochrome *f* and plastocyanine. The oxidized Photosystem II mediates another important reaction — water oxidation to produce oxygen, catalyzed by a $CaMn_4O_4$ cluster [6–8].

Inspired by nature, the development of renewable carbon-free energy using the sun is a major scientific and technological challenge in meeting the energy needs of the future. Efficient solar cells (that is, solid state photovoltaic devices and dye-sensitized solar cells) and solar-driven water splitting systems represent two major objectives in utilizing solar energy [9]. While solar cells can directly convert solar radiation into electricity, they cannot store energy [10]. On the other hand, solar-driven water splitting can store energy in the form of fuel ($H_2$) and oxidant ($O_2$) [11,12]. Energy storage in chemical bonds is most efficient, and as a consequence, this strategy for solar energy storage has attracted great attention during the past three decades. Hydrogen is an environmentally-friendly energy carrier because its only oxidation product is $H_2O$. Through widespread use of $H_2$ as a fuel, generated either directly in an artificial photosynthetic system or by electrolysis using solar-generated electricity, dependence on fossil fuels can be decreased, with a corresponding decrease in $CO_2$ emissions.

Water splitting is actually an oxidation–reduction reaction that can be divided into its two half reactions — the reduction of water protons to $H_2$ and the oxidation of water to $O_2$. For each half reaction, the following components are needed: (1) a light absorber that undergoes electron transfer upon excitation; (2) an electron relay or
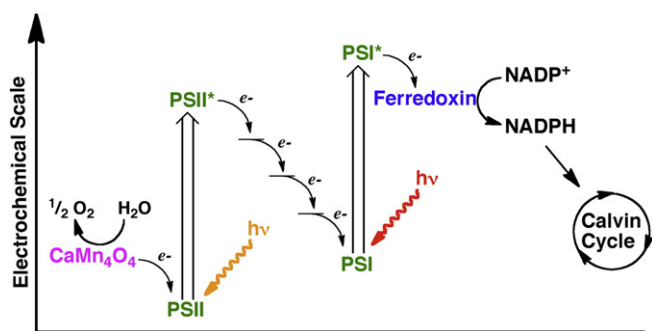
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**Fig. 1.** Z-scheme of biological photosynthesis.

pathway that proceeds favorably in one direction so that reducing equivalents or oxidizing equivalents are transferred to the respective catalysts; and (3) a catalyst for carrying out the desired oxidative or reductive half reactions. The half reaction systems may also have other components such as an antennae assembly so that a greater fraction of incident photons are absorbed with the energy subsequently transferred to the light absorber that undergoes electron transfer upon excitation.

It is generally acknowledged that because water oxidation to $O_2$ involves an overall four-electron transformation coupled with the loss of four protons from two water molecules and the formation of an oxygen–oxygen bond [13], it is the more difficult half reaction to carry out. However, a viable system for the light driven generation of $H_2$ from water has not been achieved to date in terms of the levels of activity and robustness for real development into a practical water splitting system.

In order to study each half-reaction system in detail and optimize the performance of individual components contained therein, a source of electrons for the reductive side or oxidizing equivalents (holes) for the oxidation side is added to the system as well. If this is done by the addition of another chemical component to the system, it is best done with a compound that undergoes irreversible decomposition upon oxidation or reduction to prevent back electron transfer. If the former, the component is a sacrificial electron donor, and if the latter, it is a sacrificial electron acceptor, but neither of these components is capable of driving the respective half reaction from a thermodynamic standpoint.

The key challenge for each light-driven half reaction includes the following: (1) whether the excited state of the light absorber is capable of electron transfer at the potential need for the particular catalyst to carry out the half-reaction; (2) whether the catalyst is capable of accumulating charge for the desired transformation; (3) the long-term stability of all system components during irradiation to see if they are viable for long-term operation; (4) the levels of activity for photoinduced electron transfer and product generation; and (5) the mechanism by which the system operates to prolong overall system stability.

In earlier studies of the light-driven generation of $H_2$, colloidal Pt was employed as the catalyst, either stabilized in solution by different polymers such as polyvinyl alcohol or polyvinylpyrrolidone or attached to semiconductor nanoparticles by platinization (one example is platinized $TiO_2$). Platinum as an electrode material has a low overpotential for the electrochemical generation of $H_2$ in aqueous or aqueous/organic solutions of different levels of acidity, and it was found to operate satisfactorily in colloidal form for the light-driven production of $H_2$ from water. However, it is widely accepted that platinum must be replaced by cheaper materials because of its high price and very low earth abundance [14]. Hence, the development of efficient catalysts for water reduction to $H_2$ made from of inexpensive, earth-abundant elements has become a prime focus of research on artificial photosynthesis and light-driven hydrogen generation.

During the past 15 years, efforts on this front have focused on complexes of iron, nickel and cobalt as possible catalysts [15–17].

The studies involving iron-containing catalysts are generally related to models of the active sites of hydrogenase enzymes that feature two iron atoms bridged by a dithiolate ligand such as 2-aza-1,3-propanedithiolate or benzene-1,2-dithiolate. The other ligands bound to the iron centers in these model compounds include CO and $CN^-$ with other coordination sites occupied by cysteine or phosphine. A second class of hydrogenase enzymes contain Fe and Ni ions, which are similarly bridged by thiolate donors and contain CO and possibly $CN^-$ bound to the Fe center. The catalytic properties of Ni complexes for $H_2$ generation electrocatalytically has been developed most extensively over the past decade by DuBois and coworkers beginning with a mononuclear complex that possesses chelating ligands capable of functioning in a manner similar to 2-aza-1,3-propanedithiolate for proton delivery to a Ni-bound hydride ligand. The chemistry and electrocatalytic studies of the Fe hydrogenase model compounds is reviewed in Chapter 8 while the Ni systems are covered in Chapter 9.

In this section, we focus on the recent progress achieved using cobalt complexes as artificial hydrogenases for the generation of $H_2$ from protons and electrons. Complexes of cobalt, their interactions with hydrogen and the existence of cobalt hydride species have a long history from the original discoveries of $Co_2(CO)_8$ reacting with $H_2$ to form $CoH(CO)_4$ by Hieber [18] and the seminal work on hydrogenation catalysis by $Co(CN)_5^{3-}$ that involved the formation of $CoH(CN)_5^{3-}$ [19–21]. In the 1970s, work by Schrauzer on model compounds for the active site of Vitamin $B_{12}$ led to the study of bis(dimethylglyoximate)cobalt complexes termed cobaloximes (Fig. 2), hydridocobaloximes and the observation of hydrogen evolution from such species [22]. In 1986, Espenson and Connelly found that hydrogen was formed by reaction of the related complex **3** (Fig. 4) with $Cr^{2+}$ reductants in an acidic medium [23]. These reports set the stage for the numerous studies that have been published in the past decade dealing with hydrogen generation promoted by cobalt complexes upon electrochemical reduction or as part of photochemical systems in which electrons are supplied chemically by a sacrificial electron donor. Different series of Co catalysts that have been employed in electrocatalytic and photocatalytic water splitting will be described in detail, and the mechanisms of the catalysis of hydrogen formation will be analyzed based on most recent information. A review article by Artero has recently been published on the electrocatalytic generation of $H_2$ using Co complexes, but much of the emphasis in that article is on studies in non-aqueous media in which protons are supplied in the form of weak or strong acids [24]. In this section, we will concentrate more on both photochemical and electrochemical work in which the proton source is water or acid and either aqueous or aqueous organic solvents are employed.

### 1.2. Key considerations for $H_2$ formation in photochemical and electrochemical systems

With a number of different photochemical systems described using various Co complexes as catalysts and with an even greater
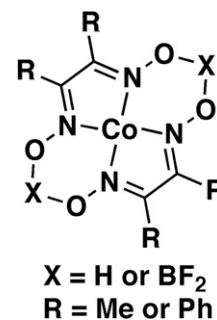


X = H or $BF_2$
R = Me or Ph

**Fig. 2.** Generic cobaloxime complex.

number of studies relating to electrocatalytic $H_2$ generation, it is valuable to compare and analyze the results regarding the mechanism of $H_2$ formation in order to gain insight for further progress on this important problem. It is important to recognize that while the photochemical and electrochemical studies of $H_2$ generation have key points in common, they also have critical differences and employ different metrics of evaluation. Overpotential and catalytic current are often used as measures of success with regard to electrochemical systems whereas quantum yield represents an important metric of efficiency photochemically. In a photochemical system, the potential at which the reducing electron is supplied to the catalyst is determined by the excited state and ground state properties of the light absorber and electron donor, respectively — it is not continuously variable as in an electrocatalytic system. There are even questions that exist in comparisons between different studies of electrocatalytic $H_2$ generation or between studies of light-driven hydrogen generation. Turnover numbers and turnover frequencies may be relevant for comparisons between systems examined under exactly the same set of conditions, but they can be difficult to compare directly from different laboratories because of subtle but significant differences such as electrode preparation and photon flux. The medium plays a critical role in defining these systems with one set of studies conducted in non-aqueous media with protons supplied by organic acids and another set of studies in aqueous or mixed aqueous organic media.

Furthermore, the use of organic acids in non-aqueous solutions has caused large inconsistencies in reporting overpotentials for catalysts [25]. The various different methods for calculating overpotential in organic media can lead to differences of up to 200 mV. Homoconjugation is a phenomenon that occurs when the conjugate base is stabilized by a hydrogen bond to the acid. It increases the acidity of this proton and leads to the calculation of an overpotential that is much smaller than the actual value. Artero and coworkers have reported a method of calculating overpotential that relies on taking the half-wave potential as the reference and correcting for the homoconjugation of the particular acid used in the study [25]. Furthermore, the $pK_a$ of the acid employed for electrochemical reduction has a substantial effect on the thermodynamic potential of proton reduction, arising from the differences in proton dissociation in various solvents [26]. Recognition of these factors is a critical step in normalizing the way that electrocatalytic performance is described.

## 2. Electrocatalytic production of hydrogen

### 2.1. Background

Numerous cobalt complexes including systems containing macrocyclic and polypyridine ligands had been reported as catalysts for hydrogen generation from proton sources upon electrochemical reduction more than twenty years ago [27–32]. In most of these early studies, the proton source was an organic acid such as triflic acid (HOTf) or anilinium salts, rather than water. In one of the earliest of these studies, cobalt macrocyclic complexes (Fig. 3, **1** and **2**) were studied for indirect electrocatalytic reduction of $CO_2$. It was found in this study that the presence of water was essential for $CO_2$ reduction and both CO and $H_2$ were produced [27]. The potentials at which the reductions occurred were $-1.5$ to $-1.6$ V vs. SCE, with up to 93% current efficiency, but total turnover numbers (TON) and turnover frequencies (TOF) were low.

### 2.2. Cobalt tetraimine ($CoN_4$) complexes

Based on the studies by Espenson and coworkers on the chromous ion reduction of **3** to give hydrogen [23], Peters and coworkers [33,34] examined **3** as an electrocatalyst for proton reduction in nonaqueous media with trifluoroacetic acid (Fig. 4). The complex was found to function very effectively for hydrogen generation with a very low
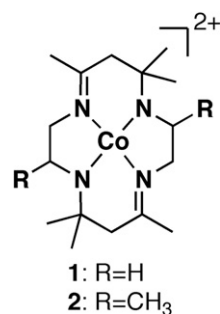


**Fig. 3.** Cobalt complexes used for electrocatalytic $CO_2$ reduction.

overpotential (~40 mV) for proton reduction ($E_{H+/H} = -0.55$ V vs. SCE). However, the related diphenylglyoxime complex (**4**) had a more positive $Co^{II}/Co^I$ redox couple of $-0.28$ V and exhibited lower electrocatalytic activity. This trend was validated when examining several tetraimine macrocyclic complexes (**5–7**), which had $Co^{II}/Co^I$ reduction potentials ranging from $-0.08$ to $-0.40$ V.

Complexes with more positive potentials for proton reduction were not only found to have lower activity, but also required stronger acids for the reduction to occur. In related investigations from the laboratory of Artero and Fontecave [35,36] for electrocatalytic proton reduction, the cobaloxime complexes of the type $[Co(dmgBF_2)_2(OH_2)_2]$ (**8**) and $[Co(dmgH)_2LCl]$ (**9**) were also investigated in non-aqueous media (Fig. 5). In order to understand the effect of electron donating or withdrawing substituents of the glyoxime and axial ligands on electrocatalytic activity, a series of derivative complexes were examined. It was found that substitution of phenyl for methyl on the glyoxime ligand resulted in a less cathodic electrochemical potential for the $Co^{II}/Co^I$ couple, but it was also observed that lower electrocatalytic activity resulted from this change. A similar trend was observed for the $BF_2$-modified glyoxime ligands. In this way, the complexes studied by both groups of investigators exhibited the same general trend. Subsequent work by these investigators for the *photo*chemical generation of $H_2$ using these cobaloxime catalysts is described below [37–39].

In a different study, Stubbert et al. [40] have found that a cobalt bis(iminopyridine) complex (Fig. 6, **10**) in which the ligand is redox active exhibits good activity for proton reduction in aqueous media. Faradaic hydrogen yields up to $87 \pm 10\%$ were obtained under constant potential electrolysis at $-1.4$ V vs. SCE in aqueous buffered solutions. The complex was found to be electroactive over a wide pH range with the initial step being reduction from $Co^{2+}$ to $Co^+$ in a formal sense. Several different pathways for $H_2$ formation were postulated depending on the specific pH value and the involvement of the ligand in the actual redox process. Ligand protonation is also a possible factor relative to protonation at the $Co^+$ ion in the analysis.
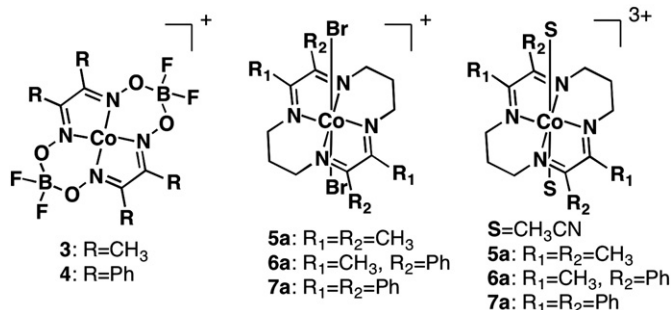


**Fig. 4.** Tetraiminemacrocyclic complexes for electrocatalytic proton reduction.
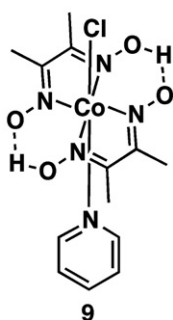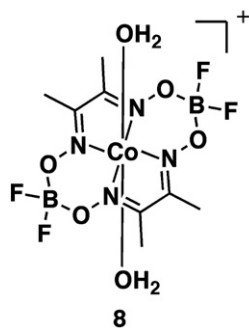
Fig. 5. Difluoroboryl- and diglyoxime cobalt complexes used as electrocatalysts.



Fig. 7. Polypyridine cobalt complexes used in electrocatalysis of hydrogen.

To combat problems associated with ligand instability of Co(dmgH)$_2$ complexes in acidic conditions, complexes **11**–**13** were examined as electrocatalysts in acidic aqueous solution. While [Co(dmgH)$_2$Br(H$_2$O)] was found to be inert in these conditions, cyclic voltammetry experiments with the di-imine diglyoximate complexes **11** and **12** showed catalytic waves at −0.76 V. The nature of the counterion in **11** and **12** (ClO$_4^-$ and coordinated Br$^-$, respectively) was inconsequential as both complexes exhibited similar activity under electrolysis conditions with a dependence of the Co$^{III}$/Co$^{II}$ potential on solution pH corresponding to approximately 60 mV per pH unit. Both complexes exhibited 80% Faradaic efficiencies for hydrogen production in controlled potentiometry experiments. Less impressive results were noted with complex **13**. A Nernstian relationship with pH suggested that the Co$^{II}$/Co$^I$ reduction was aided by protonation of the cobalt complex, possibly at the glyoxime oxygen.

## 2.3. Polypyridine cobalt complexes

Cobalt complexes bearing pyridine based ligand structures were first introduced as proton reduction catalysts by Bigi et al., using [Co(Py4)CH$_3$CN] (Fig. 7, **14**) (Py4 = 2-bis(2-pyridyl)(methoxy)methyl-6-pyridylpyridine). In conjunction with trifluoroacetic acid, current enhancements corresponding to proton reduction with 99% Faradaic yields were observed in both organic or acetonitrile:water [41]. Building on this work, as well as the recent success of [MoO(Py5Me2)] (Py5Me2 = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine) as an electrocatalyst for hydrogen production [42], [Co(Py5Me2)(CH$_3$CN)$_2$] (**15**) was found to reduce protons efficiently over a period of 60 h without signs of catalyst degradation [43]. A TON of 55,000 was calculated for this system based on the bulk concentration of catalyst but this number may not be readily comparable to other electrocatalysts based on different assumptions for the TON calculation.

## 2.4. Other cobalt complexes

In the realm of Ni complexes as active electrocatalysts for H$_2$ generation, the efforts of DuBois and coworkers using **16-Ni** (Fig. 8) and related complexes are notable [44–49]. However, the cobalt analog
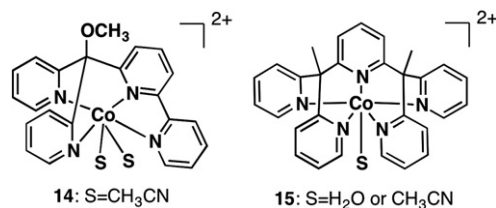


Fig. 6. Cobaloxime derivatives explored as electrocatalysts.

[Co(P$^{Ph}_2$N$^{Ph}_2$)$_2$CH$_3$CN][BF$_4$]$_2$, **16-Co**, was found to partially dissociate a P$^{Ph}_2$N$^{Ph}_2$ ligand during the course of electrocatalysis and form [Co(P$^{Ph}_2$N$^{Ph}_2$)(CH$_3$CN)$_3$][BF$_4$]$_2$. While electrocatalytically active in the presence of triflic acid in acetonitrile solution, [Co(P$^{Ph}_2$N$^{Ph}_2$)(CH$_3$CN)$_3$] [BF$_4$]$_2$ was found to have a relatively large overpotential (285 mV) when using bromoanilinium tetrafluoroborate as the proton source [46]. The turnover frequency of this complex was also low (90 s$^{-1}$) compared to the related Ni complex and its derivatives (up to 100,000 s$^{-1}$) [49]. To calculate turnover frequency, cyclic voltammetry experiments were performed in the presence of [(DMF)H]OTf, which served as a proton source. A catalytic wave was observed at −1.00 V vs. the ferrocene/ferrocenium couple corresponding to proton reduction. The relationship between the current at the top of the catalytic wave ($i_c$) and the one electron $i_p$ of the catalyst (taken in the absence of acid) provided an accurate measurement of TOF based on the equation shown below where $\nu$ = scan rate:

$$\frac{i_c}{i_p} = \frac{n}{0.4463(RTk[H^+]/F\nu)^{1/2}}.$$

This equation was further simplified by taking into account that $n = 2$ for the two electron reduction of protons to hydrogen as well as the pseudo-first order conditions with respect to nickel complex ($k[H+] = k_{obs}$). For the case with **16-Ni**, these studies were carried out in a regime where current was scan rate independent ($>5$ V/s), but the studies with **16-Co** and its tris(acetonitrile) analog were done at slower scan rates. The observed rate of hydrogen formation was therefore expressed as:

$$k_{obs} = \nu\left(\frac{i_c/i_p}{0.72}\right)^2.$$

A series of cobalt porphyrin complexes with xanthene substituents (Fig. 8, **17** and **18**) were investigated as electrocatalysts in the presence of benzoic acid and tosic acid. Measured overpotentials in these systems were much larger than other cobalt complexes mentioned above (~800 mV). Interestingly, the presence of a carboxylic acid group on the xanthene moiety positioned near the axial position of cobalt was found to have a drastic effect on catalysis, lowering overpotentials by 120 mV [50]. This "hangman effect" was found to assist proton coupled electron transfer (PCET), facilitating hydrogen production. Rates of PCET were found to be three orders of magnitude faster when a carboxylic acid functionality is present in proximity to cobalt [51].

## 2.5. Mechanistic considerations of electrocatalytic generation of hydrogen

The initial work performed to elucidate the mechanism of cobalt catalyzed hydrogen production was reported by Chao and Espenson, who examined the kinetically stabilized cobaloxime hydride [HCo$^{III}$(dmgH)$_2$P(n-Bu)$_3$] [52]. The reaction of this complex with HClO$_4$ liberates H$_2$ and a kinetics study revealed first order kinetics at low Co concentration and second order kinetics at higher [Co]. The results were interpreted to mean that two parallel paths
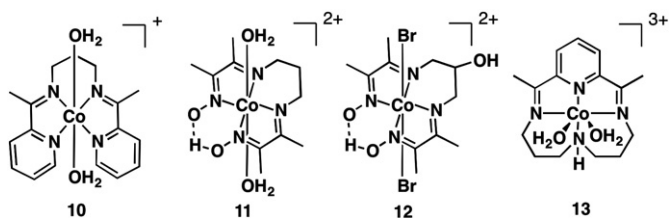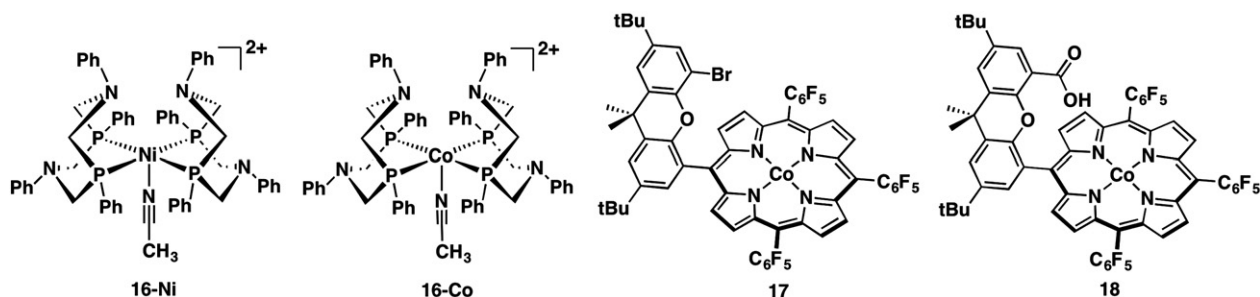
**Fig. 8.** Highly active nickel electrocatalyst, cobalt derivative, and cobalt porphyrin complexes.

for H₂ formation existed that involved heterolytic Co–H cleavage and homolytic Co-H cleavage, respectively. The former proceeded by protonolysis of the Co-H bond whereas the latter, which had a second order rate constant of $1.7 \times 10^4$ M$^{-1}$ s$^{-1}$, occurred by the coupling of two Co–H species to yield H₂ + 2 Co$^{II}$. Deuterium labeling of the hyridocobaloxime complex and analysis of the product hydrogen supported these conclusions.

Because the (dmgH)₂ "framework" of the cobaloxime complexes was acid sensitive whereas the (dmgBF₂)₂ pseudomacrocycle proved stable to H₃O⁺, subsequent studies on H₂ generation were conducted on Co complexes of the latter. Connolly and Espenson showed that hydrogen could be evolved catalytically with [Co$^{II}$(dmgBF₂)₂] in the presence of HCl with CrCl₂ as a sacrificial reductant [23]. From this work they proposed formation of [Co$^{I}$(dmgBF₂)₂]⁻, generated by reduction of Co$^{II}$ by Cr$^{II}$, as the catalytically active species. Co$^{I}$ complexes were previously reported to rapidly react in acidic conditions to yield Co$^{III}$H [53]. The relatively slow catalytic turnover was attributed to the reduction of Co$^{II}$ to the [Co$^{I}$(dmgBF₂)₂]⁻ intermediate via inner sphere electron transfer. Following protonation to HCo$^{III}$, subsequent formation of hydrogen was proposed by monometallic and bimetallic pathways as proposed for [HCo$^{III}$(dmgH)₂P(n-Bu)₃].

These observations and conclusions were used by Hu et. al. in their studies of [Co$^{II}$(dmgBF₂)₂] and its diphenyl derivative for the *electro*catalysis of hydrogen production in the presence of trifluoroacetic acid, thereby eliminating the slow step in the catalysis [33,34]. A reduction wave corresponding to the catalytic reduction of protons was observed close to the Co$^{II}$/Co$^{I}$ couple, supporting the earlier conclusion that [Co$^{I}$(dmgBF₂)₂] was indeed the catalytically active species. Furthermore, evidence of a HCo$^{III}$ was suggested due to the appearance of a quasi-reversible reduction wave after reduction of Co$^{II}$ in the presence of acid [34].

In separate studies of [Co$^{III}$(dmgH)₂(py)Cl] and [Co$^{II}$(dmgBF₂)₂] as electrocatalysts in nonaqueous media with protons provided by an organic acid, Artero, Fontecave and coworkers modeled and analyzed cyclic voltammograms. Their results pointed to a monometallic (heterolytic) pathway for H₂ generation [35,36]. The species for the final protonation was found to depend on the strength of acid used (Fig. 9). For strong acids, hydrogen was thought to evolve from the HCo$^{III}$ complex, whereas for acids with intermediate strength, final protonation occurred after reduction of HCo$^{III}$ to HCo$^{II}$. For very weak acids, Co$^{I}$ was thought to be further reduced to Co$^{0}$ before protonation to HCo$^{II}$ followed by a second protonation [36]. A theoretical analysis of the [Co$^{II}$(dmgBF₂)₂] system by Muckerman and Fujita focusing on the reduction potentials and basicity of different species proposed in hydrogen production led to the conclusion that for that system hydrogen generation proceeded by reduction of HCo$^{III}$ to HCo$^{II}$ prior to protonation to form H₂ [54]. Another analysis of similar cobalt macrocyclic complexes with N [2],N$^{2}$'-propanediylbis(2,3-butanedione 2-imine 3-oxime) indicated again a strong preference for heterolytic Co–H cleavage [55,56].

Support for the bimetallic pathway for cobalt difluoroboryl substituted glyoxime complexes was reported by Dempsey et al., by calculation of Co$^{III}$/Co$^{II}$ and Co$^{II}$/Co$^{I}$ self-exchange rates, which allowed for the

determination of activation barriers and thermodynamic driving forces for two possible pathways: the bimetallic mechanism of coupling two HCo$^{III}$ to give H₂ + 2 Co$^{II}$ and a monometallic mechanism involving protonation of HCo$^{III}$ as for strong acids in Fig. 9 [57]. A large activation barrier was found for the hydrogen-forming step in the latter path, clearly pointing to the bimetallic route as the dominant mechanism. The pathway that was not considered was that of HCo$^{III}$ reduction to HCo$^{II}$. This mechanistic route was validated by subsequent work where photoexcited bromonapthol was employed to protonate [Co$^{I}$(dmgBF₂)₂] [58]. The formation of [HCo$^{III}$(dmgBF₂)₂] was observed by transient absorption spectroscopy with a rate constant of formation of ~$4 \times 10^9$ M$^{-1}$ s$^{-1}$, in good agreement with Espenson's earlier findings. Excess Co$^{I}$ subsequently reduced the HCo$^{III}$ to HCo$^{II}$ before hydrogen was evolved via heterolytic coupling with a proton from bromonapthol. Other computational studies in addition to the work of Muckerman have also identified the monometallic pathway of HCo$^{III}$ reduction to HCo$^{II}$ prior to protonation as the most likely mechanism for hydrogen production with cobaloxime complexes [59–61].

Recent work by Marinescu et al., investigated the heavily stabilized Co$^{I}$ complex [Co(triphos)CH₃CN][PF₆] (triphos = 1,1,1-tris (diphenylphosphinomethyl) ethane) to elucidate key mechanistic details of hydrogen production [62]. Addition of tosic acid to this Co$^{I}$ complex was found to generate HCo$^{III}$, Co$^{II}$, and H₂ as observed by ¹H NMR. Conversion of HCo$^{III}$ to Co$^{II}$ was found to have second order dependence in [Co], eliminating the possibility a monometallic reaction of HCo$^{III}$ and a proton. Additionally, an inverse dependence in acid concentration indicated that bimetallic coupling of two HCo$^{III}$ complexes was unlikely to be a dominant pathway. Ultimately, kinetic modeling coupled with experimental and simulated cyclic voltammetric data unequivocally supported a mechanistic route in which HCo$^{III}$ was reduced by Co$^{I}$ to form HCo$^{II}$ and subsequent reaction with a proton to form H₂, which agrees well with the kinetic observations.
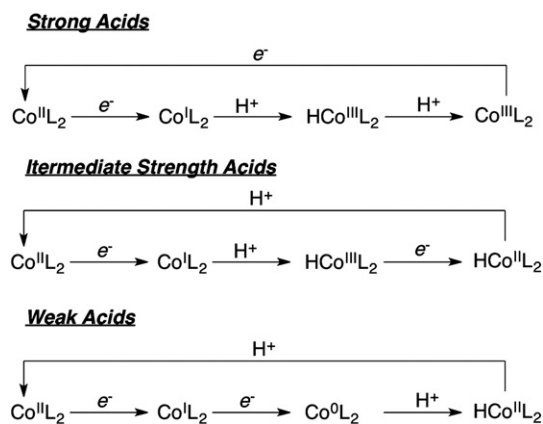


**Fig. 9.** Mechanistic dependence on acid strength.

# 3. Light-driven generation of hydrogen in systems using cobalt complex catalysts

## 3.1. Background

In the photochemical cycle, shown in Fig. 10, a photosensitizer (PS) is excited upon photon absorption, enhancing its reactivity. The excited PS (PS*) can be reductively quenched by a chemical electron donor, generating PS$^-$, followed by electron transfer to a proton reduction catalyst. On the other hand, PS* can be oxidatively quenched by either a metal centered catalyst or electron relay, producing PS$^+$, which is reduced to PS by the chemical electron donor. The relative stabilities of PS$^-$ and PS$^+$ may be quite different, a fact that seriously impacts the durability of photochemical systems as discussed further below.

## 3.2. Cobalt bipyridine complexes

In 1981, the first photocatalytic system using a cobalt complex as the catalyst was reported by Krishnan and Sutin, in which the catalyst was $[Co(bpy)_n]^{2+}$ ($n$ = undefined), $[Ru(bpy)_3]^{2+}$ (**20**) was the photosensitizer, and ascorbic acid served as the sacrificial electron donor (Fig. 11) [28]. A quantum yield of 13% was achieved for $H_2$ generation with visible light irradiation at 420 nm. During the reaction, laser flash photolysis was used to monitor the reaction intermediates and a Co(I) bipyridine intermediate was identified. The optimum pH for $H_2$ formation was 5.0, which was thought to be favorable for formation of a cobalt hydride intermediate. The generated hydrogen was confirmed to be mainly from aqueous protons through isotopic labeling studies.

The same cobalt bipyridine complex system was subsequently used for simultaneous $CO_2$ and water reduction to produce CO and $H_2$ [30]. The system employed $[Ru(bpy)_3]^{2+}$ as the photosensitizer and tertiary amines (triethylamine or triethanolamine, TEA or TEOA) as the sacrificial electron donor. Under visible light irradiation, the system produced CO and $H_2$ in the presence of $CO_2$, with the relative amounts of CO and $H_2$ proportional to the concentration of dissolved $CO_2$.

The Bernhard group recently revisited the use of $[Co(bpy)_n]^{2+}$ (**19**, $n$ = 3) as catalyst in conjunction with cyclometallated iridium-based photosensitizers of the general structure $[Ir(N^\wedge N)(C^\wedge N)_2]Cl$ (**21**) or $[Ir(P^\wedge P)(C^\wedge N)_2]Cl$ and tris(imine)ruthenium photosensitizers (**21** and **22**) [63,64]. Using TEOA as the sacrificial electron donor, all of the iridium photosensitizers showed superior activity for $H_2$ generation from water than $[Ru(bpy)_3]^{2+}$. Derivatives of **21** that were fluorinated on the cyclometallating ligand were found to be the most active of the series. Interestingly, the $[Ru(dmphen)_3]^{2+}$ complex (dmphen = 4,7-dimethyl-1,10-phenanthroline) was also found to perform substantially better than $[Ru(bpy)_3]^{2+}$, with more than 9000 TON (based on the

photosensitizer) and 74 TON (based on the $[Co(bpy)_3]^{2+}$) achieved under optimized conditions. **19** was found to efficiently quench the excited photosensitizers **21** and **22** with rate constants ranging between 1.0 and $7.0 \times 10^8$ M$^{-1}$ s$^{-1}$. However, the substantially larger electron donor *concentration* favored the reductive quenching pathway, except in the case of **22**, which was not quenched by TEOA. The limiting factor in the generation of hydrogen appears to be the stability of $[Co(bpy)_3]^{2+}$, which decomposed after less than 100 turnovers.

## 3.3. Cobaloxime complexes for light-driven generation of $H_2$

In 1983, Lehn and co-workers reported the first example of a cobaloxime catalyst (Fig. 12, **23**) for photoinduced water reduction [65], in which $[Ru(bpy)_3]^{2+}$ was employed as the photosensitizer and TEOA as the sacrificial electron donor. Hydrogen production experiments were conducted using different solvent systems. It was found that the highest rate of 16 TON per hour occurred in a DMF/$H_2O$ mixture at pH ~ 9. However, the system exhibited poor robustness; $H_2$ production ceased after a few hours. The basis of the limited durability was proposed to be the instability of the Co(II) dimethylglyoxime catalyst which quickly decomposed.

In 2008, two groups independently revisited the use of cobaloxime complexes as catalysts for photochemical hydrogen generation based on the success found for these complexes electrochemically. Both groups employed $[Co(dmgH)_2Cl(py)]$ (Figs. 5, **9**) as the catalyst for visible light-driven hydrogen production in aqueous organic media [38,66]. The Eisenberg group described a photocatalytic system using a platinum terpyridyl arylacetylide photosensitizer (**24**) and TEOA as the sacrificial electron donor in MeCN/$H_2O$ media. After 10 hours of irradiation with light of $\lambda > 410$ nm, more than 1000 turnovers were obtained at pH 8.5 [66]. During photocatalysis, the system was monitored by UV–vis spectroscopy, leading to the observation of Co$^{II}$ species as the system resting state during catalysis, as discussed in the mechanistic section. Changing the nature of the glyoxime and axial ligands shown in Fig. 13 (**25**–**29**) as well as system conditions, were found to effect to activity of the systems as follows: [67]

(1) *The axial ligands*. Complex **26** with electron-withdrawing axial ligand gave a higher rate of $H_2$ generation (238 TON after 5 h) than complex **25** with electron-donating axial ligand (106 TON after 5 h).

(2) *The ratio of water in the mixed solvents*. For complex **9**, 1000 TONs were obtained in 10 h when the ratio of MeCN/$H_2O$ was 3:2 (v/v) but increased to 2150 TONs when the ratio was changed to 24:1.

(3) *pH values*. The optimal value of pH for light-driven hydrogen production was found to be pH 8.5. As the pH is lowered, the TEOA amine donor is increasingly protonated, which in turn affects its ability to function as a sacrificial electron donor. At higher pH values, water reduction to $H_2$ becomes increasingly more difficult thermodynamically, thus decreasing the rate of $H_2$ generation.

(4) *The reduction potentials of the cobaloxime catalysts*. A correlation was found that the catalysts with more negative Co$^{II}$/Co$^I$ potentials have higher activity for water reduction and produce more $H_2$. In contrast, $[Co(dmgBF_2)_2]$ (Fig. 5, **8**), which was most effective in electrocatalytic reduction of $H^+$ to $H_2$ based on lowest overpotential, did not work in this system for light-driven $H_2$ generation. A rationalization consistent with the data was that the step after Co(I) formation is its protonation to form a Co$^{III}$ hydride. The reduction potential for **8** ($E_{Co(II)/Co(I)} = -0.29$ V vs. NHE) is relatively positive, indicating that the corresponding Co(I) species may not be reactive enough as a base to undergo protonation at pH 7.0–8.5. (The electrocatalytic work was conducted in non-aqueous media with triflic or tosic acid as the proton source.)
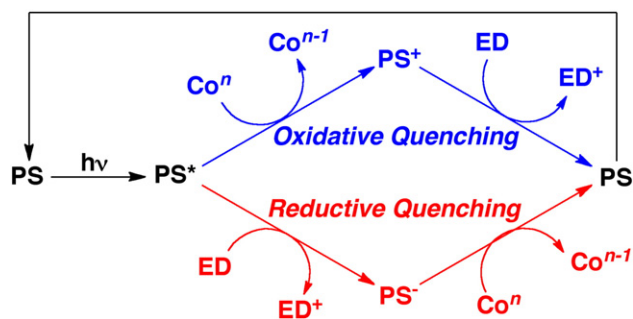


**Fig. 10.** Oxidative and reduction quenching pathways for photochemical hydrogen production.
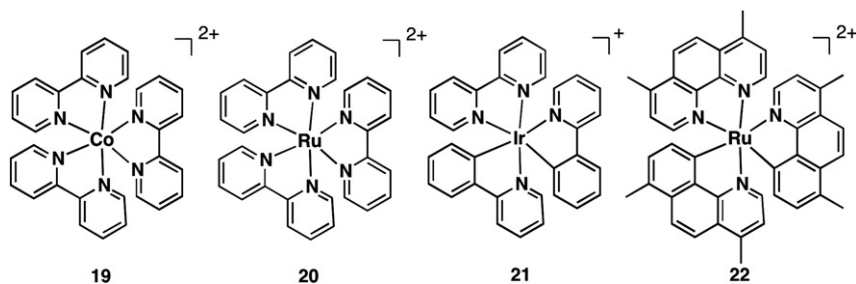
Fig. 11. First cobalt catalyst (**19**) for photochemical hydrogen production using ruthenium and iridium based photosensitizers (**20–22**).

(5) *The concentration of the cobaloxime catalysts.* The rate of H$_2$ generation was found to have a linear dependence on [Co] when concentrations were below 0.7 mM, but at higher concentrations, a similar scaling was not observed, suggesting that another step in the process becomes turnover limiting.

In further work relating to systems using Pt terpyridyl photosensitizers and cobaloxime catalysts, Castellano and co-workers examined the relationship between the rate of hydrogen production and the π-conjugation length in the acetylide ligand [68]. The photosensitizer with longer phenylacetylide π-conjugation length produced more H$_2$ gas under the same photocatalytic conditions, consistent with a longer-lived charge separation over greater distance.

Initial studies of light-driven hydrogen generation using cobaloxime catalysts were also carried out by Artero, Fontecave and coworkers who examined H$_2$ evolution with cobaloxime **8** and both [Ir(ppy)$_2$(phen)]$^+$ (ppy = 2-phenylpyridine, phen = phenanthroline) and [ReBr(CO)$_3$ (phen)] (Fig. 14, **30**) as photosensitizers in acetone solutions buffered with Et$_3$N/Et$_3$NH$^+$ that served as both the sacrificial donor (Et$_3$N) and the proton source (Et$_3$NH$^+$) [38]. A quantum yield of 16% ± 1% and 273 turnovers were achieved with **30** in a 15 h experiment (λ > 380 nm) in the presence of 600 equivalents each of Et$_3$N and Et$_3$NH$^+$.

Alberto and coworkers investigated similar Re chromophores for proton reduction with cobaloxime complexes [69]. Using the bipyridine version of the Re complex used by Artero (**31**), Probst et al., showed efficient hydrogen production in the presence of TEOA, acetic acid, and **23** in DMF. The best results, 265 TON, were achieved with a 3-fold excess of dmgH relative to catalyst, indicating ligand dissociation/decomposition. The Re chromophore was also shown to have increased longevity as compared to [Ru(bpy)$_3$]$^{2+}$, producing over double the amount of hydrogen with **23** as the proton reduction catalyst. Changing the bromide ion to thiocyanate (**32**) was found to improve the stability significantly of the chromophore with 6000 TON relative to chromophore reported [70]. An overall observed second order dependence in [Co] led these workers to postulate a bimetallic mechanism involving two HCo$^{III}$ complexes in the rate-limiting step. Finally, cationic derivatives of the
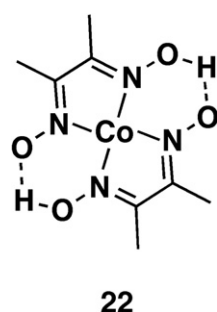
previously discussed Re chromophores were examined with a range of cobaloxime-type complexes. Further investigation into aqueous systems were conducted with different Re photosensitizers and cobalt complexes (Fig. 14) [71]. Complexes **33**, **34**, **36** and **37** were found to successfully produce hydrogen in the presence of cobalt complex **39** in water with TEOA and HBF$_4$, whereas **35** was very slow and **38** was inert. The results were rationalized in terms of the excited state lifetimes of the different photosensitizers, where the pyridine derivatives possess excited state lifetimes that are 1–3 orders of magnitude greater (200–13,000 ns) than those of the corresponding benzyl isocyanide complexes (10–60 ns). Photosensitizers with longer excited lifetimes allow for more efficient reductive quenching by the electron donor. Complexes **39–44** achieved between 2 and 12 TON (relative to Co) using **36** as a photosensitizer but complexes **45–47** produced less than 1 TON under identical conditions. Given the overall low activity of the system, structure–activity correlations were difficult to identify. Recently, in a significant improvement, TONs of approximately 100 were reported in aqueous systems using cobalt complex **40**, photosensitizer **36**, and ascorbic acid as the electron donor at pH 3.5 by the same group [72].

More recently, two cobalt glyoxime complexes have been reported as molecular catalysts for visible light-driven hydrogen generation in combination with a cyclometallated iridium photosensitizer and NEt$_3$ as the sacrificial electron donor [39]. Complex **48** (Fig. 15) is more active than the difluoroboryl complex **49**. The highest TON of 700 has been achieved in 10 h. All the reported systems show no hydrogen produced after 10 h irradiation, indicating the decomposition of the cobalt catalysts or the iridium photosensitizer. Interestingly, the addition of triphenylphosphine (PPh$_3$) to the medium results in a significant
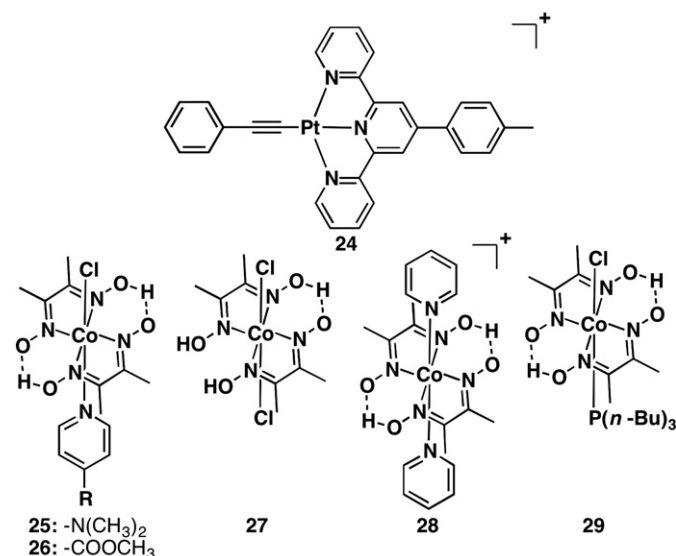




Fig. 12. First cobaloxime complex reported for photochemical hydrogen production.

Fig. 13. Cobaloxime complexes used with platinum terpyridine acetylide complexes.
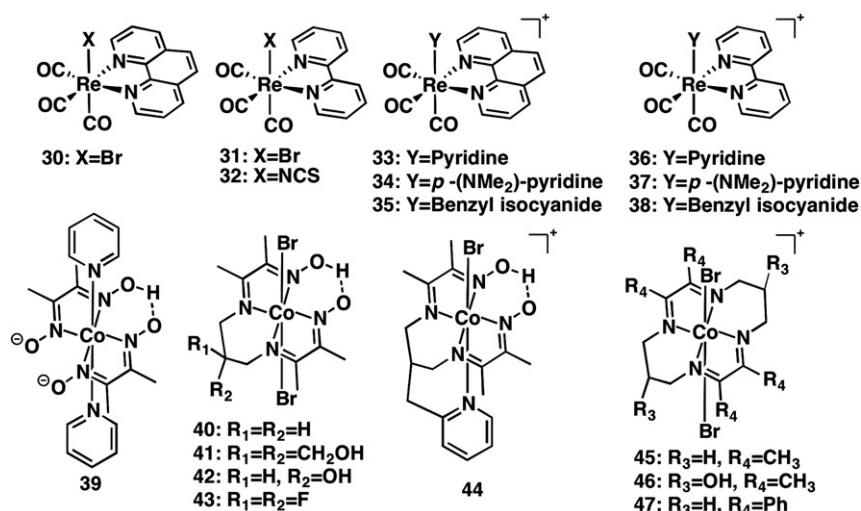
**Fig. 14.** Cobaloxime-type complexes employed in photochemical systems with Re chromophores.

improvement of the stability of the system. UV–vis spectroscopy has been used to identify a PPh₃-coordinated Co(I) intermediate (**50**) present during hydrogen production.

Cobaloxime complex **9** was also used in the introduction of the first organogold complex (Fig. 16, **51**) as a photosensitizer [73]. Under light irradiation with λ > 385 nm in the presence of TEOA, more than 350 TON were reported. Interestingly, the system also performed well in natural sunlight, achieving nearly 250 TON.

The systems described above for light-driven H₂ generation possessed the common feature of either a noble metal or 5d element-based photosensitizer. However in 2009, Eisenberg and co-workers assembled and studied the first homogeneous system based on earth-abundant elements for visible light-driven hydrogen production from water incorporating a cobalt catalyst [74]. The system contained halogenated organic dyes (Fig. 17, Eosin Y (**52**) or Rose Bengal (**53**)) as the photosensitizers, **9** as the catalyst and TEOA as the sacrificial donor. Under visible light irradiation for 15 h, more than 900 TONs were obtained in this system. When irradiating the reaction solution using a 20 nm wide bandpass filter centered at 520 nm, the Eosin Y system was relatively stable and exhibited no significant decrease of the H₂ production even after 30 h. A quantum yield of 4% was obtained for H₂ photoproduction for this system. Further studies revealed that the presence of excess dimethylglyoxime ligand (dmgH₂) improved the lifetime of the system for H₂ generation, but without any increase in the rate of H₂ generation. These observations suggested that ligand dissociation was occurring during photogeneration of H₂, a proposal that was subsequently confirmed (see below). Other studies revealed that the lowest lying triplet states of **52** and **53**, that were accessed via the heavy atom effect, play a key role for electron transfer yielding initial reduction of Co$^{III}$ to Co$^{II}$ and subsequent hydrogen production involving Co$^{I}$ and HCo$^{III}$ intermediates.

A similar system was described shortly thereafter by Sun and co-workers using **52** as the photosensitizer and BF₂-annulated cobaloximes **3** and **4**, as well as clathrochelated cobaloximes **54** and **55** (Fig. 17), as catalysts in the presence of TEOA as the sacrificial donor [75]. The maximum activity for these systems was 327 TON in 5 h upon visible light irradiation (λ > 400 nm) with catalyst **3**. The caged clathrochelated complexes showed much less activity than the cobaloxime complexes, indicating the need for ligand dissociation to allow cobalt hydride formation.

In further studies by McCormick et al., using cobaloxime catalyst **9**, up to 9000 TON were achieved (relative to photosensitizer) when rhodamine dyes (with S (**57**) or Se (**58**) in place of O (**56**) in the xanthene ring) were used as the photosensitizers [76]. The heavy atom effect, as discussed previously, increases the population of dye molecules in the longer-lived triplet excited state, thereby increasing the likelihood of an intermolecular electron transfer. These rhodamine derivatives are stable for extended periods under irradiation in solution, but were found to decompose rapidly if irradiated in the presence of a sacrificial electron donor. Quenching studies revealed that the phosphorescence of **57** was quenched by the TEOA electron donor but not by the catalyst, thereby indicating that hydrogen generation was proceeding by a reductive quenching mechanism with the formation of the reduced dye. There was thus a branchpoint in the reaction chemistry of the reduced dye. As long as an active catalyst was present, the generation of H₂ continued (and it could be prolonged by the addition of more dmgH₂), but in the absence of active catalyst, photosensitizer decomposition occurred. A supposition was offered that the glyoximate ligands were undergoing hydrogenation so that the resultant Co complex could no longer be reduced by the reduced photosensitizer.

The question of exchange between free and complexed glyoximate ligands was definitively answered in a different study by McCormick et al. [77]. Based on observations that Co(dmgH)₂Cl(py) was found to be an active catalyst for photochemical H₂ generation but that the corresponding diphenylglyoximate derivative, Co(dpgH)₂Cl(py), was a relatively poor catalyst, a series of H₂-generating experiments were conducted. Fig. 18 shows the results for four runs in which systems having the following catalysts were present: (a) Co(dmgH)₂Cl(py) + 2 dmgH₂, (b) Co(dmgH)₂Cl(py) + 2 dpgH₂, (c) Co(dpgH)₂Cl(py) + 2 dpgH₂, and (d) Co(dpgH)₂Cl(py) + 2 dmgH₂. The good yield of H₂ for run (a) and the poor yield of H₂ for (c) are clear. The mixed ligand experiments of (b) and (d) gave essentially identical results that were intermediate between (a) and (c), unequivocally establishing exchange of the glyoximate ligands during hydrogen generation.
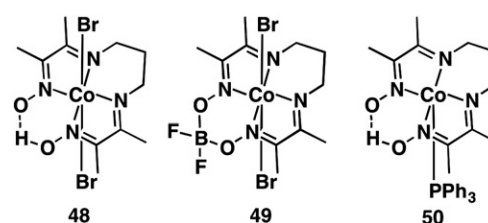


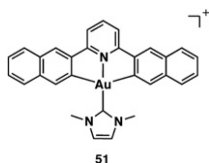**Fig. 15.** Cobaloxime derivatives used with Ir(bpy)(ppy)₂.

Fig. 16. Organogold photosensitizer.

## 3.4. Polypyridine cobalt complexes for the photogeneration of H$_2$

A cobalt(II) quaterpyridine complex (Fig. 19, **59**) has been reported as a visible light-driven catalyst for water reduction [78]. It catalyzes photo-induced hydrogen generation using as photosensitizer [Ir(III)(dF(CF$_3$) ppy)$_2$(dtbbpy)]$^+$ (dF(CF$_3$)ppy = anion of 2-(2,4-difluorophenyl)-5-tri-fluoromethylpyridine, dtbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine) in aqueous acetonitrile (λ > 420 nm). Highest TONs of 1730 have been obtained with Co(I) species observed during light irradiation. A cobalt(II) penta(pyridine) complex [(CF$_3$PY5Me2)Co(H$_2$O)](CF$_3$SO$_3$)$_2$ (**60**) (PY5Me2 = 2,6-bis(1,1-di(pyridin-2-yl)ethyl)pyridine) has also been described as a catalyst for light driven hydrogen production using either molecular or semiconductor nanowire photosensitizers [79]. Hydrogen was generated in water under photocatalytic conditions with visible light irradiation using [Ru(bpy)$_3$]$^{2+}$ as the chromophore and ascorbate as the sacrificial donor. To obtain a system based solely on Earth-abundant elements, GaP nanowires was employed to replace [Ru(bpy)$_3$]$^{2+}$. In an aqueous solution containing GaP nanowires as the light absorber and methanol as the electron donor (or hole scavenger), H$_2$ was also observed during visible light irradiation but the rate of hydrogen production rapidly decreased due to the aggregation of GaP nanowires and/or decomposition of the catalyst.

Another example of cobalt(II) penta(pyridine) complexes for catalytic hydrogen production is [Co(DPA-Bpy)(OH$_2$)](PF$_6$)$_3$ (**61**) (DPA-Bpy = N, N-bis(2-pyridinylmethyl)-2,2′-bipyridine-6-methanamine) [61]. In 1.0 M sodium phosphate buffer at pH 7.0, **61** exhibits a sequence of two redox events centered at −0.15 and −0.90 V (vs. SHE), corresponding to the Co$^{III/II}$ and Co$^{II/I}$ couples, respectively. Photocatalytic hydrogen production was investigated in a system based on [Co(DPA-Bpy)(OH$_2$)](PF$_6$)$_3$ complex as the catalyst, [Ru(bpy)$_3$]$^{2+}$ as the photosensitizer and ascorbic acid as the electron donor. The concentration of the catalyst has a great influence on the light-induced activity for photoinduced hydrogen production. When the concentration is 50 μM, the obtained TON is ~450, but at 0.5 μM, the TON increased to 4400.

## 3.5. Bis(dithiolene) complexes of cobalt for the photogeneration of H$_2$

In 2011, McNamara et al., [80] reported the first example of a cobalt dithiolene complex (Fig. 20, **62**) for both photocatalytic and electrocatalytic hydrogen production from water. The [Co(bdt)$_2$]$^-$ complex **62** is an active catalyst with up to 2700 TON (based on the
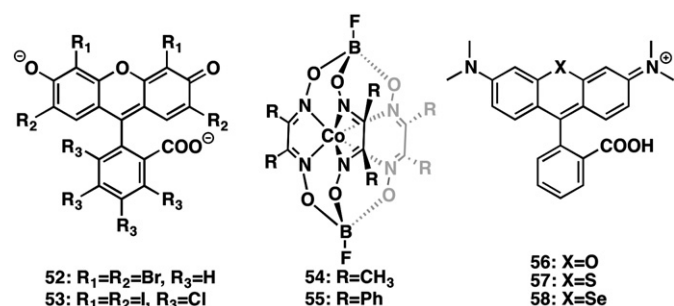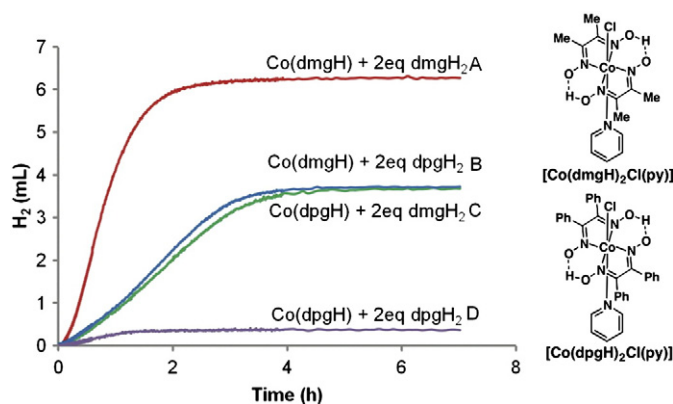


Fig. 18. Ligand exchange of cobalt–glyoxime complexes in aqueous media, reproduced with permission.

catalyst) and initial turnover rate of 880 mol H$_2$/mol catalyst/h when employed with [Ru(bpy)$_3$]$^{2+}$ as the photosensitizer and ascorbic acid as the sacrificial donor. Complex **62** was also found to be an active electrocatalyst in mixed MeCN/H$_2$O in the presence of weak acids with a Faradaic yield of >99% when the potential is held at −1.0 V vs. SCE.

A subsequent study examined a series of cobalt bis(dithiolene) complexes (**62–65**) for the light-driven reduction of protons to H$_2$ in aqueous solvent mixtures for the purpose of determining electronic effects on the reactivity [81]. The dithiolene ligands ranged in electron donating ability with three of them based on the benzenedithiolate structure. All of the complexes were active as catalysts for the light-driven reduction of protons from water when paired with [Ru(bpy)$_3$]$^{2+}$ as the photosensitizer and ascorbic acid as the sacrificial donor. The catalysts increased in activity for photochemically driven H$_2$ generation with ligand electron withdrawing ability. The complex [Co(mnt)$_2$]$^-$ (**65**), that exists in the solid state as a dimer and has the least negative reduction potential, exhibited the highest activity with turnovers up to 9000 with respect to catalyst.

While these cobalt bis(dithiolene) complexes are also active electrocatalysts in 1:1 acetonitrile/water, their relative order of activity differed from that found in the photochemical systems [81]. Specifically, while 65 was most active catalyst in light-driven systems, it exhibited the highest overpotential in electrochemical hydrogen production, as compared to **62–64**. On the other hand, the three derivatized benzenedithiolate complexes followed the same ordering for both photochemical and electrochemical activity. The mechanistic implications of the differences in activity of the cobalt bis(dithiolene) complexes for photochemical and electrochemical H$_2$ generation are discussed further below.

## 3.6. Mechanistic considerations of systems for the light driven generation of hydrogen

As mentioned above, photochemical systems are mechanistically more complex than electrochemical systems because of the possibility of different photoinduced electron transfer pathways and the reactions involving both the catalyst and the sacrificial electron donor as well as their subsequent chemistry. The oxidative quenching pathway involves PS* being oxidized by the cobalt catalyst, whereas in the reductive quenching pathway, PS* is reduced by the sacrificial electron donor. The oxidized electron donor then undergoes irreversible decomposition, which is well documented in the case of TEA [82], TEOA [83], and ascorbic acid [84]. In the decomposition pathway of TEA and TEOA, H-atom abstraction from the α-carbon leads to the formation of a highly reducing carbon-based radical, which



Fig. 17. Organic chromophores and clathrochelated cobaloxime complex.
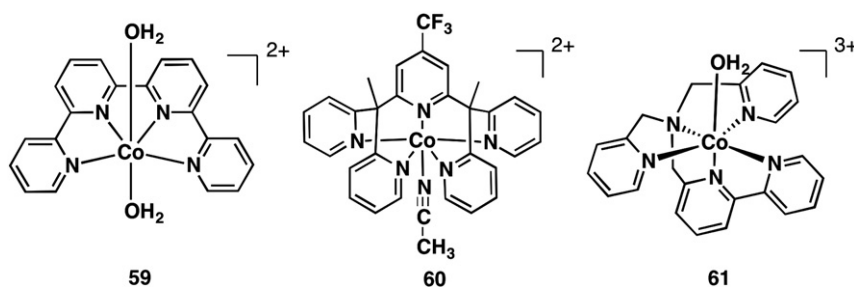
**Fig. 19.** Polypyridine complexes used in light driven proton reduction.

can serve as another reductant for the cobalt-based catalyst. In photochemical systems using these tertiary amine electron donors, one photon leads to the production of two electrons. The specific quenching pathway of a given photochemical system is determined by the excited state reduction potentials of PS*, the oxidation potential of the electron donor, the reduction potential of the catalyst, as well as the relative concentrations of the catalyst and electron donor. Even if rate constants for oxidative and reductive quenching of PS* by catalyst and electron donor, respectively, are found to be similar in magnitude, the system can be biased to a single pathway such as reductive quenching by using a much greater concentration of electron donor than of catalyst.

The charge transfer chromophores of Pt terpyridylacetylide complexes and Ir cyclometallated complexes have been shown to be capable of operating in both oxidative and reductive quenching pathways. For the Pt terpyridylacetylide complexes, both quenching pathways have bimolecular rate constants ($k_q$) with cobaloxime complexes and TEOA (diffusion controlled) that indicate that they can occur in parallel, but when using very high concentrations of TEOA relative to catalyst, reductive quenching is favored [66–68]. For Ru(bpy)$_3^{2+}$ on the other hand, quenching has been observed by ascorbic acid, but not by TEOA due to the latter's thermodynamically unfavorable oxidation potential [28,63,85–87]. Therefore, in systems with TEOA and cobalt catalysts, it typically functions by the oxidative quenching route ($k_q = 10^7$–$10^8$ M$^{-1}$ s$^{-1}$) [63]. Cyclometallated Ir choromophores also have competitive rates of quenching with cobalt complexes ($10^8$ M$^{-1}$ s$^{-1}$) and TEOA ($10^6$–$10^9$ M$^{-1}$ s$^{-1}$), and therefore the mechanism depends on the relative concentrations of catalyst and electron donor [63,78]. Systems with Re tri(carbonyl) chromophores were found to proceed solely by reductive quenching using TEOA with a rate constant near $10^8$ [69–71]. Organic chromophores, Eosin Y, Rose Bengal, fluorescein, and rhodamine derivatives were all shown to undergo reductive quenching in the presence of TEOA, and the reduced form of these dyes were generally unstable, thus contributing to the relatively short hydrogen production times of systems containing them [74–76].

As in the electrochemical systems, a formally Co$^I$ species is widely viewed as the key to H$_2$ generation. The species forms upon catalyst reduction and undergoes protonation to form a HCo$^{III}$ intermediate. Both first and second order dependences on Co concentration have

been reported for hydrogen formation, indicating the possibility of different mechanisms for the formation of H$_2$. Du et al., who employed systems containing the Pt(terpyridine)acetylide complex **24** and cobaloxime complexes **9**, **25–29**, found a first order dependence on [Co] in H$_2$O/CH$_3$CN [66,67] whereas Probst et al., observed second order kinetics with a system using a Re(CO)$_3$bpyX (X = Br, NCS) photosensitizer in DMF [69,70]. First order kinetics on [Co] supports a monometallic mechanism in which a Co hydride intermediate reacts with H$^+$ for H$_2$ formation, while second order dependence on [Co] is consistent with a coupling of two HCo$^{III}$ to give H$_2$ + 2 Co$^{II}$. The solvent medium likely plays a large role in the mechanism due to proton availability. When Alberto and coworkers reported a similar catalytic system in pure water, they observed a first order dependence, supporting this notion. Further work with cobaloxime complexes in photocatalytic systems in aqueous solvent have also shown a first order dependence on cobalt concentration [74,76].

For the systems in which cobalt bis(dithiolene) complexes function as the catalyst, one electron reduction of the catalyst and protonation likely occur in accord the with H$_2$ forming mechanism for the cobaloxime catalysts [80,81]. However, the mixed nature of the frontier orbitals in these complexes makes formal oxidation state assignments less meaningful and raises the possibility of protonation sites other than at the metal ion. The ordering of photochemical activity correlates with the Co(L$_2$)$^-$/Co(L$_2$)$^{2-}$ reduction potential from least negative to most negative. Since the cobalt bis(dithiolene) systems proceed by a reductive quenching mechanism with high concentrations of ascorbate donor, the reaction that correlates with H$_2$ producing activity is the reduction of the catalyst by the reduced photosensitizer (Ru(bpy)$_3^+$) based on the driving force (ΔE) of the reaction. This electron transfer may therefore be turnover-limiting in the catalysis. However, there is a difference in the reactivity order for the photochemical and electrocatalytic activity of the cobalt bis(dithiolene) systems, indicating that a difference in the turnover-limiting step exists between the two types of systems.

The difference between the electronic structures of the cobalt bis(benzenedithiolate) complexes and Co(mnt)$_2^-$ (**65**) may lead to differences in the site of protonation and the consequent reduction potentials of the electrocatalytic waves for these complexes. For **65**, the frontier metal and ligand-based orbitals possess similar energies, suggesting that protonation may take place at either the metal center or the ligand [88–90]. In contrast, the HOMOs for derivatives **62–64** have only 29% ligand character, thereby favoring protonation at the metal center [91]. The *electrocatalytic mechanism* was proposed to be ECEC [92], where the Co dithiolene catalysts undergo rapid protonation once they are reduced to Co(L$_2$)$^{2-}$. Subsequent reduction and reaction with H$^+$ lead to H$_2$ formation.

A further analysis of the cobalt bis(dithiolene)-catalyzed reduction of protons was offered by Solis et al., who conducted detailed calculations of electrochemical potentials and pKa values [93]. The calculations showed that complexes **62–64** are likely protonated after reduction to Co$^{II}$. The new Co$^{II}$(SH)$_2$ species (protonation at two thiolates) was theoretically shown to have a very similar
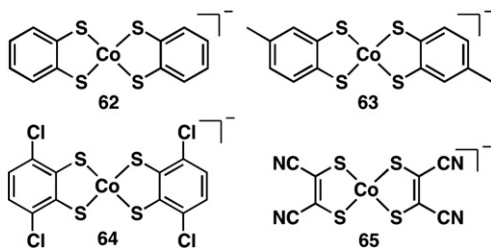


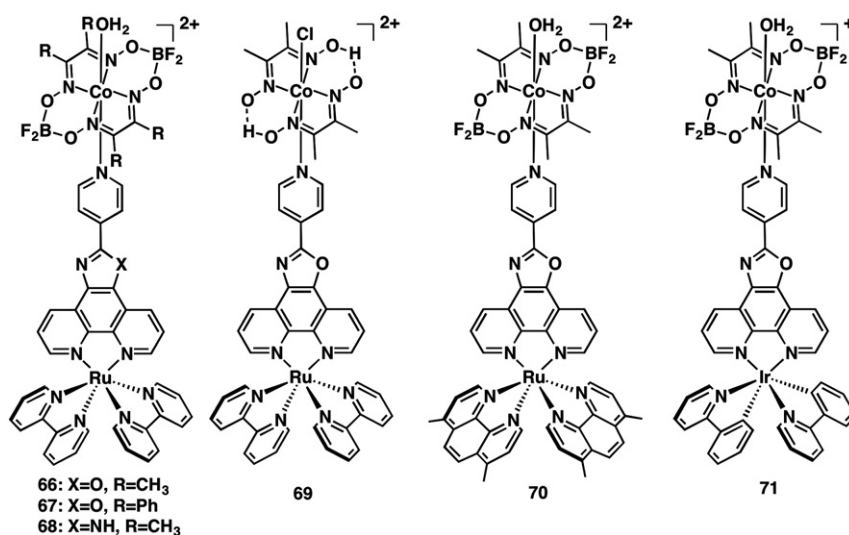**Fig. 20.** Highly active cobalt bis(dithiolene) complexes.

reduction potential as compared to the initial $Co^{III}/Co^{II}$ couple. Formation of $HCo^{III}(SH)$ by proton reduction permitted monometallic formation of $H_2$. In Fig. 21, the different catalytic species are shown as $Co^{OS}(SH)_xS_{4-x}^{n-}$ with formal metal oxidation state (OS), ligand protonation as SH, and overall complex charge of n−. The species and arrows shown in red are common to all of the dithiolene catalysts, the ones in blue are for catalyst **65**, $[Co(mnt)_2]^-$, whereas the ones in green would correspond to the bis(benzenedithiolate) complexes **62–64** that have more negative reduction potentials. Complex **65** is therefore thought to be only singly protonated before further reduction to $Co^I(SH)S_3^{2-}$ while the other catalysts are doubly protonated before subsequent reduction and hydrogen generation.

### 3.7. Integrated catalyst–photosensitizer systems using cobalt complexes

Covalent linking of the catalyst and photosensitizer has been proposed as a way of improving light-driven proton reduction systems and a number of systems based on this notion have been examined. In the first of these systems, ruthenium tris diimine complexes were connected to a cobaloxime complex via pyridine coordination to serve as the photosensitizer and catalyst, respectively (Fig. 22) [37]. Irradiation of these photosensitizer–catalyst conjugates in $Et_3N/Et_3NH^+$-buffered acetone solutions led to intramolecular electron transfer and $H_2$ generation. A total of 103 TON was achieved with **66** after 15 h of irradiation. Replacing the oxazole portion of the bridging ligand with an imidazole (**68**) led to an increased rate of hydrogen production, with 104 TON reached in only 4 h [38]. Complexes **67** and **69** were found to have less than 20 TON. No hydrogen was formed with complex **70** but a change to a cyclometallated iridium photosensitizer in **71** produced over 200 TON in 15 h. However, control experiments revealed similar activity with unlinked catalyst and chromophore systems (165 TON). In these studies, it was found that even small amounts of water significantly inhibit the system's activity, and subsequent work described below showed that pyridyl ligand dissociation from the catalyst may be facilitated with water present.

Based on the above reports for light-driven $H_2$ generation using a molecular photochemical device, other examples of photochemical devices were reported for $H_2$ production using water as the proton source. One such system contained a porphyrin moiety as the photosensitizer and the H-bridged cobaloxime bearing an axial pyridine ligand as the catalyst (Fig. 23, **72–74**) [94]. Sun and co-workers synthesized and studied systems in which the sensitizer was a porphyrin with a pyridyl group at one of the meso positions coordinated to a $Co^{III}Cl(dmgH)_2$ catalyst. Three porphyrin derivatives were examined – $Zn^{2+}$, $Mg^{2+}$ and the unmetallated porphyrin – with the Zn derivative showing the most significant activity (~22 TONs), but all systems were short-lived regarding $H_2$ production. Electron transfer from the $^3\pi\pi^*$ state of Zn porphyrins is well known, but it is likely that upon reduction of $Co^{III}$ to $Co^{II}$ in the initial steps of the catalysis, the system loses its structural integrity as mentioned above.

An iridium photosensitizer bearing a bipyridyl substituent was used to construct a cobalt tris–bipyridine complex as the catalyst (Fig. 23, **75**) [95]. However, this system exhibited only modest turnovers for hydrogen production from water with 20 turnover numbers, which was similar to the separated parts (10 TON).

An integrated system that contains a cobaloxime catalyst and an organic dye as PS was synthesized and studied by McCormick et al. [77]. In **76** as shown in Fig. 24, fluorescein is attached by an amide bond to the axial pyridine of the catalyst. While the system was found to produce $H_2$ upon irradiation in the presence of TEOA, it was less active than a control system having separate fluorescein and cobaloxime catalyst (**9**) components. The absence of any enhancement of activity by connecting PS to the catalyst led to an examination of the possibility of ligand exchange at the Co center upon photochemical reduction. Initial studies confirmed facile pyridine exchange in the presence of small amounts of $Co^{II}$, and subsequent



**Fig. 21.** Mechanistic routes available to cobalt bis(dithiolene) catalysts determined by calculations of reduction potentials and pKa values.

studies described above established that the dmgH ligands were exchanging during $H_2$ generation as well. The resting state of the catalyst during $H_2$ generation was determined to be $Co^{II}$, a labile metal ion. The observation of ligand exchange during irradiation indicates clearly the lack of structural integrity for any integrated system based on a cobaloxime catalyst in aqueous or organic aqueous media.

Although these findings clearly show the dissociation of the pyridine ligand in aqueous organic solutions, other studies have shown that similar supramolecular constructs are in fact bound in organic media by solution phase X-ray scattering [96]. However, photochemical systems such as **75**, which are less prone to dissociation into completely separated catalyst and photosensitizer units, still suffer from fairly low activity. The benefit of fast *intra*molecular electron transfer in linked systems may be undone, for example, by fast *back* electron transfer or catalyst lability, resulting in overall poor catalytic efficiency.

### 3.8. Systems employing semi-conducting materials and cobalt catalysts for light driven hydrogen production

Cobaloxime catalysts have also been investigated for attachment to heterogeneous materials for light-driven hydrogen production. Titanium dioxide ($TiO_2$) has long been known to serve as both an electron mediator and structural scaffold and to undergo photoinduced electron transfer from charge transfer chromophores such as $Ru(bpy)^{2+}$ [97–104]. Recently, a heterogeneous photochemical device based on $TiO_2$, a molecular photosensitizer and catalyst was described [105]. The cobaloxime catalyst was modified with phosphonate group on the axial pyridine ligand and $[Ru(bpy)_3]^{2+}$ was functionalized with phosphonate groups on one of the bpy ligands to anchor them to the surface of $TiO_2$, resulting in a system shown in Fig. 25. Absorption of a photon by the $[Ru(bpy)_3]^{2+}$ moiety results in electron injection into the $TiO_2$ conduction band, from which it can migrate to the cobaloxime catalyst and reduce it. Upon irradiation in pure water and TEOA (pH 7), the modified $TiO_2$ was found to reduce water to produce $H_2$ gas with low TOF number of 0.005 $s^{-1}$. The system had modest activity at about 400 mmol $H_2$ $h^{-1}(g\ TiO_2)^{-1}$. While control experiments showed that less hydrogen was produced with the phosphonate-free cobaloxime (**9**) complex, the observation of ligand exchange with such catalysts brings into question the durability of the integrated system.

Chen and coworkers used the same cobaloxime complex to create a catalytically active site on a CdSe/ZnS core-shell nanocrystal [106]. The nanocrystal or quantum dot absorbs light directly and electron transfer to the cobaloxime complex was determined to occur in 105 ps by transient absorption spectroscopy. Recombination, which would be problematic for hydrogen production, was found to be

**Fig. 22.** Integrated photosensitizer–catalyst "devices" for light driven hydrogen production.

relatively slow. In toluene with $HNEt_4Cl$ as the proton source and TEOA as the electron donor, over 10,000 turnover numbers per quantum dot were achieved in 10 h of irradiation but the system exhibited limited durability that was traced to catalyst decomposition.

### 3.9. Semi-biological systems

Lastly, Tiede and co-workers reported a photochemical system that blurred the lines of "artificial photosynthesis." [107] Addition of cobaloxime complex **9** to naturally produced Photosystem I (PSI), harvested from cyanobacteria *Synechococcus leopoliensis* or *Synechococcus lividus*, resulted in a self-assembled hydrogen producing device (Fig. 26). Using sodium ascorbate as the sacrificial electron donor, rates of hydrogen formation as high as 170 TON per minute were observed with activity leveling off after only 1.5 h. The reason for cessation of activity was thought to be due to cobaloxime dissociation from PSI, from metal analysis comparison before and after the photolysis.

### 4. Conclusions and challenges

Catalysts are one of the key factors for efficient solar energy conversion by water splitting and artificial photosynthesis. For $H_2$ generation and the reductive side of water splitting, great progress has been achieved in the past decades using Co complexes as catalysts and artificial hydrogenases in which the reaction is driven either electrochemically or photochemically. In the most active photochemical systems for hydrogen generation with molecular cobalt catalysts, 9000 TON (relative to [dye]) have been reported for using cobaloxime complexes with organic dyes as the photosensitizers and 9000 TON per catalyst have been found for cobalt bis(dithiolene) systems. These results on the reductive side of water splitting are complemented by significant progress on the oxidation of water to give $O_2$ using cobalt water oxidation catalysts (WOCs), most notably by Nocera and co-workers [108–113]. In the latter, the work has primarily been electrochemical in nature, raising the challenge of developing a true robust and active system for water splitting in which each half-reaction is
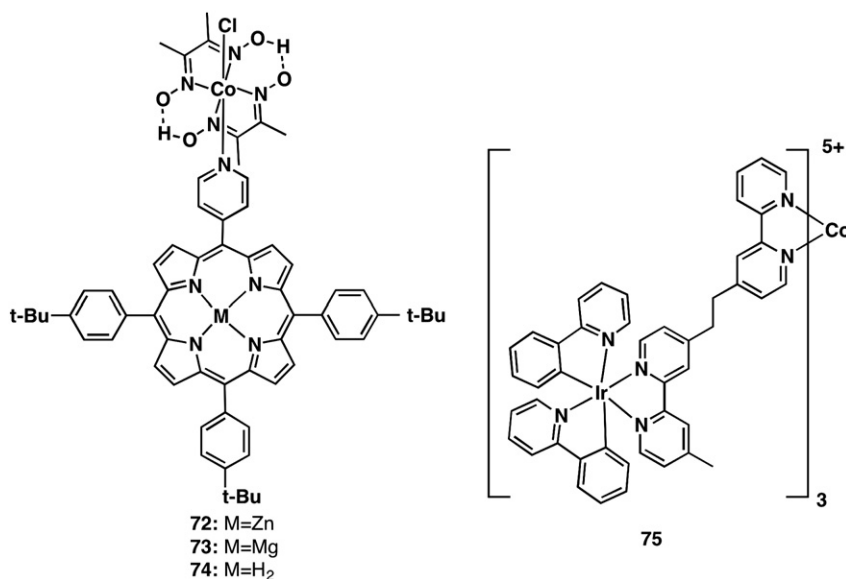


**Fig. 23.** Linked systems based on cobalt proton reduction catalysts.
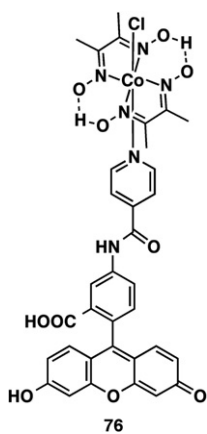
**Fig. 24.** Cobaloxime complex linked to fluorescein.

light-driven with the two half-reaction systems connected by means of pathways for both electron transfer and proton transfer.

Clearly, more progress needs to be achieved to increase the activity, efficiency and robustness of catalysts based on earth-abundant elements. With regard to Co complexes for hydrogen generation, durability under hydrogen generating conditions continues to be a major concern, in light of the fact that reported lifetimes for systems containing Co molecular catalysts range from several minutes to several days under irradiation with visible light. Often the catalysts stop functioning during $H_2$ generation, possibly as a result of ligand reaction or of sacrificial donor decomposition. The practical lifetime for viable systems needs to be long enough to accommodate at least $10^7$–$10^9$ turnovers, or systems must be developed that have

"self-repair" as part of their chemistry. For artificial photosynthetic systems, self-repair may be defined as linked equilibria that can return a catalyst to a functioning form if it is rendered inactive by a secondary reaction pathway.

Air-sensitivity is another major problem for $H_2$ generating systems. For water reduction systems, the reduced forms of molecular catalysts, especially in organic media, are generally air-sensitive, with atmospheric $O_2$ able to oxidize them rapidly. The ideal water reduction catalyst should promote hydrogen production much faster than oxygenation to avoid decomposition or deactivation pathways. Water tolerance is an important concern for many reported $H_2$-generating catalysts. While some molecular catalysts are reported to work well in organic solvents, their activity is in general diminished by even small amounts of water. However, for viable water splitting in solar energy conversion, it is essential that water serves as the solvent of choice.

For electrocatalytic splitting of water, the ideal working potential should be as close as possible to the thermodynamic potentials of the two half-reactions for water reduction and water oxidation at the system's pH. If the working potential has too large an overvoltage, significant energy is lost in the process (that is, the difference between the working potential and the required minimal potential) and the half reaction loses efficiency. However, often decreasing overpotential leads to a decrease in overall activity. How to decrease the overpotential to a minimum value for water reduction while maintaining activity is a continuing challenge for the design of better electrocatalysts.

For light-driven half-reactions, however, the concern about overpotential and reaction barriers changes. In the photogeneration of $H_2$, the excited state photosensitizer PS* will undergo electron transfer quenching which can be either by electron transfer from PS* to the
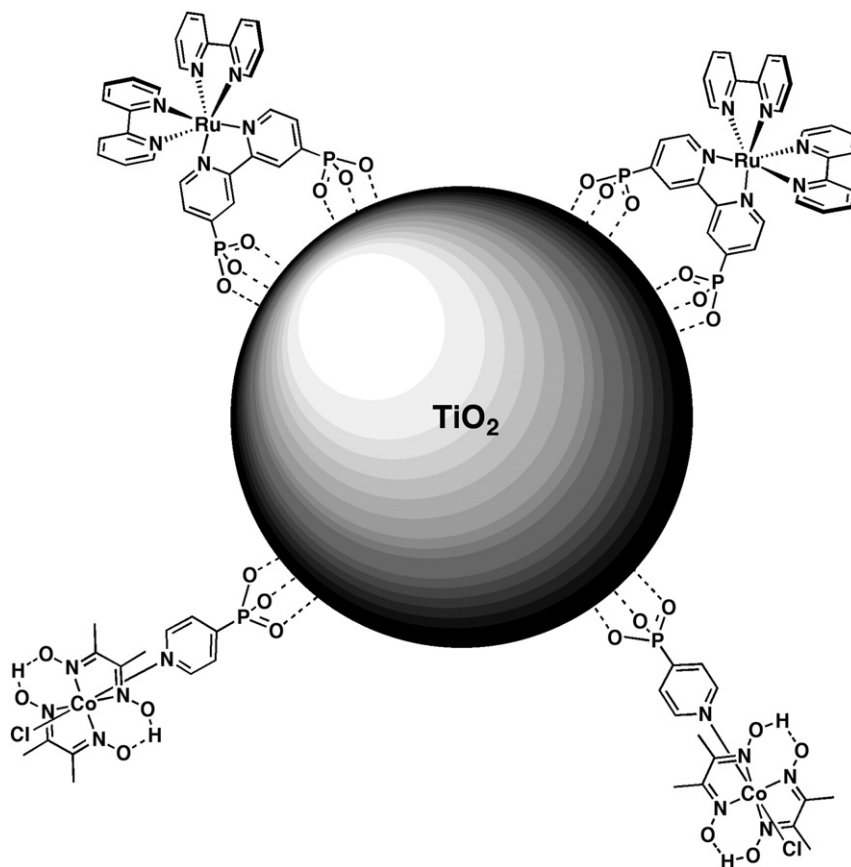


**Fig. 25.** Titanium dioxide with Ru(bpy)$_3^{2+}$ and a cobaloxime complex anchored to the surface with phosphonate groups.
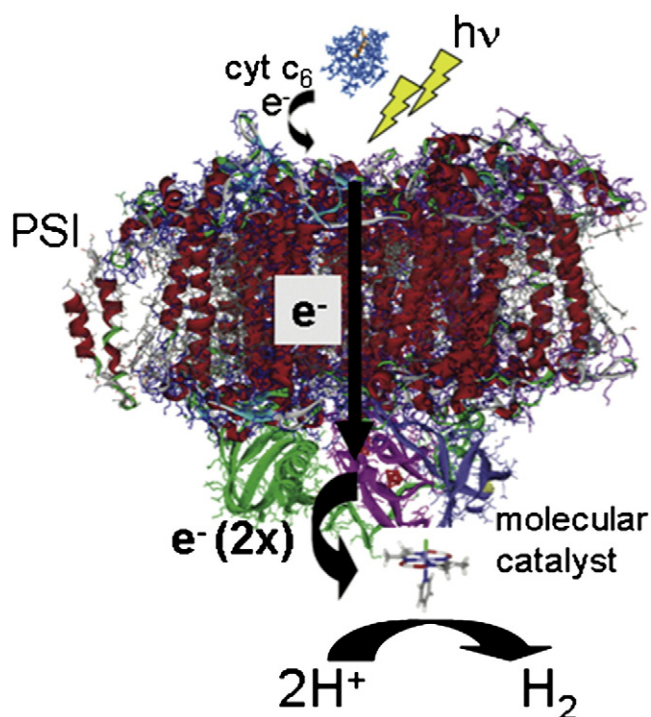
**Fig. 26.** Photosystem I and cobaloxime photochemical proton reduction system, reproduced with permission.

Whether water splitting is achieved by electrolysis using electricity generated by photovoltaic devices or dye-sensitized solar cells, or by artificial photosynthesis remains at this point unclear. While technology for the former is at a better developed stage at this point, an artificial photosynthetic system for water splitting has promise of greater simplicity and efficiency. The durability, scalability, cost and efficiency will in the long run decide which approach to water splitting and hydrogen generation will win this competition. For catalyst development, efforts over the past decade have focused on compounds and materials of earth-abundant elements. Compounds of no other metal have been as extensively studied in this context as those of Co, although both Fe and Ni are found in different classes of hydrogenases and model systems based on them have shown some success. Much of the Co work was stimulated by earlier studies involving glyoximate and bipyridine complexes, but recent studies have uncovered other sets of Co complexes that will merit further investigation. Additionally, compatibility of these complexes with other system components will be essential to provide the needed robustness and activity to achieve water splitting on the scale needed for meaningful solar energy conversion.

catalyst (oxidative quenching) or by electron transfer from the sacrificial donor to PS* (reductive quenching). The feasibility of each step is determined by the reduction potentials of the catalyst, the sacrificial donor and the excited photosensitizer PS*, and the relative rates of the oxidative and reductive quenching paths will be controlled by the particular quenching rate constant and the quencher concentration. Substituent variation for each PS group can be used to modify the excited state redox potentials of PS* that in turn will affect the relative rates of oxidative and reductive quenching. In systems such as these, the overpotential of the catalyst for generating $H_2$ *electrochemically* is not the best measure of relative activity. Instead, it may just help to determine which photochemical path may be followed.

In the research described in this article, we have focused mainly on molecularly-based systems with Co catalysts for doing one of the half-reactions of water splitting, the reduction of protons to $H_2$. The primary objective in these studies has been to develop compatible components in a visible light-driven system to be active, efficient and robust. Actual energy storage in studies dealing with the water splitting *half*-reactions is not, or should not be, the prime research objective. In many cases involving light and a sacrificial electron donor or acceptor, net energy storage is not even achieved. In fact, for proton reduction to $H_2$, the oxidation of a sacrificial donor such as a tertiary amine might provide most of the potential energy required to produce hydrogen, and for water oxidation to $O_2$, electron acceptors such as persulfate are chemically strong enough oxidants so that there is no need for light to drive the reaction. While the consumption of a sacrificial donor/acceptor may seem like a major disadvantage for a half-reaction system, it is through these studies of the water splitting half-reactions that actual systems for solar energy storage by water splitting can be developed. Once systems for performing the two half-reactions have been developed sufficiently in terms of robustness and activity, they will need to be joined through a conductive membrane. The system will also need to allow protons to move from one half-reaction compartment to the other so that a significant proton gradient does not occur.

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