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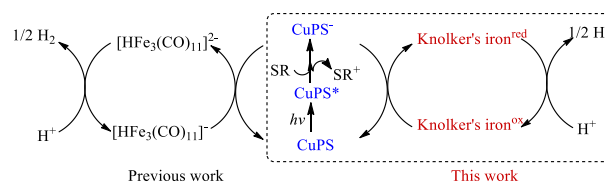
Efficient Photocatalytic Water Reduction Using in Situ Generated Knölker's Iron Complexes

Yuan-Yuan Sun,^[a] Hai Wang^[b], Nan-Yu Chen^[a], Alastair J J Lennox^[a, c], Aleksej Friedrich^[d], Liang-Min Xia^[a], Stefan Lochbrunner^{*,[d]}, Henrik Junge^[c], Matthias Beller^{*,[c]}, Shaolin Zhou^{*,[b]} and Shu-Ping Luo^{*,[a]}

Abstract: In situ generated iron-based Knölker complexes were found to be efficient catalysts in a fully non-noble metal Cu-Fe photocatalytic water reduction system. These mono-nuclear iron catalysts resulted in up to fifteen times faster hydrogen generation compared to previously reported Fe₃(CO)₁₂. A reductive quenching mechanism was shown to operate by fluorescence experiments.

Artificial photosynthesis (AP) is considered to offer solutions for the current energy crisis and to decrease environmental pollution, because it directly converts sunlight energy into chemical energy. Among the various concepts, the most direct and clean method to convert photochemical energy into chemicals is the splitting of water into O₂ and H₂.¹ Despite tremendous effort in this area,² there still exists significant challenges for its application, due to low efficiencies of light absorption materials,³ redox catalysts⁴ and full-cell systems.⁵ In order to improve current systems and to gain better understanding of the overall water-splitting process, the individual half reactions (proton reduction and water oxidation) are generally studied separately. Over the past decades numerous, highly active, water reduction catalysts (WRC) for photocatalytic hydrogen generation have been developed,⁶ most of which are derived from precious metals such as platinum,⁷ palladium,⁸ rhodium⁹ and ruthenium.¹⁰ Due to the high price and limited availability of these precious metals, the development of WRC based on bio-relevant or earth abundant transition metals is highly desirable. Recently, non-noble metal alternatives, e.g. cobalt¹¹ and nickel¹² complexes have been examined as active hydrogen generation catalysts. In addition, nature developed an iron-based hydrogenase (with up to 9000 molecules of H₂ per second and site) for proton reduction,¹³ which makes it appealing for WRC applications.¹⁴ In 2009, we demonstrated that simple, cheap, and readily available iron carbonyls can act as WRCs.¹⁵ In combination with a noble metal photosensitizer (PS), [Ir(bpy)(ppy)₂]PF₆ (ppy:

2-phenylpyridine), high activities were achieved. This was followed by a new non-noble metal water reduction system that employed Fe₃(CO)₁₂ as WRC and a heteroleptic copper complex as PS. Both oxidative and reductive quenching pathways of the excited state of CuPS were confirmed in this Cu-Fe system.¹⁶ Herein, we envisioned mono-nuclear iron tricarbonyl cyclopentadienone complexes might become an efficient substitute for Fe₃(CO)₁₂. In general, Knölker's precursor complexes are stable under contact with air and water, and easily accessible from simple and cheap precursors.¹⁷ Importantly, Knölker's complexes can easily be produced in situ and have been successfully applied in various organic redox reactions.¹⁸ Due to their uniquely powerful redox catalyst properties, they have great potential to serve as efficient WRCs, Scheme 1. In the presence of a heteroleptic copper(I) PS (CuPS), we report herein on the use of a series of Knölker iron complexes as mimics for mono-nuclear iron-based hydrogenases, which have proved to be highly active catalysts for water reduction. This represents the first non-noble metal photocatalytic system for water reduction employing Knölker's catalysts.



Scheme 1. The envisioned process for hydrogen generation by applying a Cu-based PS and Fe-based WRC.

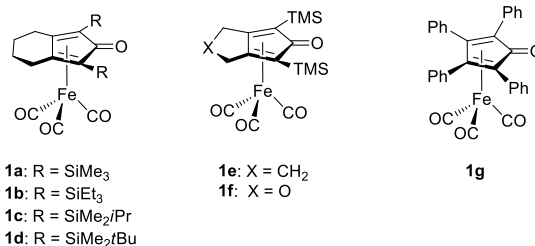


Figure 1. The iron-based Knölker catalysts **1a-1g** applied to water reduction

Initial investigations were performed under the same conditions recently applied to the Cu-Fe based water reduction system, which included the heteroleptic cationic copper(I) complex [Cu(Xantphos)(bathocuproine)PF₆] as PS, triethylamine (TEA) as sacrificial reductant (SR) in a tetrahydrofuran (THF)/water mixture (THF:TEA:H₂O = 4:3:1) (Scheme 1).¹⁹ The activities of a range of Knölker WRCs, Figure 1, were tested and the results are summarized in Table 1. The iron complex **1a** was not active in the absence of an additional base (entry 1). Therefore, several bases were applied to induce catalytic activity. Adding KOH as base resulted in a significant hydrogen generation of

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17 mL after 3 hours and a productivity (TON) of 58 (entry 2). Furthermore, K_3PO_4 , tetrabutylammonium hydroxide (Bu_4NOH) and tetraethylammonium hydroxide (Et_4NOH) were also tested (entries 3-5). The latter resulted in the best TON value (75) after 3 hours. The influence of the ratio of the amounts of catalyst **1a** and base were investigated in more detail. In this respect, 12 μmol **1a** and 12 to 20 μmol Et_4NOH proved to be optimal (Figure S2). Next, the other iron complexes **1b-1g** were tested under the same conditions applying Et_4NOH as base (entries 6-11). These experiments resulted in almost the same activities compared to **1a** except for **1d** (entry 8), which achieved 59% of the productivity of **1a**. $[Fe_3(CO)_{12}]$ (**2**) was completely deactivated in the presence of additional base (entry 12) and therefore, for comparison, the reaction was repeated in the absence of Et_4NOH (entry 13). The productivity of hydrogen generation with **2** was similar to that of **1a**. However, when taking into account the maximum TON for each iron atom, it is clear **1a** is superior in terms of efficiency and rate (entry 13 vs 5). **2** provided only 3.1 mL of H_2 in 3 hours in comparison to 22 mL provided by **1a**, which is a 15 fold increase in TON. Thus, we have demonstrated the ability of Knölker type iron complexes to act as efficient WRCs.

Table 1. Application of iron-based Knölker complexes in the photocatalytic water reduction.

Entry ^[a]	Cat	Base	Time / hr	Vol. H_2 , 3 hr /mL ^[b]	Fe-TON ^[c] 3 hr ^[b]
1	1a	-	12	0	0
2	1a	KOH	12	17 (33)	58 (112)
3	1a	K_3PO_4	8	12 (30)	41 (102)
4	1a	Bu_4NOH	8	19 (29)	65 (99)
5	1a	Et_4NOH	8	22 (35)	75 (119)
6	1b	Et_4NOH	9	22(29)	75 (99)
7	1c	Et_4NOH	7	23 (29)	78 (99)
8	1d	Et_4NOH	7	13(29)	44 (99)
9	1e	Et_4NOH	8	19 (28)	65 (95)
10	1f	Et_4NOH	8	19 (24)	65 (82)
11	1g	Et_4NOH	6	18 (19)	61 (65)
12	2	Et_4NOH	15	0	0
13 ^[d]	2	-	27	3.1 (33)	8 (90)
14 ^[d]	1a	Et_4NOH	7	15 (16)	123 (131)

[a] Reaction conditions: CuPS 3.5 μmol , Cat. 12 μmol , base 12 μmol , 10 mL THF/TEA/ H_2O (4/3/1), 25 °C, Xe-light irradiation (output 1.5 W), without light filter, gas evolution quantitatively measured via gas burettes, gas analysis via GC. All given values are the averages of at least two experiments. The results differ between 1 and 20% except for volumes <10 mL (up to 40%); [b] numbers in parentheses are the volume attained after the time indicated in the previous column [c] TON (Fe) = $n(H_2)/n(Fe\text{ atom})$; [d] 5 μmol catalyst applied.

A number of control reactions were undertaken in order to gain further mechanistic insight into the system. The pH of the solvent mixture was monitored during the reaction. After the base was added, the pH increased from 11.38 to 11.49 (Table S1). Then, the pH slowly decreased during light irradiation, a trend that was also observed for the CuPS / **2** system and reflects the steady consumption of sacrificial amine base (NEt_3). By addition of further quantities of either CuPS or **1a** or both to the standard experiment after gas evolution had ceased, the activity was restored to different levels (Figure S4).

This clearly indicated that both components decomposed during the reaction, but that the heteroleptic CuPS degraded faster than Knölker's iron complex.^{19d} To test the influence of UV light on the activity of light-driven hydrogen production, our experiments were carried out with a 400 nm cutoff filter and AG1.5 filter. Indeed, the water reduction system was shown to be able to use visible light efficiently (Figure S5) with only a slight decrease in productivity and catalyst lifetimes. Thus, the light source is an important component to improve the stability of Knölker's iron catalyst system.

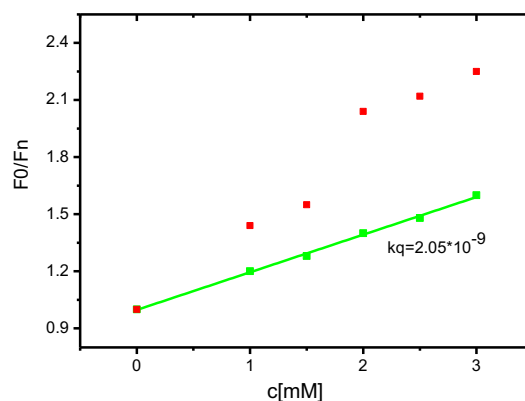


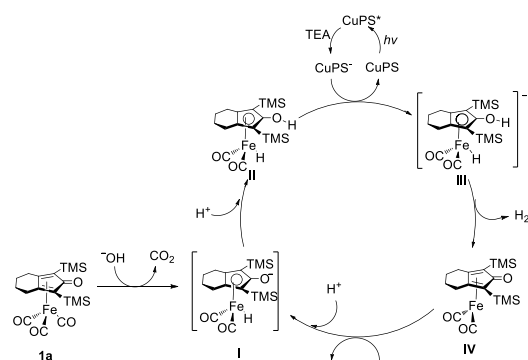
Figure 2. The Stern-Volmer curves. The concentration of CuPS is 0.35 mM in acetonitrile; quenchers: **1a** (red) and TEA (green).

Table 2. Lifetime measurements of CuPS, with **1a** in THF and THF+ Et_4NOH .

Solvents	CuPS ^[a]	CuPS ^[a] + 1a ^[b]
THF	3.2 μs	3.8 μs
THF + TEA (5:3)	350 ns	360 ns
THF + Et_4NOH	440 ns	660 ns
(THF + Et_4NOH) + TEA (5:3)	270 ns	<265 ns ^[c]

[a] The concentration of CuPS is 0.1 M – 0.35 mM; [b] The concentration of **1a** is 0.04 mM – 0.1 mM; [c] Amplitude weighted average lifetime. The fit resulted in two lifetimes: $\tau_1 = 139\text{ ns}$, $\tau_2 = 351\text{ ns}$.

When applying **2** to the reaction, the quenching of the excited state of CuPS has been previously reported to undergo a reductive quenching pathway.^{19c} We wanted to perform the corresponding experiments to establish the quenching mode of the PS excited state under the newly optimized conditions (entry 5). Using **1a** as the quencher, evolution of the fluorescence ratio of CuPS was found not to be linear (red curve, Figure 2). The data deviated from the Stern–Volmer equation since the catalyst has non-negligible absorption at both the excitation and fluorescence wavelengths. However, when the quencher was TEA, the evolution of the fluorescence ratio was linear (green line, Figure 2) and an apparent quenching rate constant of $k_q = 2.05 \times 10^{-9}\text{ L mol}^{-1}\text{ s}^{-1}$ was obtained. Due to three orders of magnitude higher concentration of TEA compared to **1a**, it is predicted that the reductive quenching mode is dominant. This conclusion was confirmed by lifetime measurements of the CuPS excited state in the presence of **1a** in THF and THF+ Et_4NOH (Table 2). The lifetime of *CuPS was recorded to be about 3 μs in THF. The precatalyst **1a** did not quench the luminescence lifetime of *CuPS , but the lifetime decreased in the presence of TEA to 350 ns and then to 265 ns under the reaction conditions and in the presence of the catalyst.



Scheme 2. Plausible mechanism

Considering our mechanistic studies, and previous work in the groups of Knölker and Casy, regarding the reduction reactions applying Knölker's iron complexes,²⁰ the following water reduction mechanism is proposed (Scheme 2). Under basic conditions the water gas shift reaction converts the pre-catalyst **1a** into the hydride iron complex **I**. This active complex **I** showed an enhanced reduction current in cyclic voltammogram experiments (Figure S7), and was detected by ESI-MS (Figures S12-S15). CO₂ as the byproduct was neutralized by the base (Figure S19). When water was added, protonation occurred to form hydride complex **II** and the reduction current increased many times over in comparison to complex **I**. During light irradiation, Knölker's iron WRC **III** is formed by an electron transfer from CuPS⁻. This is followed by hydrogen generation through hydrolysis of the iron hydride. In the last step the 16-electron iron (0) **IV** species is reduced by another CuPS⁻ to provide the hydride iron complex **I** again. Although a few particles were formed at the end of the reaction, the pure liquid phase mixture, separated by the centrifuge method, kept the same activity after CuPS was added (Figures S17 and S18). This fact indicates that the particles are most probably from the photosensitizer, also confirming that the homogeneous Knölker's iron complex is the active WRC.

In summary, we have developed a novel non-noble metal system for the photocatalytic reduction of water at room temperature. It uses in situ generated Knölker's iron complexes as water reduction catalysts, which perform at a rate four to fifteen times that of [Fe₃(CO)₁₂]. These new mono-nuclear iron WRCs are cheap, readily available from commercial sources and stable at ambient conditions, thus rendering them very attractive catalysts. Further developments to increase the stability are currently being carried out in our laboratories.

Notes and references

All catalytic experiments were carried out under an argon atmosphere with exclusion of air. THF, TEA, and water were degassed and purified by standard laboratory methods prior to use. The catalyst and copper(I) complex were synthesized according to a literature procedure (see Supporting information). The amount of gas liberated was measured by a gas burette (see Supporting information). Details on the equipment and the experimental set-up have been published elsewhere.^{19d} The relative composition of the evolved gas was determined by GC (gas chromatograph Fuli 9790II, carboxen 1000, TCD, external calibration). The light source was a 300W Xe lamp. Typical procedure for light-driven water reduction: A double-walled thermostatically controlled reaction vessel is evacuated and purged with argon. The copper photosensitizer and iron catalyst are added as solids, Et₃NOH is added as liquid. The corresponding solvent mixture (THF/TEA/H₂O) is added and the system is taken to 25 °C before switching on the light source. It is then stirred at 25 °C until no further gas

evolution is observed. All given values are the averages of at least two experiments. The results differ between 1 and 20% except for volumes <10 mL (up to 40%).

Acknowledgements

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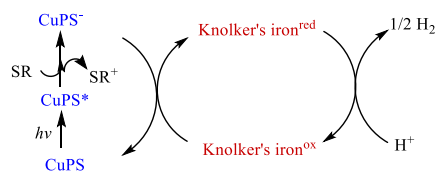
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Entry for the Table of Contents

Hydrogen Generation

Yuan-Yuan Sun, Hai Wang, Nan-Yu Chen,
Alastair J. J. Lennox, Aleksej Friedrich,
Liang-Min Xia, Stefan Lochbrunner*,
Henrik Junge, Matthias Beller*, ShaoLin
Zhou* and Shu-Ping Luo* _____
Page – Page

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