

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

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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 mononuclear iron catalysts were able to generate hydrogen up to 15 times faster than previously reported $[\text{Fe}_3(\text{CO})_{12}]$. A reductive quenching mechanism was shown to operate by fluorescence experiments.

Artificial photosynthesis 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 O_2 and H_2 .^[1] Despite tremendous effort in this area,^[2] significant challenges for its application still exist owing to low efficiencies of the light absorption materials,^[3] redox catalysts,^[4] and full-cell systems.^[5] 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 (WRCs) for photocatalytic hydrogen genera-

tion have been developed,^[6] most of which are derived from precious metals such as platinum,^[7] palladium,^[8] rhodium,^[9] and ruthenium.^[10] As a result of the high price and limited availability of these precious metals, the development of WRCs based on biorelevant or earth-abundant transition metals is highly desirable. Recently, non-noble metal alternatives, for example, cobalt^[11] and nickel^[12] complexes, have been examined as active hydrogen-generation catalysts. In addition, nature has developed an iron-based hydrogenase (with up to 9000 molecules of H_2 per second and site) for proton reduction,^[13] which makes it appealing for WRC applications.^[14]

In 2009, Beller demonstrated that simple, cheap, and readily available iron carbonyls can act as WRCs.^[15] In combination with a noble metal photosensitizer (PS), $[\text{Ir}(\text{bpy})(\text{ppy})_2]\text{PF}_6$ (bpy: 2,2'-bipyridyl; ppy: 2-phenylpyridine), high activities were achieved. This was followed by a new non-noble metal water reduction system that employed $[\text{Fe}_3(\text{CO})_{12}]$ as a WRC and a heteroleptic copper complex as PS. Both oxidative and reductive quenching pathways of the excited state of the copper(I) photosensitizer (CuPS) were confirmed in this Cu–Fe system.^[16] Herein, we envisioned that mononuclear iron tricarbonyl cyclopentadienone complexes might become an efficient substitute for $[\text{Fe}_3(\text{CO})_{12}]$. In general, Knölker's precursor complexes are stable under contact with air and water and are easily accessible from simple and cheap precursors.^[17] Importantly, Knölker's complexes can be easily produced in situ and have been successfully applied in various organic redox reactions.^[18] Owing to their uniquely powerful redox catalyst properties, they possess great potential as efficient WRCs in the presence of a heteroleptic CuPS (Scheme 1). We report herein on the use of a series of Knölker iron complexes as mimics for mononuclear 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 by employing Knölker's catalysts.

Initial investigations were performed under the same conditions as those recently applied to the Cu–Fe-based water-reduction system, which included the heteroleptic cationic copper(I) complex $[\text{Cu}(\text{Xantphos})(\text{bathocuproine})\text{PF}_6]$ as PS and triethylamine as sacrificial reductant (SR) in a tetrahydrofuran (THF)/water mixture (THF/ $\text{Et}_3\text{N}/\text{H}_2\text{O}$ = 4:3:1) (Scheme 1).^[19] The activities of a range of Knölker WRCs, according to Figure 1, were tested, and the results are summarized in Table 1. Iron complex **1a** was not active in the absence of an additional base (Table 1, entry 1). Therefore, several bases were applied to induce catalytic activity. Adding KOH as a base resulted in sig-

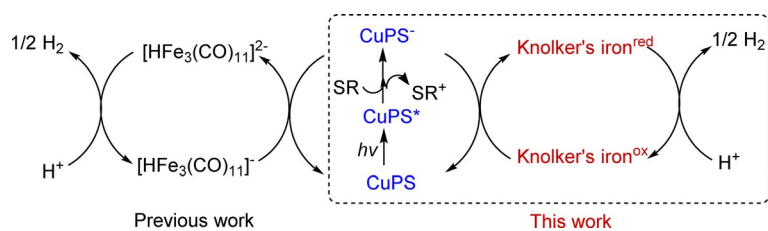
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Supporting Information (characterization of **1a–g**, experimental information on the photocatalytic reaction, and general conditions for the photophysical and electrochemical measurements) and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/cctc.201600186>.



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

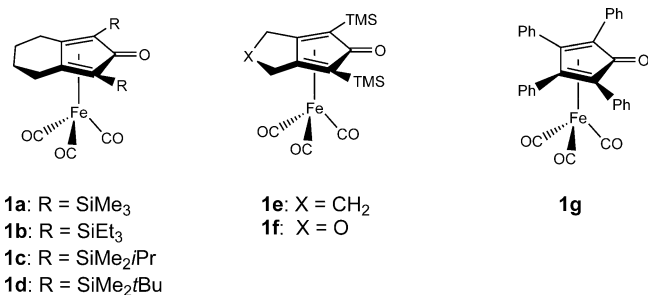


Figure 1. Iron-based Knölker catalysts **1a–g** applied to water reduction.

Table 1. Application of iron-based Knölker complexes in the photocatalytic water reduction. ^[a]					
Entry	Cat.	Base	<i>t</i> [h]	Volume H ₂ ^[b] [mL]	Fe TON ^[b, c]
1	1a	–	12	0	0
2	1a	KOH	12	17 (33)	58 (112)
3	1a	K ₃ PO ₄	8	12 (30)	41 (102)
4	1a	Bu ₄ NOH	8	19 (29)	65 (99)
5	1a	Et ₄ NOH	8	22 (35)	75 (119)
6	1b	Et ₄ NOH	9	22 (29)	75 (99)
7	1c	Et ₄ NOH	7	23 (29)	78 (99)
8	1d	Et ₄ NOH	7	13 (29)	44 (99)
9	1e	Et ₄ NOH	8	19 (28)	65 (95)
10	1f	Et ₄ NOH	8	19 (24)	65 (82)
11	1g	Et ₄ NOH	6	18 (19)	61 (65)
12	2	Et ₄ NOH	15	0	0
13 ^[d]	2	–	27	3.1 (33)	8 (90)
14 ^[d]	1a	Et ₄ NOH	7	15 (16)	123 (131)

[a] Reaction conditions: CuPS (3.5 μmol), cat. (12 μmol), base (12 μmol), THF/Et₃N/H₂O (4:3:1, 10 mL), 25 °C, Xe-light irradiation (output 1.5 W), without light filter, gas evolution quantitatively measured by gas burettes, gas analysis by 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] Values were determined after 3 h. Values at the end of the experiment are shown in brackets. [c] TON (Fe) = *n*(H₂)/*n*(Fe atom). [d] Cat.: 5 μmol.

nificant hydrogen generation of 17 mL after 3 h and a productivity (i.e., turnover number, TON) of 58 (Table 1, entry 2). Furthermore, K₃PO₄, tetrabutylammonium hydroxide (Bu₄NOH), and tetraethylammonium hydroxide (Et₄NOH) were also tested (Table 1, entries 3–5). The latter resulted in the best TON value (75) after 3 h. The influence of the ratio of the amounts of catalyst **1a** and base was investigated in more detail. In this respect, 12 μmol **1a** and 12 to 20 μmol Et₄NOH proved to be

optimal (Figure S2, Supporting Information). Next, iron complexes **1b–g** were tested under the same conditions by applying Et₄NOH as the base (Table 1, entries 6–11). These experiments resulted in almost the same activities as those obtained with **1a** except for **1d** (Table 1, entry 8), which achieved 59% of the productivity of **1a**. [Fe₃(CO)₁₂] (**2**) was completely deactivated in the presence of additional base (Table 1, entry 12), and therefore, for comparison, the reaction was repeated in the absence of Et₄NOH (Table 1, entry 13). The productivity of hydrogen generation with **2** was similar to that with **1a**. However, upon taking into account the maximum TON for each iron atom, it is clear that **1a** is superior in terms of efficiency and rate (Table 1, entry 13 vs. 5). Complex **2** provided only 3.1 mL of H₂ in 3 h in comparison to 22 mL provided by **1a**, which is a 15-fold increase in TON. Thus, we demonstrated the ability of Knölker-type iron complexes to act as efficient WRCs.

A number of control reactions were undertaken 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 is a reflection of the steady consumption of sacrificial amine (Et₃N). By adding an additional quantity of either the 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 performed with a λ = 400 nm cutoff filter and an 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 lifetime. Thus, the light source is an important component to improve the stability of Knölker's iron catalyst system.

Upon applying **2** to the reaction, the quenching of the excited state of the CuPS was previously reported to undergo a reductive quenching pathway.^[19c] We wanted to perform the corresponding experiments to establish the quenching mode of the excited state of the PS under the newly optimized conditions (Table 1, entry 5). Using **1a** as the quencher, evolution of the fluorescence ratio of the CuPS was found not to be linear (red curve, Figure 2). The data deviated from the Stern–Volmer equation, as the catalyst has non-negligible absorption at both the excitation and fluorescence wavelengths. However, if the quencher was Et₃N, the evolution of the fluorescence

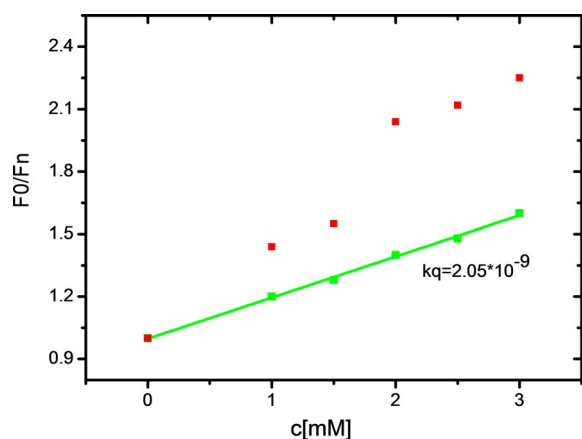


Figure 2. Stern–Volmer curves. The concentration of the CuPS was 0.35 mM in acetonitrile; quenchers: **1a** (red) and Et₃N (green).

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. Given that the concentration of Et₃N is three orders of magnitude higher than that of **1a**, it is predicted that the reductive quenching mode is dominant. This conclusion was confirmed by lifetime measurements of the excited state of the CuPS (*CuPS) in the presence of **1a** in THF and THF + Et₄NOH (Table 2). The lifetime of the *CuPS was recorded at approximately 3 μs in THF. Precatalyst **1a** did not quench the luminescence lifetime of the *CuPS, but the lifetime decreased in the presence of Et₃N to 350 ns and then to 265 ns under the reaction conditions and in presence of the catalyst.

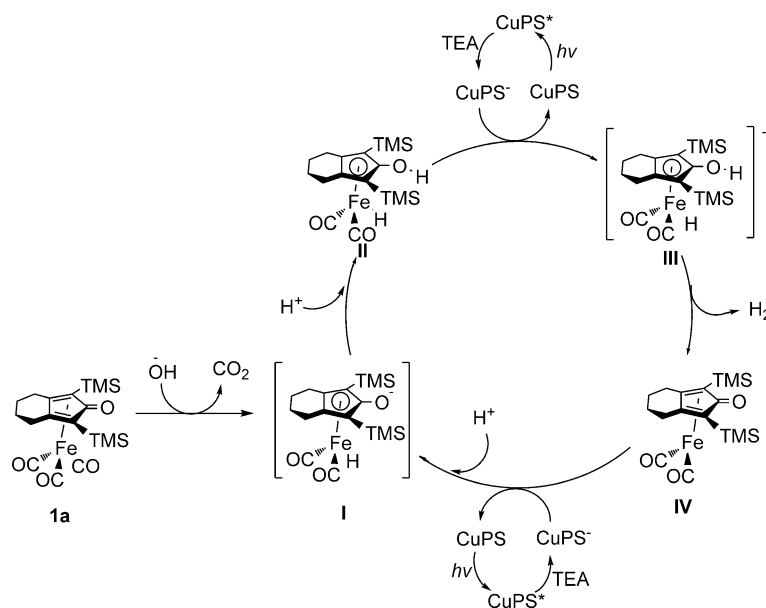
Considering our mechanistic studies and previous work in the groups of Knölker and Casy regarding reduction reactions by using Knölker's iron complexes,^[20] the following water-reduction mechanism is proposed (Scheme 2). Under basic conditions, the water gas shift reaction converts precatalyst **1a**

Table 2. Lifetime (τ) measurements of the CuPS with 1a in THF and THF + Et ₄ NOH.		
Solvent	τ [ns]	
	CuPS ^[a]	CuPS ^[a] + 1a ^[b]
THF	3200	3800
THF/Et ₃ N (5:3)	350	360
THF/Et ₄ NOH	440	660
(THF/Et ₄ NOH)/Et ₃ N (5:3)	270	< 265 > ^[c]

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

into hydride iron complex **I**. Active complex **I** shows an enhanced reduction current in cyclic voltammetry experiments (Figure S7) and can be detected by ESI-MS (Figures S12–S15). CO₂ as the byproduct is neutralized by the base (Figure S19). Upon adding water, protonation occurs to form hydride complex **II**, and the reduction current increases relative to that of complex **I**. During light irradiation, Knölker's iron WRC **III** is formed by electron transfer from CuPS[−]. This is followed by hydrogen generation through hydrolysis of the iron hydride. In the last step, 16-electron iron(0) **IV** species is reduced by another CuPS[−] again to provide hydride iron complex **I**. As a few particles were observed after finishing the reaction, the liquid phase was separated by centrifugation. In restart experiments, initiated by the addition of another aliquot of the CuPS, this liquid phase still showed significant activity (Figures S17 and S18), which thus underlines the homogeneous character of Knölker's iron complex in the water-reduction system. The particles probably arise from the photosensitizer.

In summary, we 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-



Scheme 2. Plausible mechanism.

reduction catalysts, the performance rates of which are 4–15 times faster than that of $[\text{Fe}_3(\text{CO})_{12}]$. These new mononuclear iron water reduction catalysts are cheap, readily available from commercial sources, and stable under ambient conditions, which thus render them very attractive catalysts. Further developments to increase the stability are currently underway in our laboratories.

Experimental Section

General methods

All catalytic experiments were performed under an argon atmosphere with exclusion of air. THF, Et_3N , and water were degassed and purified by standard laboratory methods prior to use. The catalysts and the copper(I) complex were synthesized according to literature procedures (see the Supporting Information). The amount of gas liberated was measured by a gas burette (see the Supporting Information). Details of the equipment and the experimental setup are 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 300 W Xe lamp.

Typical procedure for light-driven water reduction

A double-walled thermostatically controlled reaction vessel was evacuated and purged with argon. The copper photosensitizer and the iron catalyst were added as solids, and Et_4NOH was added as a liquid. The corresponding solvent mixture (THF/ $\text{Et}_3\text{N}/\text{H}_2\text{O}$) was added, and the system was taken to 25 °C before switching on the light source. The mixture was then stirred at 25 °C until no further gas evolution was 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%).

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