## Hydrogen Production

# Photo- and Electrocatalytic H<sub>2</sub> Production by New First-Row Transition-Metal Complexes Based on an Aminopyridine Pentadentate Ligand

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Abstract: The synthesis and characterisation of the pentadentate ligand 1,4-di(picolyl)-7-(p-toluenesulfonyl)-1,4,7-triazacyclononane (Py2<sup>Ts</sup>tacn) and their metal complexes of general formula  $[M(CF_3SO_3)(Py_2^{Ts}tacn)][CF_3SO_3], (M = Fe (1_{Fe}),$ Co  $(1_{co})$  and Ni  $(1_{Ni})$  are reported. Complex  $1_{co}$  presents excellent H<sub>2</sub> photoproduction catalytic activity when using  $[Ir(ppy)_2(bpy)]PF_6$  (**PS**<sub>Ir</sub>) as photosensitiser (PS) and Et<sub>3</sub>N as electron donor, but  $\mathbf{1}_{Ni}$  and  $\mathbf{1}_{Fe}$  result in a low activity and a complete lack of it, respectively. On the other hand, all three complexes have excellent electrocatalytic proton reduction activity in acetonitrile, when using trifluoroacetic acid (TFA) as a proton source with moderate overpotentials for  $\mathbf{1}_{co}$  (0.59 V vs. SCE) and  $\mathbf{1}_{Ni}$  (0.56 V vs. SCE) and higher for  $1_{Fe}$  (0.87 V vs. SCE). Under conditions of CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (3:7:0.2),  $\mathbf{1}_{co}$  (5  $\mu \textrm{m}),$  with  $\mathbf{PS}_{ir}$  (100  $\mu \textrm{m})$  and irradiating at 447 nm gives a turnover number (TON) of 690  $(n_{\rm H_2}/n_{\rm 1co})$  and initial turnover frequency (TOF) (TON $\times$ t<sup>-1</sup>) of 703 h<sup>-1</sup> for H<sub>2</sub>

## Introduction

Hydrogen has gained special attention as the most promising fuel for the future use in transport and energy storage in terms of sustainability, carbon neutrality and energy conversion. However, there are many challenges that still remain; one of the most important is its efficient production. Water splitting promoted by sunlight is the most widely desired energetic pathway for hydrogen production.<sup>[11]</sup> In nature, iron and nickel hydrogenase enzymes<sup>[2]</sup> produce H<sub>2</sub>, but they are inconveniently instable under aerobic conditions making their application in H<sub>2</sub> production devices difficult.<sup>[3]</sup> Many efforts have been devoted to develop biomimetic catalytic systems of such enzymes, producing stimulating examples of H<sub>2</sub> production enzymatic models, but usually such catalysts have a tendency to be unstable against O<sub>2</sub> and operate generally at relatively high negative potentials.<sup>[4]</sup> On the other hand, in the last years an

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production. It should be noted that  $\mathbf{1}_{co}$  retains 25% of the catalytic activity for photoproduction of H<sub>2</sub> in the presence of  $O_2$ . The inexistence of a lag time for  $H_2$  evolution and the absence of nanoparticles during the first 30 min of the reaction suggest that the main catalytic activity observed is derived from a molecular system. Kinetic studies show that the reaction is -0.7 order in catalyst, and time-dependent diffraction light scattering (DLS) experiments indicate formation of metal aggregates and then nanoparticles, leading to catalyst deactivation. By a combination of experimental and computational studies we found that the lack of activity in photochemical water reduction by 1<sub>Fe</sub> can be attributed to the  $\mathbf{1}_{Fe}^{II/I}$  redox couple, which is significantly lower than the  $\mathbf{PS}_{\mathbf{Ir}}^{\mathbf{III/II}}$ , while for  $\mathbf{1}_{\mathbf{Ni}}$  the pK<sub>a</sub> value (-0.4) is too small in comparison with the pH (11.9) imposed by the use of Et<sub>3</sub>N as electron donor.

intense search has been dedicated to find earth-abundant transition-metal complexes able to catalyse the reduction of protons to hydrogen at low overpotentials or by using light as a source of energy.<sup>[5]</sup> Earth abundant molecular complexes based on cobalt,<sup>[5a]</sup> nickel,<sup>[6]</sup> iron<sup>[7]</sup> and molybdenum<sup>[8]</sup> have been shown to be able to reduce the protons of water to H<sub>2</sub> under electro- and photochemical conditions in an efficient manner. However, a comparative study of the factors that affect the reactivity in catalytic water reduction among a series complexes based on different metals with the same ligand framework to the best of our knowledge has not been explored in detail so far.<sup>[9]</sup>

Very often water reduction requires intermediates in which metals are in a low oxidation state, and which are frequently stabilised by oxygen-sensitive or easily hydrolysable ligands. It is then crucial to develop catalysts that are active in water as the reaction media, are resistant to oxygen and which could operate at a low overpotential and by light-driven. In this regard, previous studies,<sup>[10-12]</sup> relying on abundant metals and robust polypyridyl ligands are encouraging for the electrocatalytic and photocatalytic reduction of water. More recently, more versatile amino pyridine ligands have also shown impressive catalytic performance. Up to now, systems that contain from five chelating pyridines to three pyridines and two amines have been studied (Figure 1).

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Figure 1. Selected polypyridine and polypyridinamine cobalt complexes studied in proton and water reduction.  $^{[9_{0},10,12e]}$ 

We are interested in developing robust catalysts that could retain their molecular nature under catalytic conditions with the aim to study reaction mechanisms. In this regard, we previously reported a highly efficient water oxidation catalysts based on iron complexes and highly chelating tetradentate aminopyridine ligands.<sup>[13]</sup> In particular, 1-pyridine-4,7-dimethyltriazacyclononane (Pytacn) has been particularly useful to investigate the reaction mechanism due to the conferred high stability of its iron coordination complexes.

It is known that the triazacyclononane (tacn) moiety is a highly electron-donating, redox-innocent, ligand moiety that stabilises high oxidation states at metal centres. In principle, the application of ligands derived from this unit to water reduction are counterintuitive considering the mechanisms proposed for molecular complexes with polypyridine ligands that usually require reduction of the metal centre to M<sup>I</sup> or even M°.<sup>[14]</sup> In this regard, the introduction of electron-withdrawing substituents could decrease the ligand stabilisation and favour the low oxidation states, but preserve the high chelating nature of the moiety. More interestingly is to explore catalysts for both water oxidation (WO) and water reduction (WR) reactions based on analogous ligand structures. To date, only a few examples of catalysts have been reported that can carry out both WO and WR catalysis.<sup>[15]</sup> Water splitting devices could be favoured by the use of both WO and WR catalysts build from comparable structural motifs in order to achieve compatibilities and synergies among homogeneous systems.

With this aim, herein we present a robust platform assembled by appending on the N atoms of the tacn ring with one electron-withdrawing tosyl group and two methylpyridine arms, giving a pentadentate ligand, as well as their corresponding iron, cobalt and nickel complexes. The resultant Co complex is active in both electro- and photochemical H<sub>2</sub> production, while the Fe and Ni complexes are only electrocatalytically active. The comparative study among complexes with the same ligand framework allows us to establish basic principles for water reduction based on aminopyridine ligands.

## **Results and Discussion**

The synthesis of the ligand 1,4-di(picolyl)-7-(p-toluenesulfonyl)-1,4,7-triazacyclononane (Py<sub>2</sub><sup>Ts</sup>tacn) has been achieved in excellent yield (82%) from a direct dialkylation of the monotosylated 1,4,7-triazacyclononane with two equivalents of 2-(chloromethyl)pyridine hydrochloride. The reaction of the Py<sub>2</sub><sup>Ts</sup>tacn ligand with one equivalent of M(OTf)<sub>2</sub>·2 CH<sub>3</sub>CN (M = Co, Fe and Ni) in THF at room temperature afforded the M<sup>II</sup> five-coordinate monocationic complexes of general formula [M-(CF<sub>3</sub>SO<sub>3</sub>)(Py<sub>2</sub><sup>Ts</sup>tacn)][CF<sub>3</sub>SO<sub>3</sub>], M=Co (1<sub>Co</sub>), M=Fe (1<sub>Fe</sub>) and M= Ni (1<sub>Ni</sub>) (Scheme 1).



Scheme 1. Synthesis of ligand  $Py_2^{Ts}$ tacn and complexes  $1_{Co'}$   $1_{Fe}$  and  $1_{Ni}$ .

All three  $M^{\parallel}$  coordination complexes  $1_{Co}$ ,  $1_{Fe}$  and  $1_{Ni}$  showed broad signals in their <sup>1</sup>H NMR spectra that expand from -10 to 140 ppm, indicative of paramagnetic species (see Supporting Information, Figures SI.3, SI.4 and SI.5). High-resolution electrospray ionisation mass spectrometry (HR-ESI-MS) shows the monocharged molecular peak (673.1054 m/z for  $[1_{Co}-OTf]^+$ , 670.1069 *m*/*z* for  $[1_{Fe}$ -OTf]<sup>+</sup> and 672.1058 *m*/*z* for  $[1_{Ni}$ -OTf]<sup>+</sup>) and the double charged molecular peak of the complexes without the triflates (262.0766 m/z for  $[1_{co}-2OTf]^{2+}$ , 260.5804 *m/z* for  $[1_{Fe}-2 \text{ OTf}]^{2+}$  and 261.5797 *m/z* for [1<sub>Ni</sub>-2OTf]<sup>2+</sup>). In agreement, X-ray diffraction analysis of monocrystals from  $1_{Co}$  and  $1_{Ni}$  confirm the formation of distorted octahedral complexes formed by a pentacoordinate ligand bonded to the metal by the three amines of the triazacyclononane unit and two different pyridines; the last coordination site occupied by a labile triflate anion (Figure 2). The selected bond lengths and angles are summarised in Figure 2. M-N bond lengths are in the range of the expected values for the two pyridines (ca. 2.10 and 2.05 Å for  $1_{co}$  and  $1_{Ni}$ , respectively) and the alkyl amines (ca. 2.14 and 2.07 Å for  $\mathbf{1}_{co}$  and  $\mathbf{1}_{Ni^{\prime}}$  respectively), but considerably larger for the tosylated amine (2.320 and ca. 2.264 Å for 1<sub>co</sub> and 1<sub>Ni</sub>, respectively).

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**Figure 2.** ORTEP structures with ellipsoids set at the 50% probability level of  $1_{co}$  (top) and  $1_{Ni}$  (bottom) from the X-ray diffraction analysis. Hydrogen atoms have been omitted for clarity. Relevant distances [Å] and bond angles [°] for  $1_{co}$ : Co(1)–O(1), 2.034(1); Co(1)–N(1), 2.141(2); Co(1)–N(2), 2.093(2); Co(1)–N(3), 2.320(2); Co(1)–N(4), 2.130(2); Co(1)–N(5), 2.133(2); O(1)-Co(1)-N(1), 172.39(6); N(2)-Co(1)-N(4), 2.130(2); Co(1)–N(5), 159.09(6); N(1)-Co(1)-N(2), 80.05(6); N(1)-Co(1)-N(3), 81.61(6); N(1)-Co(1)-N(4), 82.20(6); N(1)-Co(1)-N(5), 96.47(6); N(2)-Co(1)-N(3), 101.95(6); N(4)-Co(1)-N(5), 79.31(7) and for  $1_{Ni}$ : Ni(1)–O(1), 2.0488(17); Ni(1)–N(1), 2.071(2); Ni(1)–N(2), 2.042(2); Ni(1)–N(3), 2.264(2); Ni(1)–N(4), 2.076(2); Ni(1)–N(5), 2.066(2); O(1)-Ni(1)-N(1), 73.15(7); N(2)-Ni(1)-N(4), 83.67(8); N(1)-Ni(1)-N(4), 84.51(8); N(1)-Ni(1)-N(2), 82.18(8); N(1)-Ni(1)-N(3), 83.67(8); N(1)-Ni(1)-N(4), 84.51(8); N(1)-Ni(1)-N(5), 96.52(8); N(2)-Ni(1)-N(3), 100.46(7); N(4)-Ni(1)-N(5), 80.75(8).

### Photocatalytic water reduction to H<sub>2</sub>

### Effect of the metal

First, we tested the catalytic activity of  $\mathbf{1}_{Fe}$ ,  $\mathbf{1}_{Co}$  and  $\mathbf{1}_{Ni}$  under light-driven conditions by using a photosensitiser and a sacrificial electron-donor under irradiation ( $\lambda = 447$  nm). Hydrogen evolution was monitored online by the difference of pressure between the reaction vessel containing the mixture of the reaction and a blank sample under the same conditions, but lacking the metal complex. Reactions were carried out by using an acetonitrile/water mixture; acetonitrile was used to ensure the complete solubilisation of the photosensitiser. The amount of hydrogen obtained at the end of the reaction was established in every case by analysing an aliquot of the headspace using gas chromatography with a thermal conductivity detector (GC-TCD).

The comparison among the activity of the three complexes was carried out by irradiation of a mixture containing the complex  $1_{M}$  (50  $\mu$ M), [lr(ppy)<sub>2</sub>(bpy)]PF<sub>6</sub> (**PS**<sub>Ir</sub> 250  $\mu$ M, ppy: phenyl pyridine) as photosensitiser and Et<sub>3</sub>N (200  $\mu$ L) as a source of electrons, in water/acetonitrile (7:3 mL) mixture. Under these conditions complex  $1_{co}$  is highly active, producing 3.2 mL of H<sub>2</sub> after 1.5 h of reaction with a TON<sub>cat</sub> ( $n_{H_2}/n_{complex}$ ) and TOF<sub>cat</sub>

 $(TON_{cat}h^{-1})$  values of 260 and 174  $h^{-1}$  (2.1 mL(H<sub>2</sub>) $h^{-1}$ ), respectively. In contrast, complex  $\mathbf{1}_{Ni}$  produces small amounts of hydrogen (6 TON<sub>cat</sub>) and 1<sub>Fe</sub> does not show any photocatalytic activity (see the Supporting Information, Figure SI.7). This is a very interesting result, but the difference among the activities of the complexes is difficult to rationalise at this point and will be discussed in more detail in the following sections. Control experiments show that the three components are needed for the photocatalytic H<sub>2</sub> evolution. Furthermore, when the reaction was performed in dark conditions, no gas production could be detected. Finally, only negligible amounts of H<sub>2</sub> where measured when using  $Co(OTf)_2 \cdot 2 CH_3 CN$ , Ni-(OTf)<sub>2</sub>·2CH<sub>3</sub>CN and Fe(OTf)<sub>2</sub>·2CH<sub>3</sub>CN under analogous photochemical conditions. Therefore, these results provide strong evidence that the H<sub>2</sub> obtained in our experiments cannot be attributed to the activity of free metal in solution, and therefore we conclude that the catalytic activity arises from the metal complex.

#### Photosensitiser

H<sub>2</sub> production by  $\mathbf{1}_{co}$  was drastically reduced when photosensitisers such as  $[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$  ( $\mathbf{PS}_{Ru}$ ) or erythrosine B ( $\mathbf{PS}_{EB}$ ) were used instead of  $\mathbf{PS}_{Ir}$  (TON<sub>cat</sub> = 20 with an initial TOF<sub>cat</sub> of 26 h<sup>-1</sup> and negligible, respectively) (see Figure SI.8 in the Supporting Information). This can be rationalised by the reduction potentials of the photosensitiser ( $\mathbf{PS}_{Ir}$ : -1.55,<sup>[16]</sup>  $\mathbf{PS}_{Ru}$ : -1.34,<sup>[17]</sup> and  $\mathbf{PS}_{EB}$ :  $-1.05 V^{[18]}$  vs. SCE). The redox potential  $E^{\circ}(\mathbf{1}_{co}^{II/})$ , measured by cyclic voltammetry, was found -1.10 V versus SCE. Therefore  $\mathbf{PS}_{Ir}$  has a higher reduction potential, and it is appropriate to account for the catalytic activity.

#### Effect of the sacrificial electron donor and the solvent mixture

The light-driven hydrogen production catalysed by  $1_{co}$  is also dependent on the amount of sacrificial electron donor and the solvent mixture. For instance, the yield of H<sub>2</sub> production is lower at higher Et<sub>3</sub>N loadings than 2% in volume of the reaction mixture (Figure 3). This reduction in activity can be rationalised by the increase in pH due to the increase on concentration of Et<sub>3</sub>N (from pH 11.9 using 1% of Et<sub>3</sub>N to pH 12.6 using 15% of Et<sub>3</sub>N), which may hinder either the formation of the Co–H intermediate or the reaction of Co–H with protons to form H<sub>2</sub>. Likewise, the ratio water/CH<sub>3</sub>CN modifies the catalytic activity due to the need to adjust the polarity of the medium to have all the components well solubilised. The highest activity was found at 70% (v/v) of water in acetonitrile (TON: 260, TOF: 174 h<sup>-1</sup>) (Figure 3).

## Effect of the photosensitiser and catalyst concentration

The increase of the  $[\mathbf{PS}_{Ir}]$  had a positive impact in the total amount H<sub>2</sub> obtained. The TON<sub>cat</sub> increases linearly with the concentration of the chromophore; however, the TON<sub>PS</sub> ( $n_{H_2}/$  $n_{PS}$ ) is almost independent of the photosensitiser concentration. For instance, TON<sub>cat</sub> values of 68 and 327 and TON<sub>PS</sub> values of 68 and 55 were found when using 50 and 300 µm of

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All efforts to regenerate the catalytic activity at the end of the were unsuccessful. reaction Indeed, further addition of any of the reaction components (PS<sub>Irr</sub>  $1_{co}$  or Et<sub>3</sub>N) at the end of the reaction did not restart the catalytic activity. Furthermore, the combined addition of catalyst and Et<sub>3</sub>N or **PS**<sub>Ir</sub> and Et<sub>3</sub>N results in negligible H<sub>2</sub> evolved. Only 25% of the catalytic activity could be restored upon addition of more catalyst and PS and 40% when all three components were added at the same time (see the Supporting Information, Figure SI.9). Altogether, these results suggest that the catalytic activity degradation over time may be due to a poisoning of

 $\mathbf{PS}_{irr}$  respectively (Figure 3). The loss of activity at  $\mathbf{PS}_{irr}$  concentrations higher than 300 µm can be attributed to the limited PS<sub>Ir</sub> solubility under these conditions. Initial reaction rates calculated at 10% of conversion versus the [PS<sub>Ir</sub>] revealed firstorder dependence (Figure 4), which is an indication that the reduction of the cobalt complex by the photoreduced **PS**<sub>Ir</sub> <sup>II</sup> controls the H<sub>2</sub> production rate.

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Afterwards, we studied the dependence of the H<sub>2</sub> production versus the concentration of  $1_{co}$ . Experiments were carried out varying the concentration of catalyst (5–100 μм) and fixing the concentration of  $PS_{Ir}$  (100 µM) with CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (2:8:0.2) as solvent mixture (Figures 3 and 4). The activity clearly increases with the decrease of the  $\mathbf{1}_{\mathsf{Co}}$  concentration. At low catalyst concentrations ( $1_{Co}\!=\!5~\mu\text{m},~\text{PS}_{\text{Ir}}\!=\!100~\mu\text{m})$  a TON $_{1_{Co}}$  of 690 and a  $\text{TOF}_{1_{\text{co}}}$  of 703  $h^{-1}$  were obtained. At lower catalysts concentrations, higher TON are clearly produced; however, the inaccuracy of the measurements under these conditions avoids further analysis. On the other hand, at higher catalyst concentrations (100 µm) the hydrogen production rate is still remarkable (1.46 mLh<sup>-1</sup> of H<sub>2</sub>). Initial reaction rates shows that the reaction becomes faster at lower  $\mathbf{1}_{co}$  concentration. The double In plot of the  $k_i$  versus  $1_{co}$  concentration shows an inverse catalytic-activity/metal-complex concentration correlation (Figure 4, top, inset). This might suggest the formation of inactive dimers or oligomeric species, but also cobalt nanoparticles, although the mononuclear species may have the higher activity and increase in number when the concentration is decreased.

Figure 4. Plots of on-line pressure monitored versus time for reactions using CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (2:8:0.2) as solvent mixture under irradiation at  $\lambda =$  447 nm. Тор: PS<sub>Ir</sub> (100 µм) and [1<sub>со</sub>] from 5 µм to 100 µм. Inset: double-In plot of initial H<sub>2</sub> evolution rates versus [ $1_{Co}$ ]. Bottom:  $1_{Co}$  (50  $\mu$ M) and [**PS**<sub>Ir</sub>] from 25  $\mu$ M to 125  $\mu$ M. Inset: double-In plot of initial H<sub>2</sub> evolution rates versus  $[\mathsf{PS}_{\mathsf{lr}}].$ 

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Figure 3. Study of the effect of solvent mixture,  $[Et_3N]$ ,  $[PS_{tr}]$  and  $[1_{co}]$  in the photocatalytic H<sub>2</sub> formation by  $1_{co}$ .

effect of the CH<sub>3</sub>CN/H<sub>2</sub>O solvent mixture (total volume 10 mL), Et<sub>3</sub>N (0.2 mL),  $1_{co}$  (50 μм),  $PS_{Ir}$  (250 μм). Bottom left: TON<sub>1Co</sub> and TON<sub>PS</sub> as a function of [**PS**<sub>Ir</sub>] in CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (2:8:0.2 mL),  $1_{co}$  (50  $\mu$ M). Bottom right: TON<sub>1Co</sub>

and TON<sub>PS</sub> as a function of  $[1_{co}]$ , CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (2:8:0.2 mL), **PS**<sub>Ir</sub> (100  $\mu$ M). TON<sub>cat</sub> =  $n_{H_2}/n_{catr}$ , TON<sub>PS</sub> =  $n_{H_2}/n_{PS_{Ir}}$ 

Top left: effect of Et<sub>3</sub>N% v/v in the solvent mixture, CH<sub>3</sub>CN/H<sub>2</sub>O (2:8 mL),  $1_{co}$  (50  $\mu$ M) and PS<sub>Ir</sub> (250  $\mu$ M). Top right:

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the catalytic system by decomposition products formed during the  $H_2$  evolution.

## Effect of the O<sub>2</sub> presence in the catalytic activity

One of the main problems of the water reduction catalysts is that for most catalysts the presence of O<sub>2</sub> inhibits completely the  $\rm H_2$  formation.  $^{\rm [10b]}$  Interestingly, the reactions of  $\rm 1_{Co}$  under air retain a significant amount of photoinduced H<sub>2</sub>-evolution activity. For instance, a reaction carried out with  $\mathbf{1}_{co}~(50~\mu\text{m})$ and  $PS_{Ir}$  (250  $\mu$ M) under air in a solvent mixture of CH<sub>3</sub>CN/H<sub>2</sub>O/  $Et_3N$  (3:7:0.2) gives a TON<sub>cat</sub> value of 63, and a TOF value of 44 h<sup>-1</sup>. Nevertheless, the same reaction carried out under strict inert conditions produce a total TON<sub>cat</sub> value of 259 and a TOF value of 147  $h^{-1}$ . Despite the fact that O<sub>2</sub> clearly reduces the evolution of H<sub>2</sub>, up to 25% of the activity is maintained (see the Supporting Information, Figure SI.10). Recently, Reisner et al. reported the first first-row transition-metal catalyst that can produce hydrogen in presence of high levels of O<sub>2</sub>.<sup>[19]</sup> This was achieved by using a homogeneous catalytic system based on a cobaloxime type of catalyst and eosin Y as photosensitiser.<sup>[20]</sup> Nevertheless, our system operates under distinct conditions.

### Mechanistic studies

To get insight into the first steps of the mechanism we studied the reaction of the reduced pho- $(PS_{lr}^{\parallel} = [lr^{\parallel}(ppy)_{2}]$ tosensitiser  $(bpy)][PF_6]; ppy=2-phenylpyri$ dine) with  $\mathbf{1}_{M}$  (M = Co, Ni and Fe) by UV/Vis spectroscopy. **PS**<sub>Ir</sub> was generated in situ by irradiation of a solution containing PS<sub>ir</sub><sup>III</sup> (0.1 mм) and Et₃N (1000 equiv) in anhydrous CH<sub>3</sub>CN under N<sub>2</sub> atmosphere. Reactions were performed at -20°C to minimise the decomposition of **PS**<sub>Ir</sub><sup>II</sup>, which occurs fast at 25 °C. Upon irradiation, three bands located at 385, 495 and 527 nm belonging to the **PS**<sub>Ir</sub><sup>II</sup> raised (Figure 5 and Figure SI.12 in the Supporting Information). After quantitative formation of **PS**<sub>Ir</sub><sup>II</sup> (ca. 30 s) one equivalent of  $\mathbf{1}_{M}$  was added. At this point, the addition of  $1_{co}$ (1 equiv) produced the vanishing of the spectral features corresponding to **PS**<sub>Ir</sub><sup>II</sup> in approximately 1.5 s (Figures SI.13 and SI.15 in the Supporting Information) with a concomitant recovery of **PS**<sub>Ir</sub><sup>III</sup>, as judged by UV/Vis

changes. Therefore, this implies the reduction of  $1_{co}$  by  $PS_{Ir}^{II}$  is a one-electron process. Continuous irradiation of the solution produced the recovery of  $\mathbf{PS}_{Ir}^{II}$ . In the case of the addition of  $\mathbf{1}_{Ni}$  (1 equiv), again the UV/Vis features of  $\mathbf{PS}_{Ir}^{II}$  vanished with a concomitant rising of a new broad band with a  $\lambda_{max}$  at 523 nm, which was attributed to the reduction of the  $1_{Ni}$  complex by one electron (Figure SI.13 and SI.16 in the Supporting Information). However, in the case of the addition  $1_{Fe}$  (1 equiv) only partial loss and then only partial recovery of PS<sub>Ir</sub><sup>II</sup> occurs under continuous irradiation (Figure SI.13 and SI.14 in the Supporting Information). This clearly indicates that PS<sub>I</sub>" do not have enough potential to reduce 1<sub>Fe</sub>. The extent of the reactivity with the  $\textbf{PS}_{Ir}^{~II}$  follows the order  $\mathbf{1}_{Co}\!\approx\!\mathbf{1}_{Ni}\!\gg\!\mathbf{1}_{Fe^{\prime}}$  which is in agreement with the redox potentials measured in CH<sub>3</sub>CN  $(E(\mathbf{1}_{co}^{II/I}) = -1.10, E(\mathbf{1}_{Ni}^{II/I}) = -1.07 \text{ and } E(\mathbf{1}_{Fe}^{II/I}) = -1.38 \text{ V} \text{ vs.}$ SCE). This behaviour infers that under catalytic conditions the formation of reducing species in case of  $\mathbf{1}_{Co}$  and  $\mathbf{1}_{Ni}$  is favoured, while is unlikely for  $\mathbf{1}_{Fe}$ . Consequently, one of the reasons of photochemical inactivity in  $H_2$  production of  $1_{Fe}$  is the inability of PS<sub>Ir</sub><sup>II</sup> to generate the necessary reduced species of 1<sub>Fe</sub>.



**Figure 5.** UV/Vis monitoring of  $PS_{Ir}^{III}$  (0.1 mm) reductive quenching with Et<sub>3</sub>N (1000 equiv) to form  $PS_{Ir}^{II}$  at  $\lambda = 447$  nm, and subsequent addition of one equivalent of  $1_{Fe}$ ,  $1_{Co}$  or  $1_{Ni}$  in anhydrous CH<sub>3</sub>CN at  $-20^{\circ}$ C, under N<sub>2</sub> atmosphere.

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Additional UV/Vis spectroscopic experiments were performed monitoring the amount of H<sub>2</sub> produced under catalytic conditions (CH<sub>3</sub>CN/H<sub>2</sub>O (3:7) at 25 °C). The irradiation of the sample ( $\lambda$  = 447 nm) forms **PS**<sub>Ir</sub><sup>II</sup>. Further stoichiometric addition of **1**<sub>co</sub> produced a clear consumption of the reduced photosensitiser (**PS**<sub>Ir</sub><sup>II</sup>) with a concomitant formation of H<sub>2</sub>, up to 170 µL H<sub>2</sub> were formed after 1.5 h of irradiation. Most importantly no induction time was observed (Figure 6, bottom/inset). This is very relevant, since it is an indication that **1**<sub>co</sub> is the competent catalytic species. In contrast, when **1**<sub>Ni</sub> was added, 20 µL H<sub>2</sub> were formed, while in case of **1**<sub>Fe</sub> no H<sub>2</sub> was detected (Figure 5), which qualitatively correlates with the [**PS**<sub>Ir</sub><sup>II</sup>] decay in each case, as judged by the UV/Vis.



**Figure 6.** Top: UV/Vis monitoring of the reductive quenching of  $\mathbf{PS_{r}}^{II}$  species generated by irradiating at  $\lambda = 447$  nm, upon addition of one equivalent of  $\mathbf{1_{Fe}}$ ,  $\mathbf{1_{Co}}$  and  $\mathbf{1_{Ni}}$ . Conditions:  $[\mathbf{PS_{r}}] = 0.1$  mm, Et<sub>3</sub>N = 1000 equiv, reaction volume = 2 mL, CH<sub>3</sub>CN/H<sub>2</sub>O (0.6:1.4) at 25 °C. Bottom: Time-dependent photocatalytic H<sub>2</sub> evolution activities measured in the UV/Vis cell upon addition of one equivalent of  $\mathbf{1_{Fe}}$  ( $\blacktriangle$ ),  $\mathbf{1_{Co}}$  ( $\blacklozenge$ ) and  $\mathbf{1_{Ni}}$  ( $\blacksquare$ ). Inset: Magnification in the case of  $\mathbf{1_{Co}}$ .

#### Study of nanoparticle formation during catalysis

Dynamic light scattering (DLS) experiments and tracking analysis of nanoparticles (NTA) were performed during the reaction to ascertain whether catalyst degradation could result in nanoparticle formation during the irradiation time.<sup>[21]</sup> DLS analysis on catalytic reactions of  $1_{co}$  (50 and 200 µM), in which **PS**<sub>Ir</sub> (200 µM) is used as a chromophore and Et<sub>3</sub>N (2% v/v) as a sacrificial electron-donor reagent, reveal the formation of nanoparticles that increase in size during the reaction (from 1 nm at 30 min irradiation to 100 nm after 3 h of irradiation) (Figure SI.17 in the Supporting Information). Since no clear evidence of nanoparticles were found during the first 30 min of the reaction and no induction time is observed under the same conditions, we conclude that the H<sub>2</sub> production activity is molecular. Moreover, we found that the concentration of nanoparticles in solution was very low, usually at the limit of detection for this instrument (the lowest nanoparticle concentration that can be detected for a reliable measurement > 0.1 ppm), and it was not always possible to have a reliable size distribution measurement. The same conclusions were reached by studying the same experimental conditions by using nanoparticle tracking analysis (NTA). NTA showed values of nanoparticles mL<sup>-1</sup> in the  $1 \times 10^8$ – $1 \times 10^9$  range. We note that nanoparticle concentration did not significantly vary before and after irradiation (ca. 1.5- to 2-fold increase), with oscillations under the same order of magnitude. Moreover, the same experiments conducted in the presence of Hg<sup>0</sup> reduce the nanoparticle concentration by a similar proportion. Furthermore, if we consider the obtained concentration of  $1 \times 10^8$ – $1 \times$ 10<sup>9</sup> particles ml<sup>-1</sup> by NTA as being responsible for the catalytic water reduction, a TOF value of  $10^6 - 10^7 \, s^{-1}$  is obtained. This value is evidently unrealistic and hence the low concentration of nanoparticles formed can be excluded as being responsible for the observed catalytic activity.

DLS analysis on catalytic reactions of  $1_{co}$  under high concentration conditions (500  $\mu$ M) and typical concentrations of  $PS_{Ir}$  (200  $\mu$ M) and Et<sub>3</sub>N (2% v/v), reveal more clearly the formation of nanoparticles, which again increase in size during the reaction (Figure 7). NTA under these conditions reveal nanoparticle



**Figure 7.** Number of nanoparticles distribution after different irradiation times: before irradiation, 5 min, 30 min, 1 h and 2 h. Conditions:  $1_{co}$  (500  $\mu$ M), **PS**<sub>Ir</sub> (200  $\mu$ M), CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (5:5:0.2) as solvent mixture irradiated at 447 nm.

concentrations in the  $10^9$  order of magnitude, which again imply an unrealistic TOF. DLS and NTA experiments suggest that the loss of the catalytic activity overtime may be related with the decomposition of the molecular system to form nanoparticles, which is in agreement with the -0.7 reaction order obtained for the  $1_{co}$ .

Finally, following a reviewer suggestion, to investigate the effect on the catalytic activity of possible nanoparticles formed during the reaction was evaluated by poisoning experiments with a large excess of Hg<sup>0</sup> (1000 equiv or even 1.5 mL which

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corresponds to the 15% of the total reaction volume) added 5 min before starting the irradiation. Experiments in triplicate were carried out under standard conditions ( $1_{co}$  (50 µM), PS<sub>Ir</sub> (250 µM), CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (3:7:0.2 mL)) and with and without

(250  $\mu$ M), CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (3:7:0.2 mL)) and with and without Hg<sup>0</sup> for comparison reasons (see Figure SI.17 in the Supporting Information). The results evidenced the same catalytic behaviour of H<sub>2</sub> production independently of the amount of Hg<sup>0</sup> used, within the experimental error. Furthermore, we also examined the effect of addition of Hg<sup>0</sup> during the reaction (2 × 0.5 mL, 10% v/v), which did not produce any significant effect on the time-profile nor on the hydrogen production TOF (see Figure SI.17 in the Supporting Information). Arguably, nanoparticles are unlikely to be responsible for the observed hydrogen evolution activity; however, these results could also indicate that the formation of nanoparticles may be related with the catalyst decomposition and should be considered.

## Electrochemical proton reduction to H<sub>2</sub>

To get further insight into the capacity of metal complexes  $1_{Fer}$ ,  $1_{Co}$  and  $1_{Ni}$  in the production of  $H_{2r}$ , we explored the reduction of protons under electrochemical conditions. First, redox potentials were determined for  $1_{Fer}$ ,  $1_{Co}$  and  $1_{Ni}$  (depicted in Figure 8) by using a glassy carbon as working and a saturated



**Figure 8.** CVs of  $1_{Fe'}$   $1_{Co}$  and  $1_{Ni}$ . Experimental conditions:  $Bu_4NPF_6$  (0.1 m) as supporting electrolyte in acetonitrile, using a glassy carbon as working and SCE as reference electrodes. Scan rate of 100 mV s<sup>-1</sup>.

calomel (SCE) as reference electrode in  $CH_3CN$  containing  $Bu_4NPF_6$  (0.1 M) as supporting electrolyte. A summary of the  $M^{1/0}$ ,  $M^{11/1}$  and  $M^{11/11}$  reduction potentials is presented in Table 1.

Complex  $\mathbf{1}_{Fe}$  presents the lowest reduction potential  $M^{II/I}$  from the series (-1.38 V), and therefore it is the less favoured to be reduced to oxidation state (I). In both cases  $\mathbf{1}_{Co}$  and  $\mathbf{1}_{Ni}$  showed similar reduction potentials for the  $M^{II/I}$  couple (-1.10 and -1.07 V, respectively). The CV of the same complexes in the solvent mixture used in the photocatalysed H<sub>2</sub> formation (CH<sub>3</sub>CN/H<sub>2</sub>O 3:7) experiments exhibit a reduction in the redox potentials for the  $M^{II/I}$  couple in the range of 100–200 mV. This is slightly accentuated by the basification of the media after the addition of Et<sub>3</sub>N. We note that the ligand alone does not show any reduction wave above -1.8 V. The trend found in the relative reduction potential  $M^{II/I}$  among the three com-

**Table 1.** Redox potentials for the studied complexes  $1_{Fer}$   $1_{Co}$  and  $1_{Ni}$  in anhydrous CH<sub>3</sub>CN, and CH<sub>3</sub>CN/H<sub>2</sub>O mixtures. Glassy carbon and SCE were the working and reference electrodes, scan rate = 100 mV s<sup>-1</sup>. Potentials are quoted versus SCE.

	<i>E</i> [V] M <sup>1/0</sup>	CH₃CM <i>E</i> [V] M <sup>11/1</sup>	E [V] M <sup>III/II</sup>	$\eta_{ extsf{TFA}}$ [V] $^{ extsf{[b]}}$	CH <sub>3</sub> CN/H <sub>2</sub> O (3:7) <sup>[c]</sup> <i>E</i> [V] M <sup>11/1</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O/Et <sub>3</sub> N (3:7:0.2) <sup>[d]</sup> <i>E</i> [V] M <sup>11/1</sup>
1 <sub>Fe</sub>	-1.68	-1.38	1.14	0.87	-1.58	-1.63
1 <sub>co</sub>	-1.49	-1.10	0.72	0.59	-1.23	-1.34
1 <sub>Ni</sub>	-	-1.07	1.75	0.56	-1.20	-1.21
[a] CV measured in CH <sub>3</sub> CN containing Bu <sub>4</sub> NPF <sub>6</sub> (0.1 м) as supporting elec-						

[a] CV measured in CH<sub>3</sub>CN containing Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as supporting electrolyte (SE). [b] H<sub>2</sub> reduction overpotentials ( $\eta$ ) were calculated considering the protons reduction of TFA as proton source, which is  $E^{o}_{(TFA/H_2)} = -0.51$  V (see section SI.3.1 in the Supporting Information). [c] CVs measured in CH<sub>3</sub>CN/H<sub>2</sub>O (3:7) containing KNO<sub>3</sub> (0.1 M) as SE. [d] CVs measured in CH<sub>3</sub>CN/H<sub>2</sub>O/Et<sub>3</sub>N (3:7:0.2) containing KNO<sub>3</sub> (0.1 M) as SE.

plexes is the expected and can be understood from the general increase in ionisation energies from left to right across a period in the d block.

The electrocatalytic proton reduction capacity of the three complexes was studied in acetonitrile after addition of increasing amounts of trifluoroacetic acid (TFA,  $pK_a = 12.7$  in acetonitrile)<sup>[22]</sup> as the proton source. The CV of all three  $1_{\rm M}$  complexes presents the appearance of new irreversible cathodic waves upon the addition of increasing amounts of TFA triggers (Figure 9). The grown of the reduction peak versus increase of acid concentration is a clear indication of electrocatalytic behaviour of proton reduction to H<sub>2</sub>. At low acid concentrations the shape of the catalytic wave was similar to the wave of the respective complex in the absence of acid; however, at higher acid concentrations the electrocatalytic wave becomes broader and more intense.

In all cases the onset of the catalytic wave matches the potential of the M<sup>II/I</sup> redox couple, and therefore this is consistent with M<sup>I</sup> species as the active ones in electrocatalysis through the formation of M<sup>III</sup>–H by protonation.<sup>[11,23]</sup> The proton reduction overpotential ( $\eta$ ) for complexes 1<sub>co</sub> (590 mV) and 1<sub>Ni</sub> (560 mV) turned to be considerable lower than for 1<sub>Fe</sub> (870 mV) (Table 1).

The dependence of the peak intensity versus the concentration of acid gives valuable information about the H<sub>2</sub> formation mechanism. In this regard, we studied the  $i_{cat}/i_p$  ratio as a function of the TFA concentration in a 1 mm solution of  $\mathbf{1}_{Co}$ ,  $\mathbf{1}_{Fe}$ and  $\mathbf{1}_{Ni}$  in acetonitrile, (in which  $i_{cat}$  stands for the peak current in the presence of acid and  $i_p$  for the peak current in the absence of acid). As shown in Figure 9, the  $i_{cat}/i_p$  ratio of currents of  $\mathbf{1}_{Co}$  increases with the acid concentration until it becomes independent versus the concentration of protons. Below a TFA concentration of 100 mm the  $i_{cat}/i_p$  versus [TFA] is linear and consistent with a second-order process on [H<sup>+</sup>] (Figure 9). At a TFA concentration higher than 100 mm,  $i_{cat}/i_p$  it is independent of the [TFA] (Figure 10), suggesting that under these conditions the rate-limiting step is an intramolecular proton transfer or an elimination of H<sub>2</sub>.

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**Figure 9.** Successive CVs of  $1_{Fe}$  (top),  $1_{co}$  (middle) and  $1_{Ni}$  (bottom) (1 mM) in acetonitrile containing Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) in the presence of TFA (0–60 mM). Scan rate = 100 mV s<sup>-1</sup>, glassy carbon as working electrode. Insets:  $i_{cat}/i_p$  versus [TFA].

On the other hand, complexes  $\mathbf{1}_{Fe}$  and  $\mathbf{1}_{Ni}$  have similar behaviours at low acid concentration (up to 40 mm for  $\mathbf{1}_{Fe}$ , and 60 mm for  $\mathbf{1}_{Ni}$ ), while at higher acid concentration the  $i_{cat}/i_p$  dramatically decreases, which may be due to catalyst degradation provoked by the high concentration of protons in the reaction medium.

To ensure that the electrocatalytic behaviour of  $1_{co}$  corresponds to a molecular catalytic activity and thus discarding an electrodeposition process over the surface of the glassy carbon electrode, we first measured the CV of  $1_{co}$  (1 mm) in the presence of TFA (100 mm), and then after rinsing the sur-





**Figure 10.**  $i_{cat}/i_p$  ratio as a function of the [TFA] in a 1 mm concentration solution of  $\mathbf{1}_{Fer}$ ,  $\mathbf{1}_{Co}$  or  $\mathbf{1}_{Ni}$ . Scan rate = 100 mV s<sup>-1</sup>. Glassy carbon working electrode and SCE as reference.  $i_{cat}/i_p$  values were measured at the M<sup>IM</sup> redox potential.

face of the working electrode, a new CV was recorded form a freshly prepared TFA (100 mm) solution, which did not contained  $\mathbf{1}_{co}$  (Figure SI.20 in the Supporting Information). In this case, the electrocatalytic wave completely disappeared. Consequently, the  $i_{cat}/i_p$  values obtained cannot be attributed to electrodeposition of cobalt species.

The good electrochemical behaviour of  $1_{co}$  facilitates the calculation of the electrocatalytic rate constant for hydrogen production,  $k_e$  (95 m<sup>-2</sup> s<sup>-1</sup>) and the corresponding turnover frequency (TOF =  $k[H^+]^2 = 3420 \text{ mol}(H_2) \text{ mol}(1_{co})^{-1} \text{ h}^{-1})$  by plotting the slopes obtained of  $i_{cat}/i_p$  versus [TFA] at different scan rates ( $\nu$ ) as a function of  $\nu^{-1/2}$  (Figures 10 and 11 and Figures SI.21–SI.30 in the Supporting Information).<sup>[11]</sup>



**Figure 11.** Top: plots of  $i_{cat}/i_p$  versus [TFA] for a 1 mM solution of 1<sub>co</sub> at different scan rates. Bottom: Plot of the  $i_{cat}/i_p$  slopes at different scan rates versus [TFA] as function of the  $\nu^{-1/2}$ .

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**Figure 12.** Successive CVs at increasing  $[1_{co}]$ . Conditions: [TFA] = 100 mM, Supporting electrolyte: Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M), scan rate = 100 mV s<sup>-1</sup>, GC working electrode. Inset: Electrocatalytic current versus  $[1_{co}]$  (0.1–0.8 mM) showing a first order kinetics.

In addition, the dependence of the catalytic current on the concentration of catalyst at sufficiently high TFA concentration (100 mm) was found to be first-order (Figure 12). In summary, these studies lead us to formulate an overall rate law for the production of hydrogen of  $v = k_e [H^+]^2 [1_{co}]$ .

Finally, complex  $1_{co}$  was soluble and stable in pure aqueous solution. The cyclic voltammograms in water showed a redox couple Co<sup>II/I</sup> at -1.29 V versus SCE. This is slightly shifted to lower potentials in comparison with the one obtained in CH<sub>3</sub>CN (-1.10 V vs. SCE). The addition of TFA to a 1 mm solution of  $1_{co}$  causes an increase of the electrocatalytic current near the Co<sup>II/I</sup> couple (Figure 13) comparable to the previously



**Figure 13.** Successive CVs of  $1_{co}$  (1 mM) in water containing KNO<sub>3</sub> (0.1 M) and TFA acid: from bottom to top 0, 1, 3, 10, 20, 40, and 60 mM. Scan rate = 100 mV s<sup>-1</sup>, glassy carbon as working electrode.

observed in CH<sub>3</sub>CN. Remarkably, the  $i_{cat}/i_p$  in water (65 at 60 mm) was found to be significantly higher than in acetonitrile (48 at 60 mm). The  $i_p$  was measured in a non-pH-buffered aqueous solution of KNO<sub>3</sub> (0.1 m, pH 6) and therefore a part of the  $i_p$  value could be partly associated with H<sub>2</sub> generation activity. Consequently,  $1_{co}$  is not only stable in water, but also is more electrocatalytically active for proton reduction to H<sub>2</sub> than in pure acetonitrile.

## Mechanistic considerations

Complexes  $\mathbf{1}_{M}$  (M = Co, Ni and Fe) are all electrocatalysts for  $H_2$ production, while only 1<sub>co</sub> is highly active under photochemical conditions. Under the latter conditions,  $\mathbf{1}_{Ni}$  presents much reduced activity and  $\mathbf{1}_{Fe}$  is completely inactive. The inactivity of 1<sub>Fe</sub> under photochemical conditions could be attributed to the low redox potential observed that it is needed for the formation of the Fe<sup>I</sup> species. This was shown by the reaction of the in situ generated  $\mathbf{PS}_{Ir}^{\ II}$  with  $\mathbf{1}_{\scriptscriptstyle M}$  complexes. Complexes  $\mathbf{1}_{\scriptscriptstyle Ni}$  and  $1_{co}$  instantaneously react with  $PS_{ir}^{II}$ , while  $1_{Fe}$  apparently is mainly inert to  $\mathbf{PS}_{\mathbf{Ir}}^{II}$ . This was also consistent with the  $M^{II/I}$  reduction potential of  $\mathbf{1}_{Fe}$  in acetonitrile and the observed electrocatalytic H<sub>2</sub> production, which only occurs at very low potentials. However,  $\mathbf{1}_{Ni}$  presents similar  $M^{II/I}$  reduction potential and overpotential in electrocatalytic  $H_2$  formation as  $1_{co}$  and moreover reacts instantaneously with in situ generated PS<sub>I</sub>". Therefore, other limitations should be considered for the low H<sub>2</sub> production under photochemical conditions exhibited by 1<sub>Ni</sub>. One must consider that electro- and photochemical conditions are rather different. For instance, the electrochemical studies were performed in organic solvents or water, but evaluating the electrocatalytic current based on the [H<sup>+</sup>], usually provided by the addition of an strong acid (TFA in our case). This acid supply sets up the medium to a low pH. In contrast, in photochemical reactions the electrons are provided by the incorporation of a sacrificial agent (Et<sub>3</sub>N in our case). This makes the reaction medium highly basic (pH  $\approx$  12). The large pH differences between electro- and photochemical conditions, makes pH as one of the factor which diverged the H<sub>2</sub> formation activity among complexes and conditions (1<sub>Ni</sub> and 1<sub>co</sub>). Electro- and photochemical experiments provided evidence that under these conditions both  $\mathbf{1}_{Ni,Co}$  are reduced by one electron to form M<sup>I</sup> species. Then, subsequent protonation of those species will generate M<sup>III</sup>−H intermediates and further protonation will produce H<sub>2</sub>. Alternatively, under certain conditions M<sup>III</sup>−H intermediates may not be enough reactive to produce H<sub>2</sub> (for instance under basic conditions) and will first require an additional reduction by one electron to form M<sup>II</sup>-H, which then by protonation produce  $H_2^{[12c]}$ 

To provide some light on the reactivity differences among the  $1_{M}$  series of complexes, structures of M<sup>I</sup>, M<sup>II</sup>, M<sup>II</sup>–L, M<sup>II</sup>–L (L=H<sub>2</sub>O or CH<sub>3</sub>CN) and M<sup>III</sup>–H species were DFT modelled with the Gaussian 09 program<sup>[24]</sup> using the B3LYP hybrid exchangecorrelation functional and taking into account the effect of water solvation and London dispersion effects (see the Supporting Information section SI.4 for complete details of the employed methodology). Theoretical efforts focused on the evaluation of the solvent coordination, the M<sup>II/I</sup> reduction potentials and the p $K_a$  values of hydride species to explore the energetic accessibility of the proposed intermediates as well as their relative stability. The results are summarised in Tables 2 and 3.

Under photochemical conditions ( $CH_3CN/H_2O$  3:7 solvent mixture) the metal centre may interact with both solvent molecules and the redox activity of the resulting aqua or acetoni-trile complexes could be substantially different. Therefore, the

<b>Table 2.</b> Computed free energy ( $\Delta G$ ) for coordination of CH <sub>3</sub> CN and H <sub>2</sub> O to $1_{M}$ and for ligand exchange reactions. <sup>[a]</sup>						
	$\Delta G$ [kcal mol <sup>-1</sup> ]					
	Fe'	⊦e"	Co	Co"	Ni	Ni"
$[M^{II/I}(Py_2^{Ts}tacn)] + L \rightarrow [M^{II/I}(Py_2^{Ts}tacn)(L)]$						
$L = CH_3CN$	2.9	3.4	-0.2	-1.1	5.5	-5.1
$L = H_2 O$	2.2	1.8	3.9	4.1	9.6	-1.9
$CH_3CN + [M^{11/1}(Py_2^{Ts}tacn)(H_2O)] \! \leftrightarrow \! [M^{11/1}(Py_2^{Ts}tacn)(CH_3CN)] + H_2O$						
	-0.6	1.6	-3.8	-5.1	-4.1	-3.2
[a] All values have been obtained using the ground spin state for each structure.						

Table 3. DFT computed reduction potentials [V] and $pK_a$ values of the second	the
proposed cobalt, nickel and iron intermediates. <sup>[a]</sup>	

	M=Fe	M=Co	M=Ni
<i>Е</i> ° (М <sup>II/I</sup> ) <sup>[b]</sup>	-1.42	-0.86	-0.97
p <i>K</i> <sub>a</sub> (M <sup>Ⅲ</sup> —H) <sup>[c]</sup>	1.8	7.0	-0.4

[a] All values were obtained using the ground spin state for each structure.  $E^{\circ}$  values correspond to the standard reduction potentials relative to the SCE electrode. [b] Complexes without solvent coordination were employed for the calculation. [c] pK<sub>a</sub> values were calculated at 298 K.

identification of the most stable aqua, acetonitrile or solventfree intermediate for each metal oxidation state is necessary to ensure a correct description of the initial redox step. In general, the energies gained by coordination of water or acetonitrile to the metal complexes in oxidation state II were only small or even disfavoured for  $1_{\rm Fe}$ . Binding of water to  $1_{\rm Co}$  was also energetically disfavoured. This trend is clearer for the oxidation state I. With some exceptions, the energies fall in the limits of the average error of the used methodology (Table 2). We can therefore conclude that the absence of solvent ligand coordinated is generally favoured for oxidation state I in both water and acetonitrile and also favoured for oxidation state II in water.

The reduction potentials  $M^{11/4}$  for  $1_{co}$ ,  $1_{Ni}$  and  $1_{Fe}$  without solvent bonded were calculated to be -0.86, -0.97 and -1.42 V (SCE), respectively, in qualitative agreement with the experimental reduction potentials of -1.23, -1.20 and -1.58 V (SCE), respectively. Although these values are 150-250 mV lower than the experimental results, they still fall in the usual range of the method accuracy.

Experimental and computational results determine that both  $1_{co}$  and  $1_{Ni}$  complexes form species with a M<sup>I</sup> oxidation state upon reacting with the reduced  $PS_{Ir}$ . Consequently, the origin of the photochemical inactivity of nickel species for H<sub>2</sub> production may be due to other factors such as the inaccessibility of the  $[Ni^{III}-H]$  species under basic pH, since under electrocatalytic acidic pH conditions the H<sub>2</sub> evolution reaction does take place. In this regard, the DFT calculated pK<sub>a</sub> values for  $[Co^{III}-H]$  and  $[Ni^{III}-H]$  were 7.0 and -0.4, respectively. This clearly underlines the more acidic character of the  $[Ni^{III}-H]$ . We should note that under photocatalytic conditions the pH of the mixture is

in the range of 11–12. Therefore, these results suggest that the protonation is disfavoured, thus blocking the H<sub>2</sub> production. In contrast, the reduction potential of -1.42 V for the Fe<sup>IIVI</sup> couple agree with the electrochemically observed of -1.58 V, revealing that the Fe<sup>I</sup> species may not be photochemically generated. This situation bans the possible formation of Fe<sup>III</sup>–H species (pK<sub>a</sub> 1.8, also disfavoured), and then the capacity to photoproduce H<sub>2</sub> when using **PS**<sub>Ir</sub> as photosensitiser (Scheme 2).



**Scheme 2.** Differences in reactivity among  $\mathbf{1}_{Fe'} \mathbf{1}_{Co}$  and  $\mathbf{1}_{Ni}$  in single-electron reduction process to  $M^{I}$  species and the subsequent protonation to yield the  $M^{III}$ -H species under photochemical conditions.  $pK_{a}$  values have been obtained by DFT calculations.

## Conclusion

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We synthesised and characterised a new ligand 1,4-di(picolyl)-7-(*p*-toluenesulfonyl)-1,4,7-triazacyclononane (Py<sub>2</sub><sup>Ts</sup>tacn) and the corresponding metal complexes  $1_{Fe}$ ,  $1_{Co}$  and  $1_{Ni}$ . All showed to be good electrochemical catalysts for proton reduction to H<sub>2</sub>. However, only  $1_{Co}$  is an efficient catalyst for water reduction when using [Ir(ppy)<sub>2</sub>(bpy)]PF<sub>6</sub> as photosensitiser and Et<sub>3</sub>N as electron donor. In contrast, under the same conditions  $1_{Ni}$  presents low photochemical water reduction activity and  $1_{Fe}$  is inactive. More interestingly, to some extent the catalyst  $1_{Co}$  can operate as photocatalyst for H<sub>2</sub> production in presence of O<sub>2</sub>.

The active species during the photocatalytic water reduction are molecular. This was clear by the lack of lag time in the  $H_2$  evolution, and the absence of nanoparticles during the first minutes of the reaction, when the system was most active. Moreover, the formation of nanoparticles is ascribed to the reduction of catalytic activity.



Mechanistic investigations, electrochemical studies and DFT calculations allowed us to elucidate the factors that control the activity among the three complexes with the same aminopyridine ligand. The  $Py_2^{Ts}$ tacn ligand not only controls the relative stabilisation of the metal oxidation state, but also the basicity. Both factors are important and should be considered for the boundary reaction conditions imposed by the photosensitiser, electron donor and pH. Indeed, the use of  $[Ir(ppy)_2(bpy)]PF_6$  as photosensitiser allows the one-electron reduction of  $1_{co}^{II}$  and  $1_{NI}^{II}$ , but not in the case of  $1_{Fe}^{II}$ . On the other hand, the use of  $Et_3N$  as electron donor basifies the media making the protonation of the M<sup>I</sup> metal centre for  $1_{Ni}$  difficult and, therefore, the H<sub>2</sub> evolution. Altogether, this study gives light on important factors to be considered for the development of more efficient first-row transition-metal catalysts for water reduction.

## **Experimental Section**

## **General methods**

All procedures were carried out under N<sub>2</sub> using standard vacuum line, Schlenk, and inert atmosphere glovebox techniques. Reagents and solvents were purchased from commercial sources as used as received unless otherwise stated. Triethylamine (Et<sub>3</sub>N)  $\geq$  99% purity and ascorbic acid ( $\geq$  99%) were purchased from Sigma–Aldrich® and used without further purification. 1-(*p*-Toluensulfonyl)-1,4,7-triazacyclononane (<sup>Ts</sup>tacn),<sup>[25]</sup> and [Ir(bpy)(ppy)<sub>2</sub>]PF<sub>6</sub><sup>[26]</sup> were synthesised according to the literature procedures. Anhydrous acetonitrile was purchased from Scharlab. Water (18.2 MΩcm) was purified with a Milli-Q Millipore Gradient AIS system. All the solvents were strictly degassed and stored in anaerobic conditions. All water reduction catalytic reactions were performed under N<sub>2</sub> otherwise notified.

## **Physical methods**

NMR spectra were recorded on Bruker spectrometers operating at 300 or 400 MHz as noted at 300 K. All <sup>1</sup>H chemical shifts are reported in ppm and were internally calibrated to the monoprotio impurity of the deuterated solvent. The coupling constants are measured in Hz. The  $^{\rm 13}{\rm C}$  chemical shifts were internally calibrated to the carbon atoms of the deuterated solvent. All experimental procedures were conducted at ambient temperature under nitrogen atmosphere and using degassed acetonitrile. A standard three-electrode configuration was employed in conjunction with CH Instruments potentiostat interfaced to a computer with CH Instruments 600D software. Using a one-compartment cell, all voltammetric scans were recorded using glassy carbon working electrode, which was treated between experiments by means of a sequence of polishing with MicroPolish Powder (0.05 micron) before washing and sonification. A saturated calomel electrode (SCE) and Pt wire were used as reference and counter electrodes, respectively. All materials for electrochemical experiments were dried at room temperature before use. UV/Vis spectra were recorded on an Agilent 8453 diode array spectrophotometer (190-1100 nm range) in 1 cm quartz cells. A cryostat from Unisoku Scientific Instruments was used for the temperature control. Electrospray ionisation mass spectrometry (ESI-MS) experiments were performed on Bruker Daltonics Esquire 3000 Spectrometer, by introducing samples directly into the ESI-source using a syringe. DLS and NTA experiments were performed on a Zetasizer Nano ZS, Malvern Instruments (particlesize distribution from 0.6 to 6.000 nm) and Nanosight LM20 (particle-size distribution from 1 to 2000  $\mu m$  ). The analyses were carried out in the Institut de Ciència dels Materials de Barcelona.

## X-ray crystallography

Single crystals of  $1_{co}$  and  $1_{Ni}$  were mounted on a nylon loop for Xray structure determination. The measurements were carried out on a BRUKER SMART APEX CCD diffractometer using graphitemonochromated Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å). Programs used: data collection, Smart version 5.631 (Bruker AXS 1997-02); data reduction, Saint+ version 6.36A (Bruker AXS 2001); absorption correction, SADABS version 2.10 (Bruker AXS 2001). Structure solution and refinement was done using SHELXTL Version 6.14 (Bruker AXS 2000–2003). The structure was solved by direct methods and refined by full-matrix least-squares methods on  $F^2$ . The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically optimised position and forced to ride on the atom to which they are attached.

CCDC-957199 ( $1_{co}$ ) and CCDC-957198 ( $1_{Ni}$ ) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

## Gas-evolution monitoring studies

All catalytic reactions were performed in a 15 mL vial caped with a septum. Each experiment was conducted in a volume-calibratedvial equipped with stir-bars and containing the solvent mixture with the reagents, and then was connected to one port of a differential pressure transducer sensor (Honeywell-ASCX15DN,  $\pm$ 15 psi). Each reaction had its own reference reaction, which was conducted at the other port of the differential pressure transducer sensor. The reaction and reference vials were kept under the same experimental conditions to minimise the system noise due to temperature–pressure fluctuations. In this sense, each vial was submitted and located just over a LED radiation source. Furthermore, in order to ensure a constant and stable irradiation, the LED sources were equipped with a water refrigeration system.

Just before starting the reaction, the corresponding catalyst was added by syringe through the septum from a stock solution prepared in acetonitrile. The reaction began when the LEDs were turned on. At this point, the hydrogen evolved from the reactions was monitored by recording the increase in pressure of the head-space (1 s interval). The pressure increment was the result of the difference in pressure between the reaction and reference vials. After the hydrogen evolution reached a plateau the amount of the formed gas was captured and measured, equilibrating the pressure between reaction and reference vials. The hydrogen contained in each of the reactions was measured by analysing an aliquot of gas of the headspace (0.2 mL) by gas chromatography. GC measurements of  $H_2$  corroborated the values obtained by pressure increments.

### Gas-evolution studies performed in the presence of Hg<sup>o</sup>

Catalytic reactions performed in the presence of  $Hg^0$  were carried out in a 15 mL vial capped with a septum. Each experiment was conducted in a volume-calibrated-vial equipped with stir-bars and containing the CH<sub>3</sub>CN/H<sub>2</sub>O (3:7) as the solvent mixture with all the reagents under N<sub>2</sub>. The experiments were conducted in one port of a differential pressure transducer sensor, with a reference reaction at the other port. The reaction and reference vials were kept under the same experimental conditions to minimise the system noise due to temperature-pressure fluctuations. Before starting the

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reaction Hg<sup>0</sup> was added in large excess (1000 equiv or 1.5 mL; 15% of the total reaction volume) by syringe though the septum. The solution was stirred for 5 min under and then the solution was submitted to LED irradiation at 447 nm. Hg<sup>0</sup> was left in contact with the solution during the whole catalytic assay in order to poison the heterogeneous catalyst formed during the irradiation time. The hydrogen evolved from the reaction was monitored in real time by recording the increase in pressure of the headspace (1 s interval). The pressure increment was the result of the difference in pressure between the reaction and reference vials. After the hydrogen evolution reached a plateau the amount of the formed gas was captured and measured, equilibrating the pressure between reaction and reference vials. The hydrogen contained in each of the reactions was measured by analysing an aliquot of gas of the headspace (0.2 mL) by gas chromatography. GC measurements of H<sub>2</sub> corroborated the values obtained by pressure increments.

### Parallel pressure transducer hardware

The parallel pressure transducer is composed by eight differential pressure transducers (Honeywell-ASCX15DN,  $\pm$ 15 psi) connected to a hardware data-acquisition system (base on Atmega microcontroller) controlled by a home-developed software program. The differential pressure transducer Honeywell-ASCX15DN was set with a 100 µs response, signal-conditioned (high-level span, 4.5 V) output, and a calibrated and temperature compensated (0-70°C) sensor. The differential sensor had two sensing ports that could be used for differential pressure measurements. The pressure-calibrated devices, to within  $\pm$ 0.5 matm, was offset and span calibrated by using software for a high-precision pressure transducer (PX409-030GUSB, 0.08% accuracy). Each of the eight differential pressure transducers (Honeywell-ASCX15DN,  $\pm$ 15 psi) produced voltage outputs that could be directly transformed to a pressure difference between the two measuring ports. The voltage outputs were digitalised with a resolution of 0.25 matm from 0 to 175 matm and 1 matm from 176 to 1000 matm by using an Atmega microcontroller with an independent voltage auto-calibration. Firmware Atmega microcontroller and control software were home-developed. The sensitivity of H<sub>2</sub> analytics allowed the quantification of the gas formed when low H<sub>2</sub> volumes were generated. Therefore, it could not be discarded that small amounts of H<sub>2</sub> were produced by inactive complexes.

# Gas chromatography identification and quantification of gases

Hydrogen at the headspace was analysed with an Agilent 7820 A GC System equipped with columns Washed molecular sieves 5A,  $2 \text{ m} \times 1/8''$  OD, Mesh 60/80 SS and Porapak Q,  $4 \text{ m} \times 1/8''$  OD, SS. Mesh: 80/100 SS and a thermal conductivity detector. The H<sub>2</sub> amount obtained was calculated through the interpolation of the previous calibration using different H<sub>2</sub>/N<sub>2</sub> mixtures.

## Acid concentration dependence study

A 0.8 m stock solution of TFA was prepared in a CH<sub>3</sub>CN solution of 0.1 m Bu<sub>4</sub>NPF<sub>6</sub>. Aliquots of this solution were added to a degassed solution of 1 mm catalyst in CH<sub>3</sub>CN. After the addition the solution was purged with N<sub>2</sub> before carrying out the cyclic voltammetry. The order with respect to [acid] was determined by plotting the current at the potential M<sup>II/I</sup> versus the concentration of acid.

## Catalyst concentration dependence study

TFA was added to a solution of 0.1 m Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN in an electrochemistry cell to provide an acid concentration of 100 mm. To this solution, aliquots of 20 mm stock solution of  $1_{co}$  were added and CVs were collected. The order of the proton reduction with respect to [catalyst] was determined by plotting the current at the potential M<sup>II/II</sup> versus the concentration of catalyst.

#### Syntheses

Synthesis of 1,4-di(picolyl)-7-(p-toluenesulfonyl)-1,4,7-triazacyclononane (Py<sub>2</sub><sup>Ts</sup>tacn): 2-Pycolyl chloride hydrochloride (1.16 g, 7.04 mmol), <sup>Ts</sup>tacn (1 g, 3.53 mmol) and anhydrous acetonitrile (40 mL) were mixed in a 100 mL flask.  $Na_2CO_3$  (2.05 g) and tetrabutylammonium bromide (80 mg) were added directly as solids and the resulting mixture was heated at reflux under N<sub>2</sub> for 22 h. After cooling to room temperature, the resulting orange mixture was filtered and the filter cake was washed with CH2Cl2. The combined filtrates were evaporated under reduce pressure. NaOH (2 м, 15 mL) was added to the resulting residue, and the mixture was extracted with  $CH_2Cl_2$  (4×40 mL). The combined organic layers were dried over MgSO4 and the solvent was removed under reduced pressure. The resulting residue was treated with n-hexane (100 mL) and stirred for 12 h. A fine white solid appeared which was filtered off and dried under vacuum to yield 1.34 g of the desired product (2.88 mmols, 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 300 K):  $\delta$  = 8.50 (d, J = 4.8 Hz, 2 H;  $H_2$  of py), 7.66–7.60 (m, 4 H;  $H_{Ts}$  and  $H_4$ of py), 7.47 (d, J = 7.8 Hz, 2H;  $H_{Ts}$ ), 7.26 (d, 2H; J = 8.4 Hz,  $H_{s}$  of py), 7.15-7.11 (m, 2H; H<sub>3</sub> of py), 3.86 (s, 4H; CH<sub>2</sub>-py), 3.22 (m, 4H; N-CH<sub>2</sub>-CH<sub>2</sub>), 3.12 (m, 4H; N-CH<sub>2</sub>-CH<sub>2</sub>), 2.79 (s, 4H; N-CH<sub>2</sub>-CH<sub>2</sub>), 2.40 ppm (s, 3 H; CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz, 300 K):  $\delta = 159.75$ , 149.00, 142.99, 136.40, 135.94, 129.60, 127.12, 123.23, 121.94, 63.84, 55.85, 50.87, 21.47 ppm; ESI-MS: *m/z*: 466.2 [*M*+H]<sup>+</sup>; elemental analysis calcd (%) for  $C_{25}H_{31}N_5O_2S\cdot 0.5H_2O$ : C 63.27, H 6.80, N 14.76; found: C 63.47, H 6.68, N 13.91.

**Synthesis of [Fe(OTf)(Py<sub>2</sub><sup>Ts</sup>tacn)](OTf) (1<sub>Fe</sub>):** In a glovebox, a solution of Fe(OTf)<sub>2</sub>·2 CH<sub>3</sub>CN (235 mg, 0.539 mmol) in anhydrous THF (1 mL) was added dropwise to a vigorously stirred solution of Py<sub>2</sub><sup>Ts</sup>tacn (251.2 mg, 0.539 mmol) in THF (1 mL). After few minutes, the solution become cloudy and a pale yellow precipitate appeared. After stirring for an additional 5 h the solution was filtered off and the resulting solid dried under vacuum. This solid was dissolved with CH<sub>2</sub>Cl<sub>2</sub>, and the slow diffusion of diethyl ether over the resultant solution afforded, in few days, 340 mg of a pale yellow solid (0.414 mmol, 76.9%).<sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz, 300 K):  $\delta$  = 56.62, 11.18, 8.42, 7.88, 3.45, 2.17, 1.12 ppm; HR-ESI-MS: *m/z*: 670.1069 [*M*-OTf]<sup>+</sup>, 260.5804 [*M*-2OTf]<sup>2+</sup>; elemental analysis calcd (%) for C<sub>27</sub>H<sub>31</sub>F<sub>6</sub>FeN<sub>5</sub>O<sub>8</sub>S<sub>3</sub>·0.5 CH<sub>2</sub>Cl<sub>2</sub>: C 38.21, N 8.21, H 3.74; found: C 38.54, N 8.27, H 3.73.

Synthesis of [Co(OTf)(Py<sub>2</sub><sup>Ts</sup>tacn)](OTf) (1<sub>co</sub>): In a glovebox, a solution of Co(OTf)<sub>2</sub>·2 CH<sub>3</sub>CN (236 mg, 0.537 mmol) in anhydrous THF (1 mL) was added dropwise to a vigorously stirred solution of Py<sub>2</sub><sup>Ts</sup>tacn (250 mg, 0.537 mmol) in THF (1 mL). After few minutes, the solution become cloudy and a pale pink precipitate appeared. After stirring for an additional 2 h the solution was filtered off and the resulting solid dried under vacuum. This solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the slow diffusion of diethyl ether into this solution produced 355 mg of pink crystals (0.432 mmol, 83%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300 MHz, 300 K):  $\delta$  = 118.28, 55.72, 3.92, 3.76, 2.22, 9.42 ppm; HR-ESI-MS: *m/z*: 673.1054 [*M*-OTf]<sup>+</sup>, 262.0766 [*M*-2 OTf]<sup>2+</sup>; elemental analysis calcd (%) for C<sub>27</sub>H<sub>31</sub>F<sub>6</sub>CoN<sub>5</sub>O<sub>8</sub>S<sub>3</sub>: C 39.42, N 8.51, H 3.80; found: C 39.23, N 8.56, H 3.68.

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**Synthesis of [Ni(OTf)(Py<sub>2</sub><sup>Ts</sup>tacn)](OTf) (1<sub>N</sub>):** In a glovebox, a solution of Ni(OTf)<sub>2</sub>·2 CH<sub>3</sub>CN (205.9 mg, 0.429 mmol) in anhydrous THF (1 mL) was added dropwise to a vigorously stirred solution of Py<sub>2</sub><sup>Ts</sup>tacn (200 mg, 0.429 mmol) in THF (1 mL). After few minutes, the solution become cloudy and a purple precipitate appeared. After stirring for an additional 4 h the solution was filtered off and the resulting solid dried under vacuum. This solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the slow diffusion of diethyl ether into this solution produced 285 mg of purple crystals (0.346 mmol, 80.65%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz, 300 K):  $\delta$  = 56.41, 52.13, 45.61, 15.46, 14.89, 9.21, 6.46, 5.70, 2.17 ppm; HR-ESI-MS: *m/z*: 672.1058 [*M*-OTf]<sup>+</sup>, 261.5797 [*M*-2OTf]<sup>2+</sup>; elemental analysis calcd (%) for C<sub>27</sub>H<sub>31</sub>F<sub>6</sub>NiN<sub>5</sub>O<sub>8</sub>S<sub>3</sub>·0.5 CH<sub>2</sub>Cl<sub>2</sub>: C 38.19, N 8.10, H 3.73; found: C 38.17, N 8.15, H 3.51.

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**Keywords:** cobalt • electrochemistry • homogeneous catalysis • hydrogen • photochemistry • water reduction

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## **FULL PAPER**

## Hydrogen Production

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Photo- and Electrocatalytic H<sub>2</sub> Production by New First-Row Transition-Metal Complexes Based on an Aminopyridine Pentadentate Ligand



**Cobalt is king!** The Fe, Co, and Ni complexes based on the same ligand have shown excellent electrocatalytic H<sub>2</sub> activity (see figure). While only the Co complex has excellent H<sub>2</sub> photoproduction catalytic activity, when using  $[Ir(ppy)_2(bpy)]PF_6$  (**PS**<sub>ir</sub>) as photo-

sensitiser and  $Et_3N$  as electron donor. Analytic and kinetic studies show that the catalytic activity is molecular. The lack of photochemical activity of the Fe and Ni complexes is ascribed to their redox chemistry and the  $pK_{ar}$ respectively.

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