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Phosphine Coordination to a Cobalt Diimine–Dioxime Catalyst Increases Stability during Light-Driven H_2 Production

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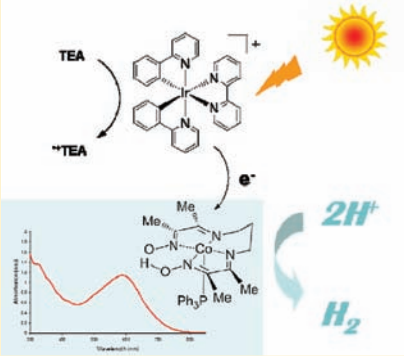
Supporting Information

ABSTRACT: The combination of cobalt diimine–dioxime complexes with a cyclometalated iridium photosensitizer gives efficient systems for hydrogen generation under visible-light irradiation using triethylamine as a sacrificial electron donor. Interestingly, the addition of triphenylphosphine (PPh_3) to the medium results in a significant improvement of the stability of the system, with up to ~700 turnovers achieved within 10 h. UV–visible spectroscopic monitoring of the reaction allows identification of a PPh_3-coordinated Co^{I} intermediate as the active species. Mechanistic issues regarding (i) the photogeneration of the Co^{I} species, (ii) the nature of the active species, and (iii) the influence of PPh_3 on the H_2-evolution mechanism are discussed.



■ INTRODUCTION

Solar power is one of the renewable solutions to the energy crisis if one can convert it into storable fuels, such as hydrogen (H_2).[1] Photoproduction of H_2 can be achieved by combining light-harvesting units for promoting local charge separation and catalysts for two-electron water reduction. Photosensitizers can be either semiconducting materials[2] or molecular compounds.[3] In the past years, the replacement of expensive and scarce noble metal catalysts, such as platinum, has been investigated using coordination complexes, such as those mimicking the active site of hydrogenases.[4,5] Cobalt-based catalysts,[6] typically cobaloximes, combined with either metal diimine photosensitizers,[7−12] organic dyes,[13−15] or photosystem I[16] have also shown interesting activities. However, such systems suffer from poor stability upon cycling and, consequently, display limited turnover numbers (TONs), thus requiring further optimization.

We recently reported a new generation of cobalt complexes incorporating a tetradentate ligand (Figure 1),[17] which were shown to be remarkable electrocatalysts for proton reduction. By combining these cobalt diimine–dioxime catalysts, $[\mathrm{Co(DO)(DOH)pnBr_2}]$ (**1**) and $[\mathrm{Co((DO)_2BF_2)pnBr_2}]$ (**2**),[17] with the cyclometalated iridium photosensitizer $[\mathrm{Ir(ppy)_2(bpy)}][\mathrm{PF_6}]$ (**PS**; Figure 1), previously shown by us and others to display an efficiency considerably higher than that of other metal bipyridyl complexes such as $[\mathrm{Ru(bpy)_3}]^{2+}$ in related homogeneous H_2-evolving photocatalytic systems,[9,18,19] we could obtain an improved photocatalytic system for the reduction of protons to H_2 with TONs based on catalysts among the highest reported so far.

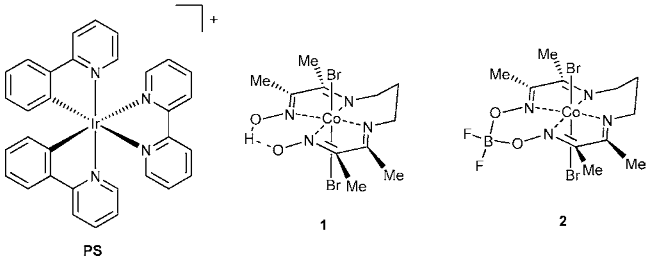


Figure 1. Photosensitizer and catalysts employed in the present study.

■ EXPERIMENTAL SECTION

Materials and Physical Methods. The ligand $N^2,N^{2\prime}$-propanediylbis(2,3-butanedione-2-imine-3-oxime) ($\{\mathrm{(DOH)_2pn}\}$)[20,21] and the complexes $[\mathrm{Co^{III}(DO)(DOH)pnBr_2}]$,[17] $[\mathrm{Co^{III}(DO)_2(BF_2)pnBr_2}]$,[17] $[\mathrm{Co^{I}(DO)(DOH)pnPPh_3}]$,[17,20,22] and $[\mathrm{Ir(ppy)_2(bpy)}](\mathrm{PF_6})$[23] were prepared according to previously reported literature procedures. Triphenylphosphine (PPh_3), triethylamine (TEA), triethanolamine (TEOA), concentrated hydrogen chloride

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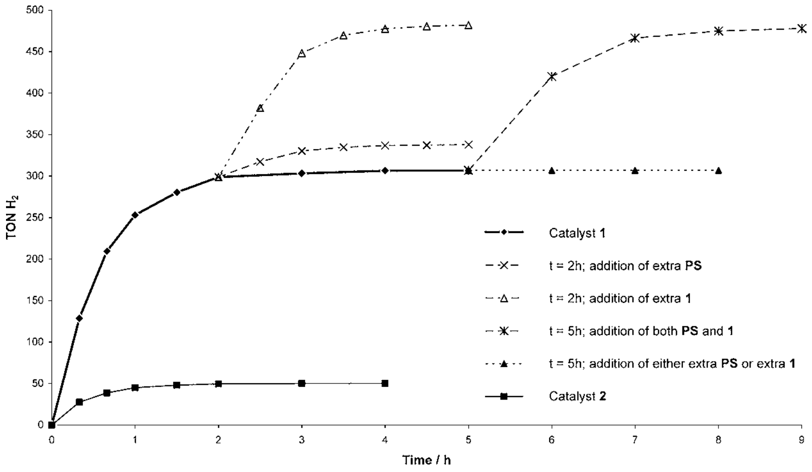

Figure 2. Photocatalytic H_2 evolution using catalyst **1** or **2**, together with regeneration of the photocatalytic system by the addition of an extra equiv of **PS** and/or **1**, after 2 or 5 h of irradiation (xenon lamp; $\lambda > 400$ nm). Conditions: $[\mathbf{1}] = 1 \times 10^{-4}$ M, $[\mathbf{PS}] = 1 \times 10^{-4}$ M, CH_3CN/H_2O (1:1, v/v), TEA (10%), pH = 10.

(HCl), CH_3CN, and cobalt bromide hydrate were used as received. All reactions in solution were carried out under an inert atmosphere of nitrogen using conventional vacuum-line and glasswork techniques. The metal complexes were, however, handled in air in the solid state. UV–visible absorption spectra have been recorded with an HP 8453 spectrophotometer.

A three-electrode cell consisting of a glassy carbon (⌀ 3 mm) disk working electrode (radiometer), an auxiliary platinum wire, and an Ag/AgCl/KCl (3 mol·L^{-1}) reference electrode, abbreviated as Ag/AgCl, was used for electrochemical measurements. Cyclic voltammograms were recorded on a EG&G PAR 273A instrument. Solution concentrations were ca. 2.0 mmol·L^{-1} for the cobalt complex and 0.1 mol·L^{-1} for the supporting electrolyte, $(n\text{-}Bu_4N)BF_4$. All potentials given in this work are with respect to the ferricinium/ferrocene (Fc^+/Fc) couple, whose potential has been measured after each experiment by adding authentic Fc to the cell. Electrochemical data from the literature have been quoted to the Fc^+/Fc couple.[24]

Typical Procedure for the Photocatalytic Experiment. The solvent mixture was prepared as follows: concentrated HCl (37%) was added to a solution of Et_3N (5 mL) in CH_3CN (22.5 mL) so as to adjust the apparent pH (measured in the solution with a glass electrode). The volume of the solution was then completed to 50 mL by the addition of distilled water. The photosensitizer (1×10^{-4} M), the catalyst (1×10^{-4} M), and PPh_3 (2×10^{-4} M) were dissolved in the above solvent mixture (5 mL) in a Schlenk tube. The solution was freeze–pump–thaw-degassed three times and then warmed to room temperature prior to irradiation. The gas-phase volume in the bottle was 64 mL. The reaction solution was irradiated at 25 °C using a xenon lamp (500 W) with a cutoff filter ($\lambda > 400$ nm). The gas phase of the reaction system was analyzed on a GC 7890T instrument with a 5 Å molecular sieve column, a thermal conductivity detector, and N_2 as the carrying gas. Hydrogen dissolved in the solution was not measured, and the effect of H_2 gas generated on the pressure of the Schlenk bottle was neglected for calculation of the volume of H_2 gas.

■ RESULTS

Photocatalytic Activity and Stability. Equimolar mixtures of catalysts **1** and **2** and $[Ir(ppy)_2(bpy)](PF_6)$ (1×10^{-4} M) were initially studied under visible-light irradiation ($\lambda > 400$ nm) at pH 10 in a CH_3CN/H_2O (1:1, v/v) mixture containing 10% triethylamine (TEA) used as the sacrificial electron donor (Figure 2). No H_2 is detected when one of the components—catalyst, photosensitizer, or TEA—is missing or when the reaction is carried out in the dark. Catalyst **1** proves the most active one with 307 TON H_2 (Figure 2; run 1 in Table 1) achieved after 4 h of irradiation, while only 50 TON H_2 is measured when catalyst **2** is employed under the same conditions (Figure 2; run 2 in Table 1).

Table 1. Photocatalytic H_2 Production under Various Experimental Conditions

run	catalyst	photosensitizer	time	TON
1	**1**	**PS**	4 h	307
2	**2**	**PS**	4 h	50
3[a]	**1**	**PS**	4 h	7
4[b]	**1**	**PS**	4 h	230
5[c]	**1**	**PS**	4 h	143
6[d]	**1**	**PS**	4 h	77
7[e]	**1**	**PS**	4 h	133
8	**1**	$[Ru(bpy)_3]^{2+}$	4 h	<1
9	**1**	**PS** (**PS**/**1** ratio = 1:2)	4 h	91
10	**1**	**PS** (**PS**/**1** ratio = 2:1)	4 h	348
11[f]	**1**	**PS**	5 h + 4 h	307 + 126
12[g]	**1**	**PS**	5 h + 4 h	307 + 171
13[h]	**1**	**PS**	2 h + 3 h	299 + 32
14[i]	**1**	**PS**	2 h + 3 h	299 + 127
15[j]	**1**	**PS**	2 h + 3 h	299 + 176
16	**1** + 0.5 equiv of PPh_3	**PS**	6 h	350
17	**1** + 1 equiv of PPh_3	**PS**	8 h	613
18	**1** + 2 equiv of PPh_3	**PS**	10 h	696
19	**1** + 5 equiv of PPh_3	**PS**	9 h	612

[a] TEOA instead of TEA. [b] 2:1 CH_3CN/H_2O. [c] 1:2 CH_3CN/H_2O. [d] pH = 9. [e] pH = 11. [f] An extra equiv of **PS** + 5 equiv of $\{(DOH)_2pn\}$ ligand added at $t = 5$ h. [g] An extra equiv of **PS** + an extra equiv of **1** added at $t = 5$ h. [h] An extra equiv of **PS** added at $t = 2$ h. [i] 5 equiv of $\{(DOH)_2pn\}$ ligand added at $t = 2$ h. [j] An extra equiv of **1** added at $t = 2$ h.

The following modifications of the system (runs 3–8 in Table 1) result in decreased TON, as previously observed on related photocatalytic systems: (i) replacement of the sacrificial electron donor TEA by TEOA (7 TON; Figure S1 in the Supporting Information);[14,18] (ii) modification of the water content of the solvent mixture (Figure S2 in the Supporting Information);[14,25,26] (iii) modification of the pH value of the system (no H_2 at pH = 8, 77 TON at pH = 9, and 133 TON at pH = 11; Figure S3 in the Supporting Information), in agreement with the presence of two antagonist effects:

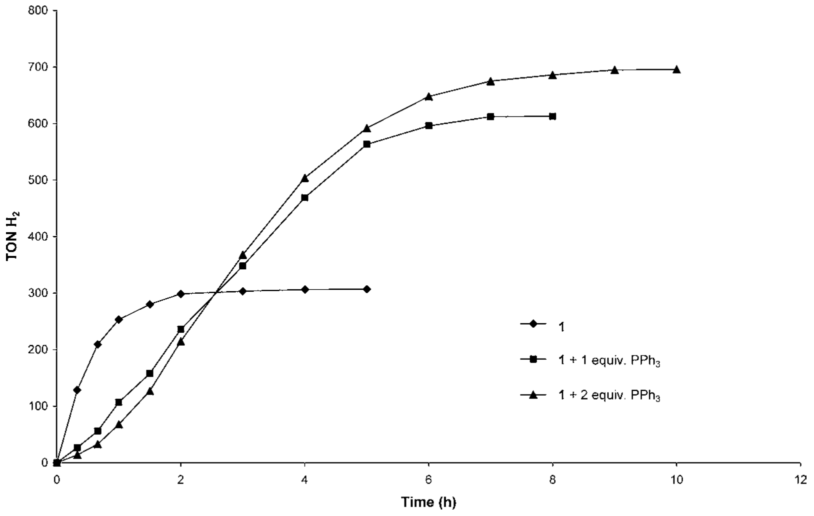

Figure 3. Photocatalytic H_2 evolution using catalyst **1** in the absence and presence of 1 and 2 equiv of PPh_3. Conditions: [**1**] = 1×10^{-4} M, [**PS**] = 1×10^{-4} M, CH_3CN/H_2O (1:1, v/v), TEA (10%), pH = 10.

increased pH results in an increased reducing power of the sacrificial electron donor (accelerating effect) and a parallel decreased concentration of the H^+ substrate (slowing-down effect);[7,10,11,13,14,27] (iv) replacement of **PS** by $[Ru(bpy)_3]^{2+}$.[9,18,19] Decreasing the **PS**/**1** molar ratio to 1:2 while keeping the concentration of **1** unchanged results in a significantly lower H_2-evolving efficiency (91 TON based on the catalyst; Figure S4 in the Supporting Information) compared to that (307 TON) obtained with a **PS**/**1** molar ratio of 1:1. In contrast, when the **PS**/**1** molar ratio is set to 2:1, the TON is increased to 348 under otherwise identical conditions.

Whereas an impressively high initial turnover frequency is observed (253 TON in the first hour; Table S1 in the Supporting Information), H_2 evolution levels off after 2 h and stops after about 4 h of irradiation. The addition then of an extra equiv of either **PS** or **1** fails to resume H_2 production under irradiation. If **PS** and **1** are added simultaneously, the activity is partially recovered, with 171 TON H_2 achieved after an additional 4 h of irradiation (Figure 2; run 12 in Table 1). If supplementation of the medium with fresh reactants is made earlier (after 2 h of reaction; Figure 2), we observe that the addition of an extra equiv of **PS** alone leads to stimulation, albeit small, of H_2 production (32 TON; run 13 in Table 1), while the addition of an extra equiv of the catalyst alone yields a much greater stimulation (176 TON over 3 h; run 15 in Table 1).[28] Previous reports on light-driven systems based on cobaloxime catalysts have indicated that the addition of the $dmgH_2$ ligand alone, instead of $[Co(dmg)_2]$, together with **PS**, was sufficient to restart H_2 evolution.[15] We also explored the regeneration ability of the diimine–dioxime ligand in our catalytic system. The addition of 5 equiv of the $\{(DOH)_2pn\}$ ligand after 2 h of irradiation restarts H_2 evolution though with a lower stability (+127 TON; run 14 in Table 1) compared to the addition of an extra equiv of **1** (Figure S5 in the Supporting Information). A similar behavior is observed when 5 equiv of the $\{(DOH)_2pn\}$ ligand and an extra equiv of the iridium **PS** are added after 5 h of irradiation compared to the addition of an extra equiv of **1** and **PS** (+126 TON; run 11 in Table 1 and Figure S5 in the Supporting Information).

Effect of PPh_3 on the Photocatalytic Activity. The addition of 1 equiv of PPh_3 has a strong influence on the course of the photocatalytic reaction (Figure 3; run 12 in Table 1). While it results in a slightly lower initial catalytic rate, it stabilizes the system with H_2 evolution sustained over 6 h at a significant rate and a doubling of the final TON. Best results in terms of stability are obtained when 2 equiv of PPh_3 is added to the reaction mixture, with up to 696 TON achieved during a 10 h experiment (Figure 3; run 13 in Table 1; Table S1 in the Supporting Information) but with comparable initial turnover frequencies. The addition of higher amounts of phosphine (5 equiv; Figure S6 in the Supporting Information) could not further improve the activity. A similar lag phase is observed when the photocatalytic experiment is run[29] using the independently prepared $[Co^I(DO)(DOH)pn(PPh_3)]$[17,20,22] complex as the catalyst (see Figure S9 in the Supporting Information).

Coordination of PPh_3 to the Cobalt Catalyst. The cyclic voltammogram of a CH_3CN solution of **1**, recorded at a glassy carbon electrode (Figure S4 in the Supporting Information), displays a first quasi-reversible system at −0.67 V vs Fc^+/Fc assigned to the Co^{III}/Co^{II} couple followed by a reversible process at −1.12 V vs Fc^+/Fc corresponding to the formation of the Co^I species (Table 2). The addition of 1 equiv of PPh_3 has no effect on the first process, showing that PPh_3 coordinates neither to the starting Co^{III} complex nor to the electrochemically generated Co^{II} species. By contrast, both cathodic and anodic waves of the second system are shifted to more positive potentials by ~280 mV (Table 2), indicating that PPh_3 strongly binds to the Co^I derivative, yielding the known $[Co^I(DO)(DOH)pn(PPh_3)]$ species.[17] The cyclic voltammogram is not modified further upon the addition of higher amounts of phosphine.

Identification of the Catalytically Active Species. The photocatalytic experiment was monitored by UV–visible spectroscopy during irradiation. Initially, absorption is only observed at high energy in the visible region (Figure 4), as expected for a Co^{III} complex in solution. Irradiation leads, after 10–20 s, to a first absorption band at 472 nm, characteristic for a Co^{II} species.[10] When PPh_3 is present in solution, a second band at 638 nm then appears and plateaus after 70 s of reaction. This band is the exact signature of the Co^I complex $[Co^I(DO)(DOH)pn(PPh_3)]$ independently recorded for comparison (Figure 4). Experiments carried out in the absence of

Table 2. Redox Properties of PS[19] and Catalyst 1 Alone or in the Presence of PPh_3[a]

	PS	1	1/PPh_3
Ir*	2.10 eV		
Ir^{IV}/Ir^{III}	+0.87 V[b]		
Co^{III}/Co^{II}		−0.67 V[b]	−0.68 V[b]
Co^{II}/Co^{I}		−1.12 V[b]	−0.84 V[b]
$\Delta G_1{}^{\circ}$[e]		−0.56 eV	−0.55 eV
$\Delta G_2{}^{\circ}$[f]		−0.11 eV	−0.39 eV
$(bpy)_{Ir}/(bpy^{\bullet-})_{Ir}$	−1.80 V[b]		
$\Delta G_3{}^{\circ}$[c]		−1.13 eV	−1.12 eV
$\Delta G_4{}^{\circ}$[d]		−0.68 eV	−0.96 eV

[a] This work (see the Supporting Information). [b] vs Fc^+/Fc. [c] The free energy of formation of the Co^{II} species by electron transfer from Ir* to Co^{III} was calculated from the equation $\Delta G_1{}^{\circ} = E(Ir^{IV}/Ir^{III}) - E(Co^{III}/Co^{II}) - E(Ir^*)$. [d] The free energy of formation of the Co^{I} species by electron transfer from Ir* to Co^{II} was calculated from the equation $\Delta G_2{}^{\circ} = E(Ir^{IV}/Ir^{III}) - E(Co^{II}/Co^{I}) - E(Ir^*)$. [e] The free energy of formation of the Co^{II} species by electron transfer from $[Ir(ppy)_2(bpy^{\bullet-})]^{3+}$ to Co^{III} was calculated from the equation $\Delta G_1{}^{\circ} = E((bpy)_{Ir}/(bpy^{\bullet-})_{Ir}) - E(Co^{III}/Co^{II})$. [f] The free energy of formation of the Co^{I} species by electron transfer from $[Ir(ppy)_2(bpy^{\bullet-})]^{3+}$ to Co^{II} was calculated from the equation $\Delta G_2{}^{\circ} = E((bpy)_{Ir}/(bpy^{\bullet-})_{Ir}) - E(Co^{II}/Co^{I})$.

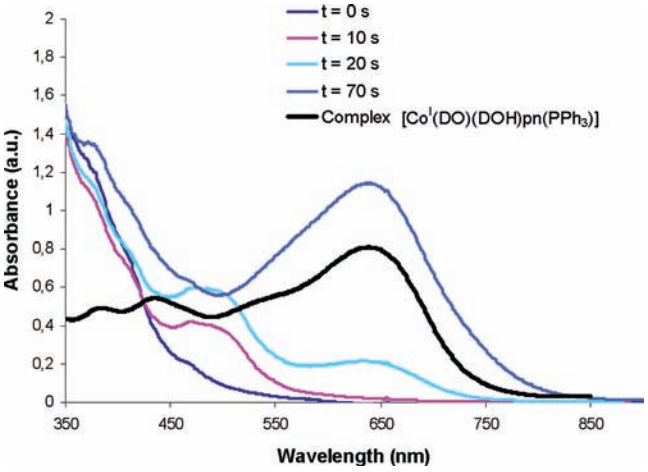

Figure 4. Time-dependent UV−visible spectra of a photocatalytic experiment in the presence of PPh_3 under irradiation. Conditions: [**1**] = 1×10^{-4} M, [**PS**] = 1×10^{-4} M, [PPh_3] = 1×10^{-4} M, CH_3CN/H_2O (1:1, v/v), TEA (10%), pH = 10.

PPh_3 display very different spectra (Figure 5). In that case, the absorption band characteristic of a Co^{II} species is replaced, after 20 s of irradiation, by two new bands at 602 and 678 nm, whose intensities reached a plateau around 60 s of irradiation. Assignment of these bands is discussed below.

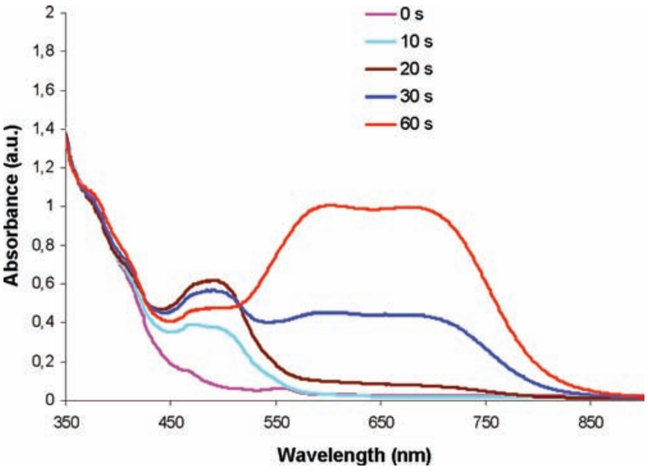

Figure 5. Time-dependent UV−visible spectra of a photocatalytic experiment in the absence of PPh_3 under irradiation. Conditions: [**1**] = 1×10^{-4} M, [**PS**] = 1×10^{-4} M, CH_3CN/H_2O (1:1, v/v), TEA (10%), pH = 10.

■ DISCUSSION

Catalytic Activity and Stability. Our results first demonstrate the potential of the new generation of H_2-evolving cobalt diimine−dioxime catalysts for light-driven H_2 production. We observe a large difference between H- and BF_2-bridged structures in terms of TONs (Table 1), which can be related to the previously noticed difference regarding protonation: catalyst **2** cannot be protonated at the oxime functions because they are engaged in covalent bonds with the boron atom, whereas protonation of the H-bridged complex **1** at close proximity of the cobalt center favors proton reduction and adjustment of the electrocatalytic potential of complex **1** to the acido−basic conditions of the solution.[17] The combination of equimolar amounts of the **PS** photosensitizer and catalyst **1** shows an impressively high initial turnover frequency but a limited stability because H_2 evolution stops after completion of ~300 TON, a number significantly higher than the one previously reported by Probst et al. for a system based on the same catalyst but working in pure water.[12] Our data show that the cobalt catalyst is the most sensitive component of the system and is more rapidly degraded than **PS** under such conditions. Partial regeneration of the H_2-evolving activity could be achieved by the simple addition of the sole $\{(DOH)_2pn\}$ ligand after 2 h of irradiation, thus regenerating the catalyst in solution. However, this does obviously not provide a sustainable solution to optimize the long-term stability of such photocatalytic systems.

We then developed a strategy to limit catalyst decomposition, based on the addition of PPh_3 to the photocatalytic medium. This ligand is known to stabilize the low redox states of the cobalt complex, which are the key intermediates in the H_2-evolution mechanism.[6,17] Stabilization of the Co^{I} state of catalyst **1** by coordination of the phosphine is confirmed by cyclic voltammetry measurements with a ~280 mV shift of the electrochemical potential shift of the Co^{II}/Co^{I} couple upon the addition of PPh_3. Under the same conditions, phosphine does not bind the starting Co^{III} compound nor the electrochemically generated Co^{II} species.

Clearly, the addition of PPh_3 considerably increases the stability of the $[Ir(ppy)_2(bpy)]^+$/**1** photocatalytic system. A 2-fold improvement of the total TON is obtained with the addition of only 1 equiv of PPh_3.[30] The addition of $PnBu_3$ has also been reported to increase the stability of a related cobaloxime-based photocatalytic system, though with the need for the simultaneous addition of excess $dmgH_2$ ligand.[7] Actually, in many reported studies, experiments are carried out with large excesses of the catalyst and/or free ligand over the photosensitizer and optimization strategies rather target the photosensitizer than the catalyst. 9000 TON_{PS} H_2 (127 TON_{Co}) was, for instance, obtained when a cobaloxime catalyst was used in combination with a new organic dye designed by Eisenberg and colleagues.[15] Tricarbonylrhenium complexes have also been successfully used as light-harvesting units in combination with cobaloximes[9,11,27] or diimine−dioxime cobalt catalysts.[12] The recently described $[Re(CO)_3(bipy)(SCN)]/[Co(dmgH)_2(OH_2)_2]$ system actually achieves up to 6000 TON_{PS} (~1000 TON_{Co} and ~200 TON_{ligand}) thanks to the presence of excess $dmgH_2$ added to repair the catalyst in the course of catalysis.[11] The introduction of excess amounts of either the photosensitizer, the catalyst, or a ligand, thereby somehow used as a sacrificial component, artificially increases the TON of the photocatalytic system but does not provide a long-term solution to the design of robust molecular-based devices. In our system, the iridium photosensitizer remains active over more than 5 h of irradiation when the catalyst is protected from decomposition by the presence of PPh_3. By comparison, it is fully decomposed after 4 h in the absence of PPh_3 (Figure 2). We assume that, under these conditions and in the absence of any electron acceptor in solution as a result of the complete decomposition of the catalyst, deactivation of the photosensitizer is accelerated.[11]

UV−visible spectroscopic analysis of the solution during photochemical experiments allows one to establish that PPh_3 binds the photogenerated Co^I derivative, yielding the known $[Co^I(DO)(DOH)pn(PPh_3)]$ species, which we believe is the initiating species in the H_2-evolution catalytic cycle.[6,17] By contrast, in the absence of PPh_3, another species is produced during the photocatalytic reaction, characterized by light absorption bands at 602 and 678 nm (Figure 5). Similar spectroscopic signatures have been reported during the course of a photocatalytic experiment employing $[Co(dmgBF_2)_2(H_2O)_2]$ as the H_2-evolving catalyst[25,26] and also observed during electrochemical[31] or chemical reduction[32,33] of $[Co(dmgBF_2)_2(CH_3CN)_2]$. In a very recent theoretical study by Fujita and Muckerman[34] on the mechanism of catalytic H_2 production by cobaloxime catalysts, a similar spectrum has been calculated for a Co^{II}−H intermediate. In our photocatalytic studies with cobalt diimine−dioxime complexes, such a Co^{II}−H species could be generated by one-electron reduction of a Co^{III}−H precursor, itself formed by protonation of the photogenerated Co^I derivative (see the Mechanistic Issues section). We thus propose that, in the presence of PPh_3 in solution, the resting state of the catalytic cycle switches from a Co^{II}−H intermediate to the Co^I−PPh_3 one. While this Co^I species stabilized by coordination of the π-acceptor phosphine ligand is stable enough to be isolated, hydridocobaloxime could only be isolated in the Co^{III} state, again thanks to stabilization of a *trans*-phosphine ligand.[35] Furthermore, under basic conditions, unstabilized hydridocobaloxime evolves through hydride transfer to a catalytically inactive cobalt complex bearing a hydrogenated dioxime ligand.[36] The above considerations provide a rationale for the positive effect of PPh_3 on the stability of the photocatalytic system.

Mechanistic Issues. In the following, we discuss mechanistic issues regarding (i) the photogeneration of the Co^I species, (ii) the nature of the active species, and (iii) the influence of PPh_3 on the H_2-evolution mechanism.

Under photocatalytic conditions, two mechanisms may account for the formation of a Co^I active species: first, an oxidative quenching process converting the photoexcited iridium complex (Ir*), by electron transfer to the catalyst, to the oxidized $[Ir(ppy)_2(bpy)]^+$ complex form, which is then reduced by the sacrificial electron donor; second, a reductive quenching process in which Ir* oxidizes the electron donor and the resulting $[Ir(ppy)_2(bpy^{\bullet -})]^+$ complex then transfers an electron to the catalyst.[6] We previously established the ability of TEA to reductively quench the excited iridium complex.[18] Considering either the Co^{III} catalyst **1** alone or in the presence of PPh_3, both oxidative ($\Delta G_1°$ and $\Delta G_2°$ in Table 2) and reductive ($\Delta G_3°$ and $\Delta G_4°$ in Table 2) processes are thermodynamically allowed for the two successive electron transfers required to generate the catalytically active Co^I species. Clarification of the mechanism at work in this system thus requires further experiments (transient absorption spectroscopy) to establish the kinetic parameters of the quenching processes. Nevertheless, because TEA is present in large excess (≈7200 equiv) with regard to **PS** and **1**, we actually favor a reductive quenching process.

The photogenerated Co^I species is the entry into the cobalt-centered H_2-evolution catalytic cycle.[6,17,32,33,37,38] Protonation then generates a Co^{III}−H intermediate as an active species for H_2 evolution. Recent theoretical studies by Fujita and Muckermann[34] or Hammes-Schiffer and colleagues[39] indicate that H_2 evolution requires further reductive activation of this intermediate to generate a Co^{II}−H active species. At this stage, two pathways could account for H_2 generation: a homolytic pathway where two hydrides react together or a heterolytic pathway where the hydride further reacts with one proton to produce H_2. Discrimination between the mechanisms at work so far proved unsuccessful at both the experimental and theoretical levels.[6,34,39] Further studies are, therefore, needed to understand the influence of phosphine coordination on the catalytic H_2-evolution mechanism. Such a modification of the cobalt coordination sphere is likely responsible for the lower initial catalytic rates observed in light-driven H_2 production catalyzed by **1** in the presence of PPh_3 (Figure 3). Because the same lag phase is observed when the photocatalytic experiment is run using $Co^I(DO)(DOH)pn(PPh_3)$ as the catalyst (see Figure S9 in the Supporting Information), we exclude that it could be due to the two initial reduction steps generating the active Co^I species from the Co^{III} precursor, as suggested for a photocatalytic system based on $Co^{III}(dmgH)_2pyCl$.[25,26]

In conclusion, the high potential of the new generation of H_2-evolving cobalt diimine−dioxime catalysts for light-driven H_2 production has been demonstrated. We also show that tuning of the coordination sphere of the catalyst can also be used as a strategy to improve the stability of such a photocatalytic system. The addition of PPh_3 indeed allows to reach up to ~700 TON_{Co} in a 10 h experiment. Importantly, our system is optimized on a 1:1 Ir/Co ratio (no need for any extra component), which opens the possibility of gaining even more stability through the development of supramolecular systems incorporating these catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Plots of photocatalytic H_2 evolution, table of TONs, and cyclic voltammograms.This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) After ~300 TON of H_2 production, the composition and pH of the medium have been modified, explaining the incomplete recovery of the activity observed after the simultaneous addition of extra catalyst and **PS**. The presence of TEA decomposition products could also account for this.
(29) With this complex being highly air-sensitive, a different irradiation setup was employed.
(30) Because the initial turnover frequencies are very similar for 1 or 2 equiv of added phosphine, we infer the slightly better stability observed in the presence of excess phosphine to a kind of inhibition of the decomposition pathways, for instance, through radical scavenging.
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