

Full paper / Mémoire

An azadithiolate bridged Fe₂S₂ complex as active site model of FeFe-hydrogenase covalently linked to a Re(CO)₃(bpy)(py) photosensitizer aiming for light-driven hydrogen production

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Abstract

In order to create photoactive catalysts for hydrogen production, a novel trimetallic Re–Fe₂S₂ complex **4** was synthesized by the coordination of the free –PPh₂ group of the ligand of the rhenium photosensitizer **6** to an azadithiolate (ADT)-bridged diiron complex **8** with the assistance of the decarbonylation reagent Me₃NO. Complex **4** was characterized by ¹H, ¹³C, ³¹P NMR and HRMS spectra. The IR, UV–vis and electrochemical data indicate some interactions between Re and Fe₂S₂ moieties, and the photo-induced electron transfer from the excited state of the Re moiety to the Fe₂S₂ catalyst is thermodynamically feasible.

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1. Introduction

The intense contemporary interest in the design and synthesis of active site models of iron–iron hydrogenases

derives from their ability to catalyse reduction of protons to hydrogen [1–3]. Much work has been performed in the past years on understanding the reaction mechanism for H–H bond formation in order to improve the efficiency of electrochemical hydrogen production catalyzed by active site model systems [4–6]. To convert the solar energy into a fuel, we are interested in light-driven proton reduction (hydrogen production) in bio-inspired chemical systems, such as FeFe-hydrogenase active site models as catalysts [7]. One way to realize this idea is the direct connection of a photosensitizer to a 2Fe2S complex, making

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the hydrogen production catalyst photoactive. Although several photoactive catalysts have been reported during the past years [8,9], they are based on noble metal ions, such as Pt or Pd, with one exception where cobalt is used [9]. Very few reports of photocatalysts based on hydrogenase active site model complexes have been published. However, we have earlier synthesized three systems where photosensitizers were covalently linked to Fe_2S_2 catalytic complexes (Chart 1) [7,10–12].

In one case (**1**), a $\text{Ru}(\text{bpy})_3$ photosensitizer was linked via an ester group to the bridge head of a propane-dithiolate (PDT)-bridged diiron catalyst. Photophysical measurements showed that the excited state of $\text{Ru}(\text{bpy})_3$ in system **1** was quenched by the Fe_2S_2 catalyst. By studying the electrochemistry of system **1**, it was found that the one-electron reduction of the Fe_2S_2 catalyst was too negative to be reached by the excited state of $\text{Ru}(\text{bpy})_3$. In the second case (**2**), a Ru bis(terpyridine) complex as the light-harvesting component and an azadithiolate Fe_2S_2 complex were coupled through a rigid link. From the value of the reduction potential of the excited state of $[\text{Ru}(\text{terpy})_2]^{2+}$ (*ca.* -0.8 V vs SCE) and relevant electrochemical data of the $2\text{Fe}_2\text{S}$ subunit (*ca.* -1.09 V vs SCE), it was apparent that the driving force for an electron transfer from the photo-generated $^*[\text{Ru}]^{2+}$ excited state to the diiron complex was uphill by about 0.59 eV, as calculated with the Rehm–Weller equation, and therefore, thermodynamically unfavorable [11]. In the third case (**3**), the $\text{Ru}(\text{bpy})_3$ photosensitizer was attached to a PDT-bridged diiron catalyst via a phosphine through ligand exchange with CO [12]. However, the same conclusion was drawn after transient

absorption measurements: only reductive quenching of the excited state of Ru -polypyridine photosensitizers by Fe_2S_2 catalysts occurred independently of the nature of the link. To overcome this reductive quenching problem, one way is to decrease the reduction potential of the Fe_2S_2 catalyst, making the desired electron transfer from the excited state of photosensitizer to the Fe_2S_2 catalyst possible. An alternative way is to increase the energy level of the excited state of photosensitizer. Since it is known that the excited states of $\text{Re}^{\text{I}}(\text{CO})_3(\text{bpy})(\text{py})$ complexes have considerably higher redox potentials [11] than the $\text{Ru}^{\text{II}}(\text{bpy})_2$ complexes, we decided to study Re complexes. We have, therefore, prepared complex **6**, which from the energy of the excited state and the $\text{Re}^{\text{I}}/\text{Re}^{\text{II}}$ redox potential has a calculated reduction potential in the excited state of *ca.* -2 V. This should in principle be sufficient for photo-induced electron transfer to an Fe_2S_2 catalyst. In addition, the use of a phosphine to coordinate to the Fe_2S_2 catalyst should permit protonation of the catalyst by shifting the redox potential towards more positive values. Based on these considerations, we have designed a new type of molecular dyad **4**, featuring a rhenium-containing subunit and an Fe_2S_2 cluster bridged with 4-(diphenylphosphinoamino)pyridine, with which it should be possible to realize the light-driven proton reduction. Because of the electronic interaction between iron and rhenium, complex **4** may also behave as a mimic of the cysteine-linked $[\text{Fe}_4\text{S}_4]$ cluster, which is part of the electron-transfer chain to and from the active site of Fe -only hydrogenases. In this paper, we report the synthesis and electrochemistry of the rhenium-containing Fe_2S_2 molecular dyad **4** (Chart 2).

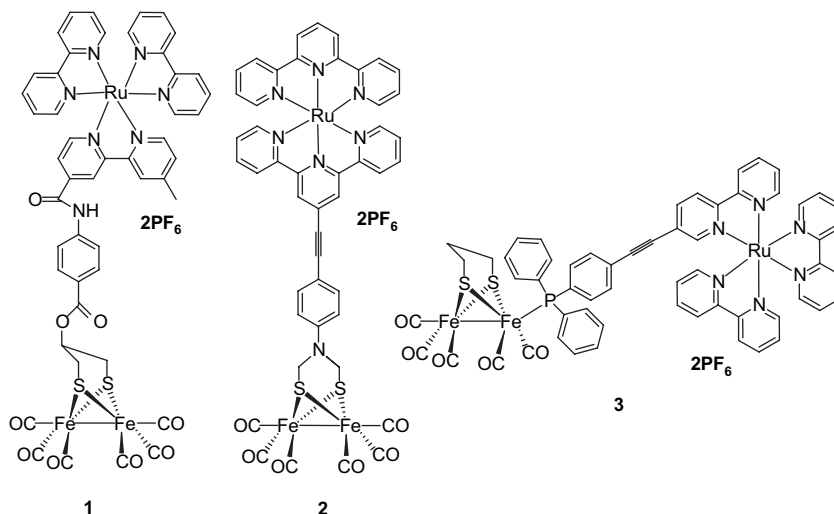
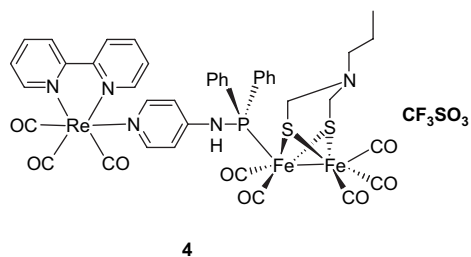


Chart 1.



4

Chart 2.

2. Results and discussion

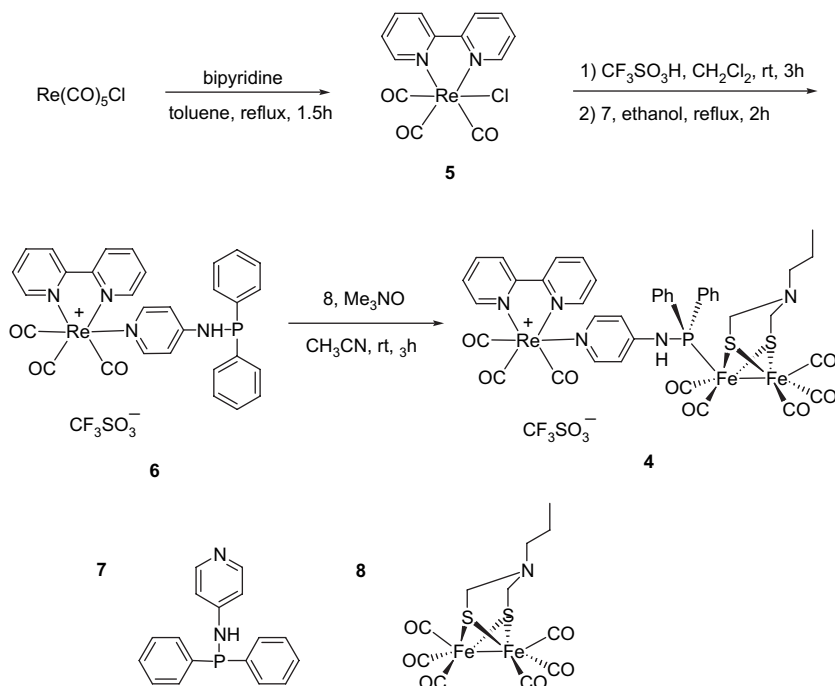
2.1. Synthesis and spectral characterizations

Prior to this research, no similar complexes have been reported, although many substitution reactions of phosphorus-containing ligands of the type PR_3 for CO have been studied [13]. The synthetic route for the preparation of target molecule **4** is depicted in Scheme 1. The commercially available $\text{Re}(\text{CO})_5\text{Cl}$ was treated with 2,2'-bipyridine (bpy) in refluxing toluene to give fac-(bpy) $\text{Re}(\text{CO})_3\text{Cl}$ (**5**). This was then coordinated to the pyridine in refluxing ethanol in the presence of $\text{CF}_3\text{SO}_3\text{H}$ to afford novel complex **6** [14]. In principle, Re can coordinate to either N or P of the ligand, but N is evidently preferred in our

case. By strict control of the reaction time to *ca.* 2 h, the coordination is selective and we could obtain complex **6** with a free phosphine ligand.

The final ligand exchange reaction of CO in **8** by the phosphine in **6** was achieved in CH_3CN with the assistance of the decarbonylation reagent Me_3NO . The carbonyl substitution reaction was accomplished in high yield with good selectivity for mono-substitution at the Fe_2S_2 unit. The trialkyl phosphine complexes are well known, while those containing NH-PR_2 ligands are rare.

With this red-colored complex **4** in hand, we have made great efforts to obtain the single crystals, but in vain. Therefore, compound **4** was identified via a combination of spectroscopic methods (^1H , ^{13}C , ^{31}P NMR, HRMS and UV–vis). The characteristic signal for methylene protons on the $2\text{Fe}_2\text{S}$ subunit (doublet at δ 2.84 and 2.94 ppm) is obvious. The protons at very low field (δ , 7.93, 8.46, 8.76 and 9.37 ppm) consist of the expected signals of bipyridine subunits. It also unambiguously shows the corresponding resonance at δ 7.53 and 7.79 ppm for phenyl protons. The most important spectroscopic feature of **4** is the ^{31}P NMR spectrum, in which the resonance signal is found at 95.5 ppm. The most intense peak observed in the mass spectrum at m/z 1105.8 corresponds to $[\text{M}-\text{CF}_3\text{SO}_3]^{+}$ (positive mode). Fig. 1 shows the IR spectra

Scheme 1. The synthetic procedure of complex **4**.

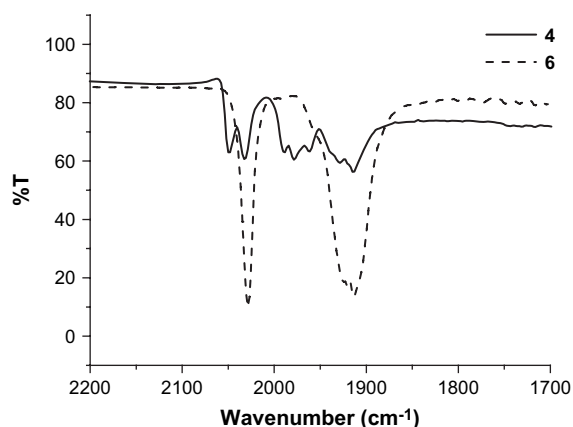


Fig. 1. The IR spectra for complexes **4** and **6**.

for complexes **6** and **4** in the carbonyl region absorptions between 1910 and 2050 cm^{-1} . By comparison, the peaks at 1914, 1926 and 2030 cm^{-1} correspond to the CO vibrations of the rhenium moiety, while those at 1956, 1978, 1986 and 2049 cm^{-1} correspond to the CO vibrations of the Fe_2S_2 moiety.

The UV–vis absorption spectra of complex **4** are shown in Fig. 2 with **6** and **8** for comparison. Both **6** and **8** have intense absorptions at 282 nm (for **6**) attributed to the ligand centered transition ($\pi_{\text{L}} \rightarrow \pi_{\text{L}}^*$), a broad band at ca. 380 nm (for **6**) due to MLCT, and 329 nm (for **8**) assigned to a $d(\text{Fe}) \rightarrow d^*(\text{Fe})$ transition. These assignments were based on comparison with data from $[\text{fac}(\text{bpy})\text{Re}(\text{CO})_3\text{Cl}]$ and $[(\text{bpy})\text{Re}(\text{CO})_3(\text{py-PTZ})]^+$ [15]. For complex **4**, however, only weak absorptions are observed, at 274 and 358 nm. The strong donor capacity of the $-\text{PPh}_2$ ligand increases the electron density of iron atoms and contributes to the $d\pi(\text{Fe}) \rightarrow \pi^*(\text{PPh}_2)$ MLCT (metal-to-

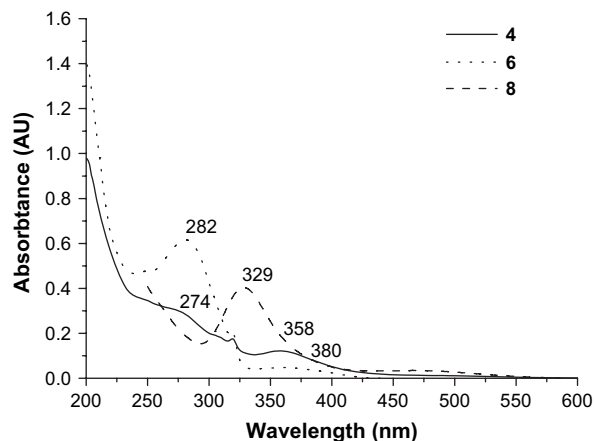


Fig. 2. The UV–vis spectra for **4**, **6** and **8** (0.01 mM) in CH_3CN .

ligand charge transfer) transition which appears at around 358 nm. The decrease of the intensity of the absorption at band 282 nm for complex **6** after coordination with **8** to form **4** may be due to decreased interaction between rhenium and the ligands (pyridine and bipyridine). The strong absorption around 329 nm disappears on the formation of **4**. Instead, an observable $d\pi(\text{Fe}) \rightarrow \pi^*(\text{PPh}_2)$ MLCT transition appears at 358 nm. We could thus see that the absorption in the near-UV region depends greatly on the coordination sphere around the iron nuclei.

2.2. Electrochemistry

The redox potentials of complex **4** were determined by cyclic voltammetry (CV) in MeCN, using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Reduction and oxidation potentials were given vs internal standard Ag/AgNO_3 and compared to those of the reference compound **6** (Table 1), which facilitates the assignment of the individual redox waves (Fig. 3).

Complex **6** exhibited clearly two reversible reduction couples at -1.54 and -1.84 V vs Ag/AgNO_3 (labeled by **1** and **2**) and one semi-reversible oxidation couple at 1.43 V (labeled by **3**). Also oxidation of the phosphine in complex **6** is observed as a shoulder at 1.14 V, which may be compared with the readily observed oxidation at 1 V of the ligand itself (compound **7**). In addition, oxidation of the solvent contributes as a strong background current. While the solvent oxidation in the absence of the Re-catalyst does not start until ca. 1.7 V (Fig. 3), the presence of the rhenium complexes **4** and **6** results in sharply increasing solvent oxidation already at 1.3–1.5 V, making the assignment of the exact value of $\text{Re}^{\text{I}}/\text{Re}^{\text{II}}$ redox couple difficult. The two reduction waves observed are described as one-electron processes for bpy/bpy^- and $\text{bpy}^-/\text{bpy}^{2-}$, respectively [16]. In the case of the trinuclear complex **4**, the first reversible reduction peak at -1.58 V (labeled by **1'**) is ascribed to a mixture of the two overlapping processes $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{I}}\text{Fe}^{\text{0}}$ and bpy/bpy^- (Fig. 4). The reduction couples at -1.80 and -1.96 V (labeled by **2'** and **3'**) are assigned as $\text{bpy}^-/\text{bpy}^{2-}$ and $\text{Fe}^{\text{0}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{0}}\text{Fe}^{\text{0}}$, respectively. The irreversible oxidation peak at 0.43 V (labeled by **4'**) is assigned to $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ and the shoulder at ca. 1.3 V (labeled by **5'**) is assigned to $\text{Re}^{\text{I}}/\text{Re}^{\text{II}}$. These data follow the general trend discussed earlier for our reported Fe_2S_2 complexes [17,18]. Because of $-\text{PPh}_2$ donor ligand, complex **4** exhibits an irreversible oxidation at a potential which is lower by ca. 300 mV compared to those of all-carbonyl analogues [11].

Table 1
Electrochemical data of complexes **4** and **6** (V vs Ag/Ag⁺)

Complex	$E_{\text{pssemi}}^{\text{ox}}$ Re ^I /Re ^{II}	$E_{\text{pir}}^{\text{ox}}$ Fe ^I Fe ^I /Fe ^{II} Fe ^I	E_{pc} Fe ^I Fe ^I /Fe ⁰ Fe ^I	E_{pc} Fe ⁰ Fe ^I /Fe ⁰ Fe ⁰	E_{pc} bpy/bpy ⁻	E_{pc} bpy ⁻ /bpy ²⁻
6	+1.43	–	–	–	–1.54	–1.84
4	ca. +1.30	+0.43	–1.58	–1.96	ca. –1.58	–1.80

Proton reduction catalyzed by complex **4** was studied by CV in the presence of a strong acid, CF₃SO₃H in CH₃CN. A new reduction peak appeared at about –1.23 V when 1 equiv of CF₃SO₃H was added (Fig. 5). As the acid concentration was increased, all the reduction peaks grew and moved to more negative potentials. These features are indicative of catalytic proton reduction. Obviously, the anodic shift on protonation (ca. 350 mV) makes the electron transfer from the excited state of Re moiety to the Fe₂S₂ unit thermodynamically feasible.

3. Experimental section

3.1. Reagents and instruments

All reactions and operations related to organometallic complexes were carried out under a dry, oxygen-free nitrogen atmosphere with standard Schlenk techniques. All solvents were dried and distilled according to the standard methods prior to use. Commercially available chemicals, including *n*-propyl amine, 4-aminopyridine, paraformaldehyde, diphenylchlorophosphine and Re(CO)₅Cl were used without further purification. The reagents LiEt₃BH and triflic acid were purchased from Aldrich.

Infrared spectra were recorded on a JASCO FT/IR 430 spectrophotometer. ¹H and ¹³C NMR (mainly

CDCl₃ solution) spectra were collected on a Varian INOVA 400 NMR spectrometer. Mass spectra were recorded on an HP1100 MSD instrument, and HRMS on an HPLC-Q-ToF MS (Micro) system.

Acetonitrile (Aldrich, spectroscopy grade), which was used for the electrochemistry, was dried with molecular sieve (4 Å) and then freshly distilled from CaH₂ under N₂. A solution of 0.05 M *n*-Bu₄NPF₆ (Fluka, electrochemical grade) in CH₃CN was used as electrolyte. Electrochemical measurements were recorded using a BAS-100 W electrochemical potentiostat. The electrolyte solution was degassed by bubbling with dry argon for 10 min before measurement. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3 and 1 μm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag⁺ electrode (1.0 mM AgNO₃ in CH₃CN) and the auxiliary electrode was a platinum wire.

3.2. Procedures

3.2.1. 4-Diphenylphosphinoaminopyridine (**7**)

A stirred solution of 4-aminopyridine (4.7 g, 50 mmol) in dry CH₂Cl₂ (40 mL) was cooled to 0 °C under an atmosphere of N₂ before diphenylchlorophosphine (4.5 mL, 25 mmol) was added over a period of

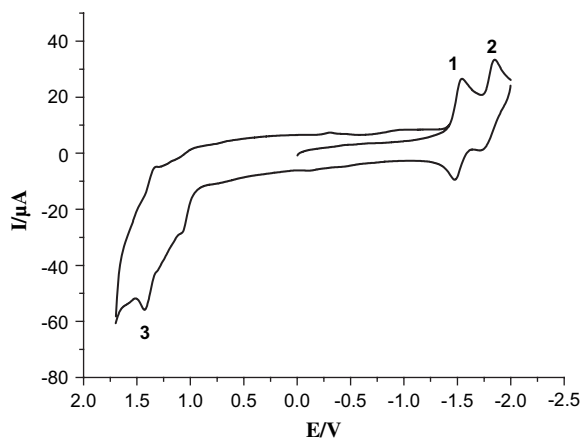


Fig. 3. Cyclic voltammogram of **6**, 1.0 mM in 0.05 M *n*-Bu₄NPF₆/CH₃CN at a scan rate of 100 mV/s with Ag/Ag⁺ as a reference electrode.

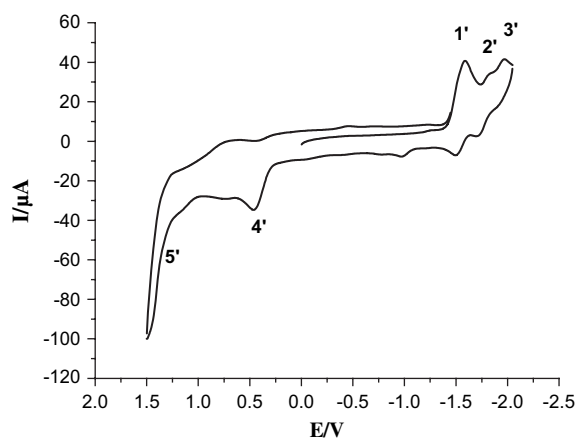


Fig. 4. Cyclic voltammogram of **4**, 1.0 mM in 0.05 M *n*-Bu₄NPF₆/CH₃CN at a scan rate of 100 mV/s with Ag/Ag⁺ as a reference electrode.

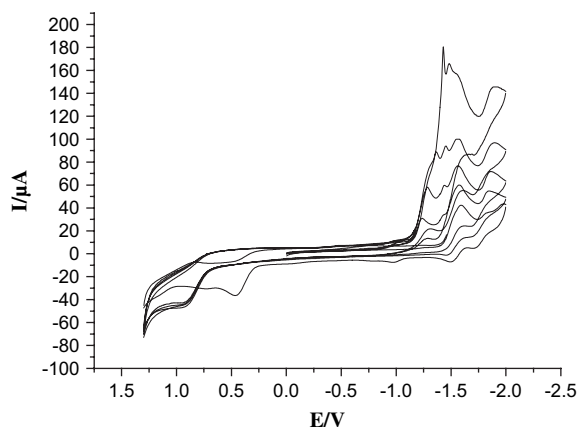


Fig. 5. Cyclic voltammograms of **4** (1.0 mM) with $\text{CF}_3\text{SO}_3\text{H}$ (0, 1, 2, 3, 4 mM upwards) in 0.05 M $n\text{-Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ at a scan rate of 100 mV/s with Ag/Ag^+ as a reference electrode.

30 min. After warming the mixture to room temperature, the aminopyridine hydrochloride salt was filtered off and the solvent was removed from the filtrate to yield crude 4-(diphenylphosphinoamino) pyridine, which was recrystallized from hexane-dichloromethane to give white pure product (5.2 g, 75%). ^1H NMR (CDCl_3): δ (ppm) 6.92 (d, $J = 12.0$ Hz, 2H), 7.37–7.47 (m, 10H), 8.19 (d, $J = 8.0$, 2H). MS (API-ES): m/z 279.3 $[\text{M} + \text{H}]^+$. ^{31}P NMR (CDCl_3): δ (ppm) 19.4 (s).

3.2.2. $[(\text{bpy})\text{Re}(\text{CO})_3\text{-4-diphenylphosphinoaminopyridine}] (\text{CF}_3\text{SO}_3)$ (**6**)

Complex **5** (185 mg, 0.4 mmol) and $\text{CF}_3\text{SO}_3\text{H}$ (0.7 mL, 8 mmol) were stirred in CH_2Cl_2 (20 mL) for 3 h. Then the solvent was removed and the residue was washed with anhydrous diethyl ether (40 mL) before filtration. A solution of **7** (111 mg, 0.4 mmol) in EtOH (40 mL) was added to the filtrate and refluxed for 2 h. Finally, the solvent was removed on a rotary evaporator and the crude product was purified by column chromatography with dichloromethane/acetone (8:1) as an eluent to give complex **6** as a yellow solid (170 mg, 50%). ^1H NMR (CD_3COCD_3): δ (ppm) 7.07 (d, $J = 6.0$ Hz, 1H, bpy), 7.26 (t, $J = 9.2$ Hz, 2H, py), 7.40–7.47 (m, 6H, ph), 7.57 (t, $J = 7.2$ Hz, 2H, ph), 7.63 (d, $J = 6.4$ Hz, 1H, bpy), 7.75–7.80 (m, 2H, ph), 7.97–8.01 (m, 2H, py), 8.31 (t, $J = 8.2$ Hz, 1H, bpy), 8.46 (t, $J = 8.0$ Hz, 1H, bpy), 8.52 (d, $J = 8.4$ Hz, 1H, bpy), 8.76 (d, $J = 8.0$ Hz, 1H, bpy), 8.99 (d, $J = 4.4$ Hz, 1H, bpy), 9.42 (d, $J = 4.4$ Hz, 1H, bpy). ^{13}C NMR (CD_3COCD_3): δ (ppm) 120.67, 123.87, 125.39, 125.80, 128.95,

129.64, 130.07, 130.65, 131.26, 132.26, 133.23, 138.42, 141.22, 142.21, 152.44, 154.86, 156.68, 158.07. ^{31}P NMR (CD_3COCD_3): δ (ppm) 111.31 (s). IR (CH_2Cl_2): $\nu(\text{CO})$ 2029, 1925 and 1914 cm^{-1} ; MS (API-ES): m/z 705.3 $[\text{M} - \text{CF}_3\text{SO}_3^-]^+$. HRMS (ES) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{N}_4\text{O}_3\text{PRE}$ 705.1065, found: 705.1055.

3.2.3. $[(\mu\text{-SCH}_2\text{N}^m\text{PrCH}_2\text{S})\text{Fe}_2(\text{CO})_5\{(\text{bpy})\text{Re}(\text{CO})_3\text{-4-diphenylphosphinoaminopyridine}\}] (\text{CF}_3\text{SO}_3)$ (**4**)

A solution of **8** (94 mg, 0.22 mmol) [18] and $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (24 mg, 0.22 mmol) in CH_3CN (40 mL) was stirred for 10 min at room temperature and **6** (187 mg, 0.22 mmol) in CH_3CN (5 mL) was added. After 3 h, the solvent was removed and the residue was washed with $\text{CH}_2\text{Cl}_2/\text{acetone}$ (3:1) as eluent to give **4** (220 mg, 80%). ^1H NMR (CD_3COCD_3): δ (ppm) 0.67 (t, $J = 7.4$ Hz, 3H), 1.14–1.18 (m, 2H), 2.26 (t, $J = 7.8$ Hz, 2H), 2.84 (d, $J = 13.6$ Hz, 2H), 2.94 (d, $J = 11.6$ Hz, 2H), 6.69 (d, $J = 6.8$ Hz, 2H, py), 7.53 (s, 6H, ph), 7.79 (t, $J = 8.8$ Hz, 4H, ph), 7.93 (t, $J = 3.4$ Hz, 2H, bpy), 7.98 (d, $J = 6.4$ Hz, 2H, py) 8.46 (t, $J = 7.6$ Hz, 2H, bpy), 8.76 (d, $J = 8.4$ Hz, 2H, bpy), 9.37 (d, $J = 5.2$ Hz, 2H, bpy). ^{13}C NMR (CD_3COCD_3): δ (ppm) 11.74, 20.02, 51.44, 61.29, 114.67, 128.46, 128.79, 129.68, 130.69, 131.94, 135.55, 136.41, 136.86, 142.71, 150.41, 151.18, 211.09, 213.04. ^{31}P NMR (CD_3COCD_3): δ (ppm) 95.49 (s). IR (CH_2Cl_2): $\nu(\text{CO})$ 2049, 2032, 1986, 1978, 1956, 1927, and 1914 cm^{-1} ; MS (API-ES): m/z 1105.8 $[\text{M} - \text{CF}_3\text{SO}_3^-]^+$. HRMS (ES) m/z calcd for $\text{C}_{42}\text{H}_{34}\text{Fe}_2\text{N}_5\text{O}_8\text{PREs}_2$ 1105.9843, found: 1105.9879. Elemental analysis (%) calcd for $\text{C}_{41}\text{H}_{34}\text{F}_3\text{Fe}_2\text{N}_5\text{O}_{11}\text{PREs}_3\text{CH}_3\text{COCH}_3$: C, 40.25; H, 3.07; N, 5.33. Found: C, 40.42; H, 3.13; N, 4.91.

4. Conclusion

In conclusion, a novel trimetallic Re–Fe complex **4** has been synthesized through the coordination of -PPh_2 of a rhenium photosensitizer to a diiron catalyst with the assistance of the decarbonylation reagent Me_3NO . Spectral data (IR, UV–vis) and electrochemistry indicate that there exists some interactions between Re and Fe moieties of complex **4**. The rhenium moiety might act as a model for the cysteine-linked $[\text{Fe}_4\text{S}_4]$ cluster, which is part of the electron-transfer chain to and from the active site of Fe-only hydrogenases, and it also gives a new model for light-driven proton reduction. Further investigations on excited-state properties and light-induced hydrogen production of system **4** are in progress.

Acknowledgements

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Appendix. Supporting information

Supplementary data associated with this article can be found in the online version, at doi:[10.1016/j.crci.2008.03.004](https://doi.org/10.1016/j.crci.2008.03.004).

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