Bio-inspired, side-on attachment of a ruthenium photosensitizer to an iron hydrogenase active site model[†]

Jesper Ekström,^a Maria Abrahamsson,^b Carol Olson,^b Jonas Bergquist,^c Filiz B. Kaynak,^d Lars Eriksson,^d Licheng Sun,^{a,e} Hans-Christian Becker,^b Björn Åkermark,^a Leif Hammarström^{*b} and Sascha Ott^{*a,b}

Received 11th May 2006, Accepted 18th July 2006 First published as an Advance Article on the web 8th August 2006 DOI: 10.1039/b606659c

The first ruthenium–diiron complex $[(\mu-pdt)Fe_2(CO)_5{PPh_2(C_6H_4CCbpy)}Ru(bpy)_2]^{2+} 1$ (pdt = propyldithiolate, bpy = 2,2'-bipyridine) is described in which the photoactive ruthenium trisbipyridyl unit is linked to a model of the iron hydrogenase active site by a ligand directly attached to one of the iron centers. Electrochemical and photophysical studies show that the light-induced MLCT excited state of the title complex is localized towards the potential diiron acceptor unit. However, the relatively mild potential required for the reduction of the acetylenic bipyridine together with the easily oxidized diiron portion leads to a reductive quenching of the excited state, instead. This process results in a transiently oxidized diiron unit which may explain the surprisingly high light sensitivity of complex 1.

Introduction

Hydrogen metabolism in nature is regulated by enzymes called hydrogenases.¹ Among these, iron hydrogenases (Fe H₂ase) catalyze the oxidation of hydrogen as well as the reduction of protons with high turnover numbers and at mild potential.² The catalytic site of the Fe H₂ase is comprised of two iron nuclei which are in bonding distance and are tethered by a bridging, non-proteic dithiolate. Biologically unusual CO and CN⁻ ligands present the low valent iron centers with remarkable electronic properties. Electrons are shuttled to and from the active site *via* a [Fe₄S₄] cluster which is directly coordinated through a cysteine to the so-

called proximal iron center Fe^P (Chart 1(a)).^{3,4} Considering the importance of the enzyme in regard to future energy technologies and the hydrogen society, it is not surprising that the bioinorganic community has developed a great interest to model the active site of these very useful enzymes.^{5,6} The objectives of this research range from the pure modeling challenges⁷ to detailed mechanistic and functional studies on the active site model.^{8–11}

We have recently become interested in the use of Fe H₂ase active site mimics as potential catalysts for the photochemical production of hydrogen and have thus introduced them as electron acceptors in multi unit assemblies.12 In the first studies, the dithiolate ligand served as the anchoring point for the attachment of the photosensitizer, and the first ruthenium diiron dyads of this type could be synthesized.^{13,14} However, the dithiolate ligand in the enzyme is believed to contain a secondary amine, the purpose of which is to shuttle protons to and from the distal iron center Fe^D.¹⁵⁻¹⁷ This important functional role is impeded in the synthetic diiron models as soon as they are functionalized at this position. Nature has chosen to leave the dithiolate "naked" and attached the electron transfer chain comprised by the $[Fe_4S_4]$ cluster via a sulfur ligand from a nearby cysteine residue to the H-cluster instead.^{3,4} Only a few examples of Fe H₂ase active site mimics where redox-active metal units are attached to one of the iron centers have been reported,6,7 however, no photo-active unit was



Chart 1

^aDepartment of Organic Chemistry, Arrhenius Laboratory, Stockholm University, 10691, Stockholm, Sweden

^bDepartment of Photochemistry and Molecular Science, Uppsala University, Box 523, 75120, Uppsala, Sweden

^cDepartment of Physical and Analytical Chemistry, BMC, Uppsala University, Box 599, 75124, Uppsala, Sweden

^dDepartment of Structural Chemistry, Arrhenius Laboratory, Stockholm University, 10691, Stockholm, Sweden

^eKTH Chemistry, Organic Chemistry, Royal Institute of Technology, 10044, Stockholm, Sweden

[†] Electronic supplementary information (ESI) available: Spectral changes of the UV/Vis spectrum of complex 1 upon exposure to room light. See DOI: 10.1039/b606659c

ever included or investigated. Inspired by this motif, we have synthesized dyad 1 in which the photosensitizer is linked to a model of the Fe H₂ase active site by a phosphine ligand in a similar sideon fashion (Chart 1(b)). The diiron complexes were investigated by crystallographic, spectroscopic and electrochemical techniques and the photophysical properties of the ruthenium diiron dyad 1 were studied by steady-state and time-resolved spectroscopy.

Results and discussion

Synthesis and IR spectroscopic characterization

Several synthetic and functional aspects have been considered in the design of complex 1. The triphenylphosphine ligand was identified as the most suitable ligand for the connection of the ruthenium and the diiron portion as it can be functionalized relatively easily and exhibits a higher stability towards oxidative degradation than trialkylphosphines. An acetylene has been chosen as the linking unit due to its appealing linear geometry and rigidity. Finally, Ru(bpy)₃ as photosensitizer displays a long excited state lifetime combined with a high excited state energy.¹⁸ Two different strategies were pursued for the synthesis of the diiron portion with the acetylenic triphenylphosphine ligand. In the first approach, the introduction of the acetylene moiety was attempted on the fully assembled $[(\mu-pdt)Fe_2(CO)_5{PPh_2(p-BrC_6H_4)}]$ where one phenyl group on the phosphine is functionalized with a bromo substituent. The second strategy relies on the synthesis of the acetylenic ligand prior to its coordination to the diiron fragment.

(*p*-Bromophenyl)diphenylphosphine was synthesized from *p*bromophenyl lithium and chlorodiphenylphosphine according to the literature procedure.¹⁹ Subsequent ligand exchange on the parent [(μ -pdt)Fe₂(CO)₆] with the functionalized phosphine using trimethylamine *N*-oxide as decarbonylation agent in CH₃CN afforded the desired mono-substituted [(μ -pdt)Fe₂(CO)₅{PPh₂(*p*-BrC₆H₄)}] **2** in 55% isolated yield (Scheme 1). The ligand substitution can conveniently be followed by a change of the carbonyl stretching frequencies in the respective IR spectra. Substitution of one carbonyl ligand shifts the frequencies from 2072, 2032, 1990 cm⁻¹ for the parent diiron hexacarbonyl starting material to 2044, 1985, 1937 cm⁻¹ for **2** (Table 1). These values are in agreement with those previously reported for related diiron complexes ligated by one triphenylphosphine.²⁰ $\label{eq:table_to_state} \begin{array}{ll} \textbf{Table 1} & Infrared \mbox{ data of } [(\mu\mbox{-}pdt)\mbox{Fe}_2(\mbox{CO})_6] \mbox{ and complexes } 1\mbox{-}\textbf{5} \mbox{ in the carbonyl stretching frequency region (measured in THF solution at 25 <math display="inline">^\circ\mbox{C}) \end{array}$

Compound ^a	$\nu(CO)/cm^{-1}$
$\label{eq:constraint} \hline \hline & [(\mu\mbox{-}pdt)Fe_2(CO)_6] \\ & [(\mu\mbox{-}pdt)Fe_2(CO)_5 \{PPh_2(BrC_6H_4)\}] \mbox{2} \\ & [(\mu\mbox{-}pdt)Fe_2(CO)_4 \{PPh_2(BrC_6H_4)\}_2] \mbox{3} \\ & [(\mu\mbox{-}pdt)Fe_2(CO)_5 \{PPh_2[C_6H_4CCH)\}] \mbox{3} \\ & [(\mu\mbox{-}pdt)Fe_2(CO)_5 \{PPh_2(C_6H_4CCH)\}] \mbox{5} \\ & [(\mu\mbox{-}pdt)Fe_2(CO)_5 \{PPh_2(C_6H_4CCH)\}] \mbox{5} \\ & [(\mu\mbox{-}pdt)Fe_2(CO)_5 \{PPh_2(C_6H_4CCbpy)\} Ru(bpy)_2]^{2+} \mbox{1}^{b} \\ & \end{tabular}$	2072, 2032, 1990 2044, 1985, 1937 2000, 1955, 1938 2043, 1980, 1934 2043, 1980, 1934 2044, 1983,
	1931 ^c
	CH CN

^{*a*} $pdt = -SCH_2CH_2CH_2S^-$. ^{*b*} As PF₆ salt. ^{*c*} Measured in CH₃CN.

The ligand exchange is sensitive to the reaction time and the used amount of Me_3NO as an increase of either one results in the formation of disubstituted $[(\mu-pdt)Fe_2(CO)_4\{PPh_2(p-BrC_6H_4)\}_2]$. This reaction is characterized by a further shift of the IR carbonyl frequencies towards lower energies (Table 1). Although well known for trialkylphosphines and phenyldimethylphosphines,²¹ only one example of double substitution with sterically more demanding triarylphosphines has been reported, but the product was not structurally characterized.²²

Introduction of the acetylene moiety at the bromophenyl substituent of **2** under classical Sonogashira cross coupling conditions with $[Pd(PPh_3)_2Cl_2]$ and CuI using either conventional or microwave heating was not successful. Similarly, an attempt to couple the acetylene to the isolated bromophenylphosphine ligand failed, reflecting the low reactivity of the electron-rich bromoarene.^{23,24}

To circumvent these problems, the acetylene was introduced at the phosphine ligand prior to the complexation of the latter to the diiron unit. Lithiation of 4-bromotrimethylsilylethynylbenzene²⁵ with butyl lithium afforded the acetylenic phenyl lithium which was subsequently reacted with chlorodiphenylphosphine to form the protected acetylenic triphenylphosphine. Without further purification, the acetylenic ligand was coordinated to the (μ -pdt)Fe₂(CO)₆ fragment, obtained from [(μ -pdt)Fe₂(CO)₆] by treatment of the latter with *n*-propylamine.²⁴ After purification by column chromatography and recrystallization, complex **4** could be isolated in 47% overall yield (Scheme 2).

Protodesilylation of 4 proceeded in a solution of THF and methanol in the presence of K_2CO_3 in good yield. With acetylene



Scheme 1 Reagents and conditions: (a) 2 eq. Me₃NO, CH₃CN, 2 h, 25 °C, 55%; (b) 10 eq. Me₃NO, CH₃CN, 2 h, 25 °C, 16%.



Scheme 2 *Reagents and conditions:* (a) 1. BuLi, THF, $-78 \degree C$, 2 h; 2. PPh₂Cl, THF, 2 h, $-78 \text{ to } 25 \degree C$; (b) *n*-PrNH₂, [(μ -pdt)Fe₂(CO)₆], THF, heat, 22 h, 47% over two steps; (c) K₂CO₃, THF–CH₃OH, 25 °C, 4 h, 81%; (d) [PdCl₂(PPh₃)₂], CuI, Et₃N, THF, CH₃CN, 85 °C, 18 h, 59%.

5 in hand, the attachment of the bipyridine ligand of the photosensitizer was targeted. First attempts to react 5 with 5bromobipyridine²⁶ under classical Sonogashira cross coupling conditions failed and no defined product could be isolated. This result is consistent with our previous findings that the iron carbonyl core is rather unstable in the presence of polypyridine ligands.²⁴ We thus turned our focus on the reaction of 5 with fully assembled [(5-Br-bpy)Ru(bpy)2]²⁺ and, most gratifyingly, we found that 5 reacted smoothly with the latter complex to afford the ruthenium-diiron dyad 1 in 59% isolated yield after column chromatography and anion exchange with PF₆. The ESI mass spectrum of 1 features an isotopic pattern typical for ruthenium complexes at m/z = 1357.11 as the base peak, corresponding to the loss of one PF₆ counter ion. Furthermore, NMR and elemental analysis data are in agreement with the assigned structure. The presence of the $Fe_2(CO)_5PPh$ portion in 1 is expressed by the characteristic IR absorptions in the carbonyl region, which are very similar to those of precursors 4 and 5.

Molecular structures of 3 and 4

X-Ray diffraction analysis of complexes **3** and **4** shows the usual square pyramidal geometry around the iron centers with Fe–Fe distances of 2.52 Å (Table 2). As shown in Fig. 1, the two triphenylphosphine ligands in **3** both reside in apical positions similar to the situation in the dimethylphenylphosphine ligands prefer a mixed apical/basal coordination mode in the solid state.²¹ It thus seems that the bulkiness of the phenylphosphines directs the ligands to the sterically least demanding apical positions.

Similarly, the acetylenic triphenylphosphine of complex **4** resides in an apical position in the solid state, (Fig. 2), consistent with the crystal structure of other mono triphenylphosphine-ligated diiron complexes.^{20,24} The acetylene with a typical bond length of 1.17 Å points in the same direction as the dithiolate ligand. The fact that the bulky triphenylphosphines exclusively prefer the apical positions is encouraging for the use of these diiron complexes as acceptors in multi unit assemblies. A defined geometry and distance should give rise to simplified photophysical properties such as monoexponential excited state decay functions.

Table 2 Selected bond lengths (\AA) for complexes 3 and 4 with estimated standard deviations

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3		4	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe1-Fe2 Fe1-P1 Fe2-P2 Fe1-S1 Fe2-S1 Fe2-S1 Fe2-S2 Fe1-C1 Fe1-C4 Fe2-C2 Fe2-C3 S1-C13 S2-C11 C1-O1 C2-O2 C3-O3 C4-O4	2.5177(14) 2.256(2) 2.247(2) 2.277(2) 2.273(2) 2.275(2) 2.275(2) 2.275(2) 2.275(2) 1.768(10) 1.761(10) 1.759(9) 1.708(9) 1.708(9) 1.850(8) 1.850(8) 1.164(8) 1.164(8) 1.180(8) 1.138(9)	Fe1-Fe2 Fe1-P1 Fe2-S1 Fe2-S2 Fe1-S1 Fe1-S2 Fe2-C1 Fe2-C2 Fe2-C3 Fe1-C4 Fe1-C5 S1-C11 S2-C13 C1-O1 C2-O2 C3-O3 C4-O4 C5-O5	$\begin{array}{c} 2.521(3)\\ 2.232(4)\\ \hline\\ 2.240(4)\\ 2.248(5)\\ 2.255(4)\\ 2.255(4)\\ 2.257(4)\\ 1.805(17)\\ 1.775(14)\\ 1.776(16)\\ 1.752(13)\\ 1.780(11)\\ 1.791(13)\\ 1.889(14)\\ 1.083(17)\\ 1.110(16)\\ 1.172(16)\\ 1.139(15)\\ 1.117(13)\\ \end{array}$



Fig. 1 ORTEP (ellipsoids at 50% probability level) of **3**. Hydrogen atoms are drawn as small circles of arbitrary radius.



Fig. 2 Molecular structure of **4** with displacement ellipsoids drawn at the 50% level. Hydrogen atoms are drawn as small circles of arbitrary radius.

Electronic absorption spectra

The electronic absorption spectra of dyad 1, of a representative diiron complex 5 and of a ruthenium reference complex $[(bpy)_2Ru(5-bpy-C\equiv C-Ar)]^{2+} 6^{27}$ (Ar = 2,5-bis(dodecyloxy)phenyl) with the same conjugated phenylethynyl bridge in the 5-position of the bipyridine as in 1, are shown in Fig. 3. Apart from a strong absorption reaching into the far UV, the spectrum of complex 5 features a strong band with a maximum at 362 nm that is typical for the (CO)₅(PPh₃) ligand set.²⁴ A broad and featureless lowintensity absorption in the visible region reaches up to 580 nm. In the spectrum of the acetylenic ruthenium reference 6, the characteristic metal-to-ligand charge transfer (MLCT) transition



Fig. 3 Electronic absorption spectra of compound 1 (—), 5 (---) and of $[(bpy)_2Ru(5-bpy-C \equiv C-Ar)]^{2+} 6^{27} (\cdots)$, recorded in CH₃CN.

can be observed around 450 nm. The broad absorption in the 350–430 nm region arises from a ligand-centered (LC) transition localized on the extended acetylenic bipyridine spacer.²⁸ The sharp peak around 290 nm is attributed to the $\pi \to \pi^*$ transitions on the auxiliary bipyridine ligands.^{18,29}

Similar to the spectrum of reference complex 6, the spectrum of 1 is dominated by strong $\pi \to \pi^*$ transitions localized on the bipyridine ligands at 287 nm.^{18,29} At least two poorly resolved absorptions can be observed in the region between 320 and 370 nm. By comparison with the spectra of complexes 5 and 6, we attribute these transitions to the $(\mu$ -pdt)Fe₂(CO)₅(PPh)₃ portion of the molecule as well as to the conjugated bpy- $C \equiv C - PPh_3$ ligand. However, the spectrum of 1 in this region is not a simple sum of the spectra of 5 and 6. Moreover, the spectrum changes considerably upon exposure of the sample to light and all spectral features in this region lose intensity (see ESI[†]). Although it is not possible to assign the degradation to either the conjugated linker or to the diiron unit, it is clear that both processes could have an impact on the photophysical behavior of the ruthenium chromophore. The longest wavelength absorption band in the spectrum of 1 between 400-500 nm is largely unaffected by the photodegradation and is attributed to the MLCT of the ruthenium chromophore, overlapping the low-intensity absorption of the diiron unit. In summary, all features of the UV/Vis spectrum of 1 have their respective counterparts in the spectra of complexes 5 and 6, although certain shifts and increased extinction coefficients can be noted when a difference spectrum is constructed. Together with the observed light-sensitivity of 1, it is clear from this data that the electronic coupling between the ruthenium and diiron portions of 1 is not negligible.

Electrochemistry

Compared to $[(\mu-pdt)Fe_2(CO)_6]$, the electrochemical reductions and oxidations of all diiron complexes described herein are shifted to more negative potentials, reflecting the electron donating properties of the introduced phosphine ligands (Table 3). The presence of two phosphines in complex 3 renders the irreversible oxidation more facile by 300 mV compared to the monosubstituted complexes. All mono-substituted complexes 1, 2, 4 and 5 exhibit comparable electrochemical behavior with an irreversible oxidation around 0.38 ± 0.02 V (all potentials herein are peak potentials of differential pulse voltammetric experiments and are given vs. $Fc^{+/0}$). A second irreversible oxidation associated with the diiron portion can be observed 300 mV after the first oxidation. Since the first oxidation is irreversible, the second process may be the oxidation of a species produced chemically after the first oxidation event. In addition to these two processes, a third reversible oxidation can be observed in the cyclic voltammogram of dyad 1 at 0.91 V. Due to the reversibility of this process and its characteristic potential,18 it can be assigned to the RuIII/II couple in 1. It therefore seems that the ruthenium portion in complex 1 is intact, despite the preceding irreversible oxidations at the diiron site.

On the reductive scan, the electronic effect of the phosphine ligands results in cathodically shifted reduction potentials of all complexes compared to $[(\mu-pdt)Fe_2(CO)_6]$, although the effect is somewhat less pronounced than in the oxidations. The most electron rich complex **3** is reduced at most negative potential

Table 3	Electrochemical	data of	[(µ-pdt)]	$Fe_2(CO)_6$]	and of c	omplexes 1	-5
Table 3	Electrochemical	data of	[(µ-pdt)]	$\operatorname{Fe}_2(\operatorname{CO})_6$	and of c	omplexes 1	-

Compound	$E_{\rm pa}({\rm Ru}^{\rm III/II})/{\rm V}$	$E_{ m pa}/{ m V}$	$E_{\rm pc}~({\rm Fe_2})/{ m V}$	$E_{\rm pc}$ (bpy)/V
$[(\mu-pdt)Fe_2(CO)_6]$		0.67	-1.60	
$[(\mu-pdt)Fe_2(CO)_5{PPh_2(BrC_6H_4)}]$ 2		0.36, 0.64	-1.76	
$[(\mu-pdt)Fe_2(CO)_4 \{PPh_2(BrC_6H_4)\}_2]$ 3		0.05	-1.92	
$[(\mu-pdt)Fe_2(CO)_5]PPh_2C_6H_4CCSi(CH_3)_3]$		0.36, 0.68	-1.74	
$[(\mu-pdt)Fe_2(CO)_5{PPh_2(C_6H_4CCH)}]5$		0.38, 0.68	-1.76	
$[(\mu-pdt)Fe_2(CO)_5{PPh_2(C_6H_4CCbpy)}Ru(bpy)_2]^{2+}$ 1	0.91	0.40, 0.65	-1.76	-1.51, -2.01

^{*a*} All potentials were recorded for deaerated, 1 mM solutions in CH₃CN containing Bu₄NPF₆ (0.3 M) as supporting electrolyte and are given *vs.* Fc^{+/0}. Anodic (E_{pa}) and cathodic peak potentials (E_{pc}) were recorded from differential pulse voltammetry ($\nu = 0.1 \text{ V s}^{-1}$). pdt = $^{-}$ SCH₂CH₂CH₂S⁻.

(-1.92 V). The irreversible reduction associated with the diiron portion in all mono-substituted complexes occurs at -1.76 V. In dyad 1, this reduction is preceded by a reversible reduction at -1.51 V. The reversibility of this wave, together with a comparison of the potential of this process with that of complex 6 (E^{red} = -1.14 vs. SCE ≈ -1.52 vs. Fc^{+/0}),²⁷ leads to the assignment of this reduction to be localized on the extended acetylenic bipyridine. Finally, a further reduction of 1 can be observed at -2.01 V and is attributed to the reduction of an auxiliary bipyridine ligand. The electrochemically most easily reduced ligand at a metal complex is usually the same ligand that is involved in the photo-induced MLCT excited state. Since, in the case of complex 1, this ligand is the acetylenic bipyridine, it appears that the excess electron would reside close to the acceptor in the lowest MLCT state. This situation is preferable and may facilitate a subsequent charge shift to the acceptor unit.

Steady-state and time-resolved spectroscopy

The highest energy peak in the vibrational progression of the emission spectrum at 77 K is known to give a good estimate of the excited state energy of a ruthenium polypyridyl complex.³⁰⁻³² Complex **1** displays an emission maximum at 616 nm in butyronitrile glass at 77 K which corresponds to an excited state energy of 2.01 eV (Table 4). This value is similar to that found for reference complex **6** (2.04 eV)²⁷ but somewhat lower than that of $[Ru(bpy)_3]^{2+}$ (2.12 eV).¹⁸ This difference in excited state energy can be rationalized by the better electron accepting capacity of the conjugated phenylethynyl bipyridine, compared to that of the unsubstituted bipyridine ligand. The excited state lifetime of complex **1** at 77 K is 2.5 µs, which is similar to that of other ruthenium(II)–polypyridine complexs.¹⁸

Complex 1 shows room-temperature MLCT-type emission centered at 670 nm, while, as expected, the diiron complex 5 shows no emission at ambient temperatures. For the reference chromophore 6 the emission maximum lies at 666 nm.²⁷ The emission yield of 1 is *ca*. 6% of that of the reference complex 6 in

Table 4Emission maxima and lifetimes, in deoxygenated acetonitrilesolutions, freshly prepared in the dark, at room temperature and inbutyronitrile glass at 77 K

	Room temperature		77 K	
Compound	$\lambda_{\rm max}/{\rm nm}$	τ/ns	$\lambda_{\rm max}/{\rm nm}$	τ/μs
Complex 1 Complex 6 ²⁷	670 666	770 1200	616 610	2.5 Not given

deoxygenated acetonitrile at room temperature, and thus it seems that the emission quenching in complex 1 is substantial. However, the room temperature excited state lifetime of a deoxygenated solution of complex 1 in acetonitrile, freshly prepared in the dark, is 770 ns. Using the excited state lifetime of complex 6 (1200 ns) as a reference,²⁷ the quenching can be calculated to be only 35%. This discrepancy in the observed excited state quenching of complex **1** is perhaps not surprising, considering the sensitivity to light already detected during the acquisition of the UV/Vis data. Even two consecutively recorded steady state emission spectra showed a substantial increase in emission intensity. A similar result could be obtained by exposing a solution of complex 1 to ambient light for less than one minute. Nanosecond time-resolved emission experiments, recording entire emission decay traces with a single laser flash excitation, revealed an even more complicated behavior. The first laser flash excitation gives an emission lifetime of 770 ns. With continued flashing, the lifetime first decreases, but subsequently increases. In parallel, a very short-lived emission (<1 ns) appears, which could also be observed in time-correlated single photon counting experiments with picosecond resolution. This behavior can be explained by photodegradation processes on either the acetylenic linker and/or the diiron unit that give rise to a changing electronic coupling between the different parts of the compound.

Although the light-sensitive nature of 1 precludes the determination of quantitative photophysical data, it can with certainty be concluded that the excited state is quenched to some degree compared to that of the reference chromophore 6. In principle, this quenching can be due to either energy or electron transfer. Since the absorption and emission spectra do not overlap substantially, Förster energy transfer is not likely to occur. Electron transfer can potentially be of oxidative or reductive nature. The driving force for electron transfer from the excited state of the ruthenium unit to the diiron site can be calculated by the Rehm-Weller equation.³³ Using the reduction potentials obtained from the electrochemical studies, the excited state energy, and omitting the work term arising from Coulombic interactions, the driving force for electron transfer from the ruthenium excited state to the diiron portion was calculated to be uphill by 0.66 V. However, a favorable driving force of 100 mV can be calculated for the reductive quenching of the excited state, resulting in a transiently oxidized diiron portion. Since the oxidation of the diiron unit is completely irreversible in the cyclic voltammetry, a similar decomposition pathway may explain the observed light-sensitivity of complex 1. In low temperature glasses, electron transfer is often hindered, which can explain why no photo-degradation was observed in the experiments conducted at 77 K.

Conclusions

With the synthesis of complex 1, we have found a viable strategy for the construction of the first model of the iron hydrogenase active site where a photosensitizer is attached to the diiron site directly via a ligand. From X-ray crystallography it appears that the triphenylphosphine ligand prefers exclusively the apical position, which results in a well-defined geometry of the RuFe₂ system. Electrochemical studies show that the bridging acetylenic bipyridine is the most easily reduced ligand. It can thus be anticipated that the light-induced MLCT excited state of 1 is localized towards the potential diiron electron acceptor which is a favorable feature to be included in future assemblies of this type. As a result of the easily reduced acetylenic ligand and the mild oxidation potential of the diiron portion, the ruthenium excited state in 1 can be quenched reductively by the diiron site. The transiently oxidized diiron site is known to be unstable which may explain the surprisingly high light-sensitivity of complex 1. In future developments of the system, the redox properties of the diiron portion have to be adjusted to more favorable values in order to fulfill the electronic requirements for electron transfer from the ruthenium chromophore to the diiron unit. Inclusion of an amine in the dithiolate linker or further ligand substitutions on the diiron core with electron donating ligands would enable protonation of the diiron site and thus render a subsequent reduction more facile. Such an electronic modulation would not only move the potential required for the reduction of the diiron site within reach of the ruthenium excited state, but would also diminish the unwanted reductive quenching of the ruthenium excited state and decrease the associated photodegradation of the system.

Experimental

NMR spectra were recorded on Varian spectrometers (300 or 400 MHz). The infrared spectra were recorded on Perkin-Elmer spectrum 1. The elemental analysis were performed in Analytische Laboratorien, Lindlar, Germany. Microwave heating experiments was performed in a SmithCreator from Biotage (Personal Chemistry AB) Uppsala, Sweden. Chromatographic purification was carried out on Merck silica gel 60 (230–400 mesh). The mass-spectrometry experiments were done on a Bruker Daltonics BioAPEX-94e superconducting 9.4 tesla FTICR mass spectrometer (Bruker Daltonics, Billerica, MA, USA) (FTICR-ESI MS). Electronic absorption spectra were measured on a Hewlett-Packard 8453 instrument, in 1×1 cm quartz cuvettes.

Single-crystal X-ray diffraction patterns were recorded with an Oxford Diffraction Excalibur diffractometer equipped with a sapphire-3 CCD on a Mo-radiation source ($\lambda = 0.71073$ Å) with ω -scans at different ϕ to fill Ewald sphere. The sample-detector distance was 50 mm. Indexing, cell refinements and integration of reflection intensities were performed with the Crysalis software.³⁴ Numerical absorption correction was performed with the program X-RED³⁵ verifying the crystal shape with program X-shape.³⁶ The structure was solved by direct methods using SHELXS97³⁷ giving electron density maps where most of the non-hydrogen atoms could be resolved. The rest of the non-hydrogen atoms were located from difference electron density maps and the structure model was refined with full matrix least square calculations on F^2 using the program SHELXL97–2.³⁸ All non-hydrogen atoms Table 5 Selected crystal data for complexes 3 and 4

	3	4
Empirical formula	$C_{48}H_{44}Br_2Fe_2O_4P_2S_2$	$C_{31}H_{29}Fe_2O_5PS_2Si$
T/K	293(2)	293(2)
$M_{\rm r}/{ m g}~{ m mol}^{-1}$	1082.41	716.42
Crystal system	Monoclinic	Triclinic
Space group	$P2_{1}/n$	$P\overline{1}$
a/Å	9.3219(9)	13.001(13)
b/Å	22.8707(16)	8.539(5)
c/Å	22.4947(17)	14.994(10)
a/°	90	90.09(5)
β/°	96.750(7)	92.35(7)
γ/°	90	90.09(6)
$V/Å^3$	4762.6(7)	1663(2)
Ζ	4	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.510	1.431
μ (Mo-K α)/mm ⁻¹	2.484	1.118
Crystal shape	Needle	Prism
T_{\min}, T_{\max}	0.41, 0.88	0.72, 0.99
$N_{\rm meas}, N_{\rm uniq}, R_{\rm int}$	32469, 14784, 0.1008	16952, 7707, 0.0930
$N_{\rm obs}, N_{\rm par}, S$ (GoF)	3150, 518, 0.745	2716, 344, 0.935
<i>R</i> 1, <i>wR</i> 2 both with $(I > 2\sigma(I))$	0.0678, 0.1624	0.1015, 0.2732
R1, $wR2$ (all data)	0.3178, 0.2224	0.2356, 0.3295
$\Delta ho_{ m min}, \Delta ho_{ m max}$ / e Å $^{-3}$	-0.609, 1.180	-0.56, 0.87

were refined with anisotropic displacement parameters and the hydrogens, which were placed at geometrically calculated positions and let to ride on the atoms they were bonded to, were given isotropic displacement parameters calculated as $nU_{eq.}$ for the non-hydrogen atoms with n = 1.5 for methyl hydrogens (-CH₃) and n = 1.2 for methylenic (-CH₂-) and aromatic hydrogens. Selected crystal data are given in Table 5 and selected bond lengths in Table 2. Molecular structures of complexes **3** and **4** are shown in Fig. 1 and 2.

CCDC reference numbers 607112 and 607113.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606659c

Electrochemical measurements were carried out in a threeelectrode cell connected to an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). The working electrode was a glassy carbon disc (diameter 2 mm, freshly polished). A graphite rod served as a counter and a non-aqueous Ag/Ag⁺ served as a reference electrode (CH Instruments, 10 mM AgNO₃ in acetonitrile, $E^{1/2} = 80$ mV vs. Fc^{+/0}). All potentials are given vs. the Fc^{+/0} couple. Solutions were prepared from dry acetonitrile (Merck, spectroscopic grade, dried with MS 3 Å) and contained ca. 1 mM of the analyte and 0.3 M tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) as supporting electrolyte. Before all measurements, the stirred solutions were purged with solvent saturated argon to remove residual oxygen and the experiments were kept under an atmosphere of argon at all times.

Steady state emission measurements were performed on a SPEX-Fluorolog II fluorimeter, and corrected for different detector sensitivity at different wavelengths. 1×1 cm quartz cuvettes were used for room temperature measurements. Steady state emission spectra at 77 K were measured in a liquid-nitrogen filled cold finger Dewar. Low temperature measurements were performed in butyronitrile, purified by distillation over P₂O₅. All samples were prepared in darkness.

Time resolved emission measurements were performed with a frequency tripled Q-switched Nd:YAG laser from Quantel

producing <10 ns flashes. Excitation light at 460 nm was obtained in an OPO. The emission was detected at right angle with a monochromator and a P928-type PMT. The PMT output was recorded on a Philips digital oscilloscope (2 Gsamples s⁻¹) and analysed with the Applied Photophysics LKS60 software or Igor Pro 5.03. Excited state lifetimes at 77 K were measured in a butyronitrile glass (distilled over P_2O_5) in a cold finger Dewar filled with liquid nitrogen.

THF was distilled over Na and CH_2Cl_2 over CaH_2 prior to use. CH_3CN was dried using molecular sieve (4 Å). [(μ -pdt)Fe_2(CO)_6],³⁹ diphenyl(4-bromophenyl)phosphine¹⁹ and 5bromo-2,2'-bipyridine²⁶ were synthesized according to literature procedures.

$[(\mu-pdt)Fe_2(CO)_5{PPh_2(BrC_6H_4)}](2)$

[(μ-pdt)Fe₂(CO)₆] (0.12 g, 0.31 mmol) was dissolved in CH₃CN (20 ml). Trimethylamine *N*-oxide dihydrate (0.070 g, 0.63 mmol) was added and the solution was stirred for 20 min. Diphenyl(4-bromophenyl)phosphine (0.21 g, 0.62 mmol) was added and the solution was stirred for 2 h. The solvent was removed under reduced pressure and the crude product was purified by chromatography on silica with pentane-toluene = 5 : 1 as eluent. The product was obtained as a red solid (0.12 g, 55%) (Found: C, 44.76; H, 2.93. C₂₆H₂₀BrFe₂O₅PS₂ requires: C, 44.76; H, 2.88%); v_{max}/cm^{-1} (THF) 2044, 1985, 1937; $\delta_{\rm H}$ (300 MHz; CDCl₃) 7.69–7.64 (m, 4 H), 7.57–7.55 (m, 4 H), 7.45–7.42 (m, 6 H), 1.76 (m, 2 H) 1.53 (m, 1 H) 1.45 (m, 2 H) 1.10 (m, 1 H).

$[(\mu-pdt))Fe_2(CO)_4{PPh_2(BrC_6H_4)}_2]$ (3)

[(μ-pdt)Fe₂(CO)₆] (0.12 g, 0.31 mmol) was dissolved in CH₃CN (20 mL). Trimethylamine *N*-oxide dihydrate (0.35 g, 3.1 mmol) was added and the solution was stirred for 20 min. Diphenyl(4-bromophenyl)phosphine (0.42 g, 1.2 mmol) was added and the solution was stirred for 2 h. The solvent was removed by reduced pressure and the crude product was purified by chromatography on silica with pentane–toluene = 1 : 5 as eluent. The product was obtained as a red solid (0.050 g, 16%). Crystals for X-ray analysis were grown by slow solvent evaporation from a THF solution of the complex at 7 °C (Found: C, 50.84, H, 3.39. C₄₃H₃₄Br₂Fe₂O₄P₂S₂ requires: C, 51.02; H, 3.39%); v_{max}/cm^{-1} (THF) 2000, 1955, 1938; $\delta_{\rm H}$ (300 MHz; CDCl₃) 7.69 (m, 8 H) 7.63–7.52 (m, 8 H) 7.40 (m, 12 H) 0.80 (m, 4 H) 0.70 (m, 2 H).

$[(\mu-pdt)Fe_2(CO)_5{PPh_2[C_6H_4CCSi(CH_3)_3]}] (4)$

To 1-bromo-4-trimethylsilylethynylbenzene (1.2 g, 4.8 mmol) in dry THF (30 ml) was added *n*-BuLi (1.6 M, 3.0 mL, 4.8 mmol) under argon at -78 °C. The solution was stirred for 2 h before chlorodiphenylphosphine (0.9 mL, 5 mmol) was added. The reaction mixture was stirred for an additional 2 h, the solvent removed by evaporation under reduced pressure and the residue dissolved in EtOAc and passed through a silica column. The resulting phosphine (an oil) and [(μ -pdt)Fe₂(CO)₆] (1.9 g, 4.9 mmol) were dissolved in dry THF (100 mL) and *n*-propylamine (10 mL) and refluxed for 22 h. The solvent was removed under reduced pressure and the crude product was purified by chromatography on silica with pentane–toluene = 4:1 as eluent. The product was obtained as a red solid (1.6 g, 47%). Crystals for X-ray analysis were grown by slow diffusion of pentane into a toluene solution of the complex at 7 °C (Found: C, 51.91; H, 4.19. $C_{31}H_{29}Fe_2O_5PS_2Si$ requires C, 51.97; H, 4.08%); v_{max}/cm^{-1} (THF) 2043, 1980, 1934; $\delta_{\rm H}$ (300 MHz; CDCl₃) 7.69–7.58 (m, 6 H), 7.51–7.47 (m, 2 H), 7.45–7.42 (m, 6 H), 1.74 (m, 2 H), 1.50 (m, 1 H), 1.40 (m, 2 H), 1.08 (m, 1H), 0.25 (s, 9 H).

$[(\mu-pdt)Fe_2(CO)_5{PPh_2(C_6H_4CCH)}] (5)$

Iron complex **4** (1.6 g, 2.3 mmol) was dissolved in a mixture of THF (70 ml) and methanol (30 ml). K_2CO_3 (7 g, 50 mmol) was added and the solution was stirred at room temperature for 4 h. The solvent was removed by rotary evaporation and the product was purified by chromatography on silica with pentane– $CH_2Cl_2 = 3 : 1$ as eluent. The product was obtained as a red solid (1.2 g, 81%) (Found: C, 52.32; H, 3.29. $C_{28}H_{21}Fe_2O_5PS_2$ requires C, 52.20; H, 3.29); v_{max}/cm^{-1} (THF) 2044, 1985, 1936; δ_H (300 MHz; CDCl₃) 7.71–7.61 (m, 6 H), 7.53 (m, 2 H), 7.47–7.42 (m, 6 H), 3.18 (s, 1 H), 1.74 (m, 2 H) 1.51 (m, 1 H), 1.43 (m, 2 H), 1.10 (m, 1 H).

 $[(5-Br-bpy)Ru(bpy)_2](PF_6)_2$ (0.21 g, 0.22 mmol) was dissolved in CH₃CN (30 ml). A solution of iron complex 5 (0.24 mg, 0.37 mmol) in THF (10 ml) was added together with [Pd(PPh₃)₂Cl₂] (0.035 g, 0.05 mmol) and Et₃N (10 mL). The solution was degassed with argon and CuI (64 mg, 0.33 mmol) was added. The reaction mixture was stirred at 85 °C for 18 h. After cooling to room temperature, the solvent was removed under reduced pressure and the product was purified by chromatography on silica using $CH_3CN-H_2O-KNO_{3(aq)} = 90 : 5 : 1$ as eluent. The resulting red product was dissolved in a small amount of CH₃CN. A saturated aqueous solution of NH₄PF₆ was added and the product was extracted with CH₂Cl₂, dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The product was afforded as a red solid (195 mg, 59%) (Found C, 46.15; H, 3.03; N, 5.73. C₅₈H₄₃Fe₂N₆O₅P₃RuS₂ requires C, 46.39; H, 2.89; N, 5.60%); $v_{\rm max}/{\rm cm^{-1}}$ (CH₃CN) 2044, 1983, 1931; $\delta_{\rm H}$ (400 MHz; CD₃CN) 8.52-8.48 (m, 6 H), 8.16 (dd, 1 H), 8.10-8.03 (m, 5 H) 7.86 (s, 1 H), 7.82 (d, 1 H), 7.73-7.66 (m, 9 H), 7.63 (s, 1 H), 7.57-7.49 (m, 8 H), 7.44–7.38 (m, 5 H) 1.78 (m, 2 H), 1.50 (m, 3 H), 1.08 (m, 1 H); $\lambda_{max}/nm (\epsilon/dm^3 mol^{-1} cm^{-1})$ (CH₃CN) 287 (64500), 323 (39700), 340 (sh, 39200), 441 (11000); m/z (ESI) 1357.11 (100%) $[M - PF_6]^+$. $[M - PF_6]^+$ requires 1356.83.

Acknowledgements

Financial support for this work was provided by the Swedish Energy Agency, the Swedish Research Council and NEST-STRP: SOLAR-H (EU contr. nr. 516510).

References

- 1 M. W. W. Adams, Biochim. Biophys. Acta, 1990, 1020, 115-145.
- 2 M. Frey, ChemBioChem, 2002, 3, 152-160.
- 3 J. W. Peters, W. N. Lanzilotta, B. J. Lemon and L. C. Seefeldt, *Science*, 1998, **282**, 1853–1858.
- 4 Y. Nicolet, C. Piras, P. Legrand, E. C. Hatchikian and J. C. Fontecilla-Camps, *Structure*, 1999, **7**, 13–23.
- 5 D. J. Evans and C. J. Pickett, Chem. Soc. Rev., 2003, 32, 268-275.

- 7 C. Tard, X. Liu, S. K. Ibrahim, M. Bruschi, L. D. Gioia, S. C. Davies, X. Yang, L.-S. Wang, G. Sawers and C. J. Pickett, *Nature*, 2005, **433**, 610–613.
- 8 F. Gloaguen, J. D. Lawrence, T. B. Rauchfuss, M. Benard and M.-M. Rohmer, *Inorg. Chem.*, 2002, 41, 6573–6582.
- 9 S. Ott, M. Kritikos, B. Åkermark, L. Sun and R. Lomoth, *Angew. Chem., Int. Ed.*, 2004, **43**, 1006–1009.
- 10 J.-F. Capon, F. Gloaguen, P. Schollhammer and J. Talarmin, *Coord. Chem. Rev.*, 2005, 249, 1664–1676.
- 11 L. Schwartz, G. Eilers, A. Gogoll, L. Eriksson, R. Lomoth and S. Ott, *Chem. Commun.*, 2006, 520–522.
- 12 L. Sun, B. Åkermark and S. Ott, Coord. Chem. Rev., 2005, 249, 1653– 1663.
- 13 S. Ott, M. Kritikos, B. Åkermark and L. Sun, Angew. Chem., Int. Ed., 2003, 42, 3285–3288.
- 14 H. Wolpher, M. Borgström, L. Hammarström, J. Bergquist, V. Sundström, S. Styring, L. Sun and B. Åkermark, *Inorg. Chem. Commun.*, 2003, 989–991.
- 15 H.-J. Fan and M. B. Hall, J. Am. Chem. Soc., 2001, 123, 3828-3829.
- 16 Y. Nicolet, A. L. D. Lacey, X. Vernede, V. M. Fernandez, E. C. Hatchikian and J. C. Fontecilla-Camps, J. Am. Chem. Soc., 2001, 123, 1596–1602.
- 17 Z.-P. Liu and P. Hu, J. Am. Chem. Soc., 2002, 124, 5175-5182.
- 18 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. v. Zelewsky, *Coord. Chem. Rev.*, 1988, 84, 85–277.
- 19 C. M. Thomas and J. C. Peters, Inorg. Chem., 2004, 8-10.
- 20 M. M. Hasan, M. B. Hursthouse, S. E. Kabir and K. M. A. Malik, *Polyhedron*, 2001, **20**, 97–101.
- 21 X. Zhao, I. P. Georgakaki, M. L. Miller, R. Mejia-Rodriguez, C.-Y. Chiang and M. Y. Darensbourg, *Inorg. Chem.*, 2002, **41**, 3917–3928.
- 22 P. Li, M. Wang, C. He, G. Li, X. Liu, C. Chen, B. Åkermark and L. Sun, *Eur. J. Inorg. Chem.*, 2005, 2506–2513.

- 23 G. J. R. Singh, J. Org. Chem., 1989, 54, 4453-4457.
- 24 (a) S. Ott, M. Borgström, M. Kritikos, R. Lomoth, J. Bergquist, B. Åkermark, L. Hammarström and L. Sun, *Inorg. Chem.*, 2004, 43, 4683–4692; (b) L. Schwartz, J. Ekström, R. Lomoth and S. Ott, *Chem. Commun.*, 2006, DOI: 10.1039/b608260b.
- 25 R. P. Hsung, C. E. D. Chidsey and L. R. Sita, *Organometallics*, 1995, 14, 4808–4815.
- 26 F. M. Romero and R. Ziessel, Tetrahedron Lett., 1995, 36, 6471-6474.
- 27 F. Chaignon, J. Torroba, E. Blart, M. Borgström, L. Hammarström and F. Odobel, New J. Chem., 2005, 29, 1272–1284.
- 28 U. H. F. Bunz, Chem. Rev., 2000, 100, 1605-1644.
- 29 J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. D. Cola and L. Flamigni, *Chem. Rev.*, 1994, 94, 993–1019.
- 30 J. Treadway, B. Loeb, R. Lopez, P. A. Anderson, F. R. Keene and T. J. Meyer, *Inorg. Chem.*, 1996, **35**, 2242–2246.
- 31 L. Hammarström, F. Barigelletti, L. Flamigni, M. T. Indelli, N. Armaroli, G. Calogero, M. Guardigli, A. Sour, J.-P. Collin and J.-P. Sauvage, J. Phys. Chem. A, 1997, 101, 9061–9069.
- 32 J. V. Caspar and T. J. Meyer, Inorg. Chem., 1983, 22, 2444-2453.
- 33 D. Rehm and A. Weller, Isr. J. Chem., 1970, 8, 259–271.
- 34 Xcalibur CCD system, CrysAlis Software system, Version 1.170, Oxford Diffraction, Oxford Diffraction Ltd, 2003.
- 35 X-RED, Absorption Correction Program, version 1.09, Stoe & Cie GmbH Darmstadt, Germany.
- 36 X-SHAPE, Crystal Optimization for Numerical Absorption Correction, version 1.2, Stoe & Cie GmbH Darmstadt, Germany.
- 37 G. M. Sheldrick, Acta Crystallogr., Sect. A, 1990, 46, 467-473.
- 38 G. M. Sheldrick, *Computer Program for the Refinement of Crystal Structures*, Göttingen, Germany, 1997.
- 39 D. Seyferth, R. S. Henderson and L. Song, Organometallics, 1982, 125– 133.