Angewandte
International Edition Chemie

DOI: 10.1002/anie.201106494

Photocatalysis

Hydrogen Production Coupled to Hydrocarbon Oxygenation from Photocatalytic Water Splitting**

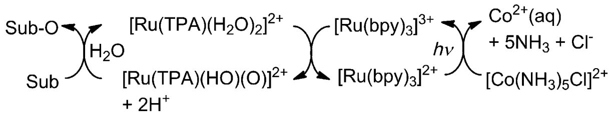
*Wangkheimayum Marjit Singh, Derek Pegram, Haifeng Duan, Diganta Kalita, Paul Simone, Gary L. Emmert, and Xuan Zhao**

Splitting of water into hydrogen and oxygen, especially with visible light, is a reaction of great challenge. H_2 generation from water has attracted much attention because of its potential use as a source of clean and renewable energy.[1] In natural photosynthesis, splitting of water to oxygen ($2H_2O \rightleftarrows O_2 + 4H^+ + 4e^-$) is driven by sunlight and carried out by the oxygen-evolving complex (OEC) in photosystem II (PSII).[1c,2]

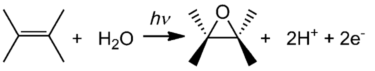
Besides water splitting, H_2 production from alternative sources such as abundant biomass has also attracted a great interest. A number of metalloenzymes such as cytochrome P450s and methane monooxygenases catalyze the oxidation of various types of hydrocarbons.[3] High-valent metal-oxo species, derived from molecular oxygen or peroxide, have been suggested as active intermediates for the oxidation of hydrocarbons.[3b,4] Recent years have seen significant progress in designing and modeling metalloproteins for highly selective and efficient oxidation of organic substrates.[5] Inspired by natural photosynthesis, oxidation of hydrocarbons with light and water has also been reported to reduce the use of hazardous chemicals and waste production.[6]

Water splitting into H_2 and O_2 involves multielectron processes for water oxidation ($4e^-$) and proton reduction ($2e^-$). There has been significant progress in developing photocatalysts for overall water splitting ($2H_2O \rightleftarrows 2H_2 + O_2$) in heterogeneous systems.[7] However, in homogeneous systems, studies of water splitting have been generally carried out separately in two half reactions: the water oxidation process using sacrificial oxidants such as Ce^{IV}, and the water reduction reaction using sacrificial reductants such as triethylamine.[8] However, for overall water splitting, sacrificial reagents should be avoided. The combination of water oxidation and proton reduction reactions in a homogeneous system remains a great challenge.

Using water as oxygen source, we and others have reported photocatalytic oxidation of organic substrates in homogeneous systems containing metal catalysts such as Ru and Mn for hydrocarbon oxidation, $[Ru(bpy)_3]^{2+}$ as photosensitizer (Ru PS; see Figure S1 in the Supporting Information), and $[Co(NH_3)_5Cl]^{2+}$ as electron acceptor.[6b,d] For example, an olefin can be oxidized to an epoxide with water as oxygen source, releasing two protons and two electrons [Eq. (1)]. As shown in Scheme 1, the electrons derived from water were eventually transferred to $[Co(NH_3)_5Cl]^{2+}$ in the photocatalytic system where $[Ru(TPA)(H_2O)_2]^{2+}$ (**1**) catalyzes the hydrocarbon oxidation.[6b] However, in artificial photosystems designed for H_2 production, protons should be the final electron acceptors [Eq. (2)].

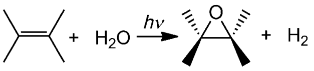


Scheme 1. Photocatalytic oxidation of hydrocarbons with water.



(1)

$$2H^+ + 2e^- \longrightarrow H_2 \quad (2)$$



(3)

In Scheme 1, if $[Co(NH_3)_5Cl]^{2+}$ is replaced with a proton reduction catalyst, it will be possible to combine the oxidation of hydrocarbons with the production of H_2 in a one-pot reaction using water as source of both oxygen and hydrogen [Eq. (3)]. As a proof of concept, we report a homogeneous multicomponent system that can photocatalytically produce H_2 by coupling the oxidation of organic substrates to the splitting of water in the absence of sacrificial reagents.

Over the past years, a number of metal complexes such as Co,[9] Ni,[10] Fe,[11] and Mo[12] have been developed for catalytic reduction of protons to hydrogen by either electrochemical or photochemical approaches.[9e,13] Beller et al. reported H_2 production catalyzed by iron carbonyls such as $Fe_3(CO)_{12}$ (**2**) in a THF/H_2O solution containing sacrificial reagent NEt_3 and photosensitizer $[Ir(ppy)_2(bpy)]^+$ (Ir PS, see Figure S1 in the Supporting Information).[14] Based on the reaction sequences in Scheme 1, our initial studies began with replacing electron acceptor $[Co(NH_3)_5Cl]^{2+}$ with **2** to test for H_2 formation. After exposing a sample containing styrene

---

[*] Dr. W. M. Singh, D. Pegram, H. Duan, Dr. D. Kalita,
Prof. Dr. P. Simone, Prof. Dr. G. L. Emmert, Prof. Dr. X. Zhao
Department of Chemistry, University of Memphis
Memphis, TN 38152 (USA)
E-mail: xzhao1@memphis.edu

[**] We acknowledge the Department of Chemistry at The University of Memphis for support. We thank Prof. Theodore J. Burkey for helpful discussions and the NSF (grant number TN EPS 1004083) for support of Haifeng Duan.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201106494.

(1 mmol), **1** (2 μmol), Ru PS (4 μmol), and **2** (8 μmol) to visible light for over 40 h, we observed very little H_2 formation. In the article by Beller and co-workers, Ir PS was used to reduce **2** for H_2 production.[14] Furthermore, it was shown that Ir PS acts as a better photocatalyst for H_2 production than Ru PS.[15] We replaced Ru PS with Ir PS and tested the H_2 formation in the presence of **2**. However, only a residual amount of H_2 was detected from analysis of the headspace gas by the GC-TCD (GC = gas chromatography, TCD = thermal conductivity detector).

Photo-induced oxidation of hydrocarbons has been achieved using Ru PS, and we tested the applicability of Ir PS for hydrocarbon oxidation.[6b] When styrene was used as a substrate, a turnover number (TON) of 28 was determined for the oxidation of styrene to benzaldehyde in a system containing **1** (1 μM), Ru PS (10 μM), and $[Co(NH_3)_5Cl]^{2+}$ (500 μM) after exposure to LED light (450 nm; LED = light-emitting diode) for 20 h. However, when Ir PS was used instead of Ru PS, we observed much less oxidation of styrene to benzaldehyde, with a TON of 7. The above-mentioned experiments suggested that Ru PS is more active than Ir PS for styrene oxidation when $[Co(NH_3)_5Cl]^{2+}$ is used as electron acceptor.

Previous studies have shown that Ru PS displays two redox potentials at 1.26 V and −1.36 V (vs. a saturated calomel electrode, SCE), assignable to $Ru^{III/II}$ and bpy/bpy$^-$, respectively. Similarly, the two redox potentials for Ir PS are at 1.25 V and −1.42 V (vs. SCE), corresponding to $Ir^{IV/III}$ and bpy/bpy$^-$, respectively.[15,16] Considering the similar redox properties of Ru PS and Ir PS, we reasoned that electron transfer between Ru PS and Ir PS should be feasible. When both photosensitizers are used, it may be possible to couple the oxidation of hydrocarbons to proton reduction. Therefore, we carried out photolysis of styrene in a THF/H_2O (9:1) solution containing **1**, Ru PS and Ir PS, and **2** as catalyst for H_2 production. As shown in Figure 1, no H_2 was detected before photolysis. After exposure to LED light (450 nm) for 3 h, a peak at 0.9 min appeared, corresponding to the formation of H_2. Residual amounts of O_2 and N_2 with retention times at 1.9 min and 3.3 min, respectively, were also observed. The peak at 0.9 min continued to increase over time and reached the maximum after 18 h of light irradiation. In the end, a TON of 77 was found for the H_2 production based on complex **1** (Table 1). Control experiments in the absence of any of the components (substrate, H_2O, **1**, Ru PS, Ir PS, **2**, or in the dark) showed no or only residual amounts of H_2 (see Figure S2 in the Supporting Information).

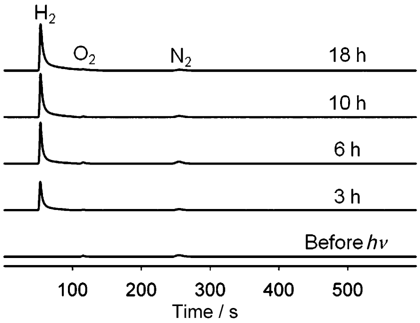


Figure 1. GC/TCD chromatogram of H_2 production over time. Conditions: Styrene (1 mmol), **1** (2 μmol), Ru PS (8 μmol), Ir PS (2 μmol), **2** (8 μmol), LED light (450 nm), 10 mL THF/H_2O (9:1), 18 h.

Table 1: Light-driven H_2 production and catalytic oxidation of hydrocarbons from water.

Substrate[a]	Product	H_2 [μmol]	TON[b]
styrene	benzaldehyde	154	77
NaSS	4-formylbenzenesulfonate	111	55
4-methylbenzyl alcohol	4-methyl benzaldehyde	56	28

[a] Conditions: Substrate (1 mmol), **1** (2 μmol), Ru PS (8 μmol), Ir PS (2 μmol), **2** (8 μmol), LED light (450 nm), 10 mL THF/H_2O (9:1), 18 h. [b] TON = $n(H_2)/n(\mathbf{1})$.

^{1}H NMR spectroscopy and GC-MS analysis of the resulting solution after photolysis confirmed the formation of benzaldehyde (see Figure S3 in the Supporting Information). As shown in Figure S4 in the Supporting Information, a molecular ion peak at 106 was observed, consistent with the formation of benzaldehyde. To confirm the source of oxygen, we carried out photocatalytic oxidation of styrene using $H_2{}^{18}O$ instead of $H_2{}^{16}O$. A molecular ion peak at 108, corresponding to the incorporation of ^{18}O into benzaldehyde, was observed with a +2 shift from the peak at 106 when $H_2{}^{16}O$ was used. This result clearly showed that water is the source of oxygen for styrene oxidation.

To determine the source of H_2 formation, we conducted the photolysis reaction using D_2O instead of H_2O. The formation of H_2 and D_2 can be distinguished by GC-TCD analysis using He as carrier gas. As shown in Figure S5 in the Supporting Information, when H_2O was used, a negative peak appeared at 0.8 min in the GC-TCD chromatogram, consistent with the formation of H_2. In contrast, a positive peak at 0.8 min was observed when D_2O was used, suggesting the formation of D_2. These results clearly showed that water is the source of hydrogen in the photolytic reaction. Therefore, our studies from both GC-MS and TCD analyses clearly demonstrated that H_2O is not only the oxygen source for olefin oxidation, but also the proton source for H_2 generation.

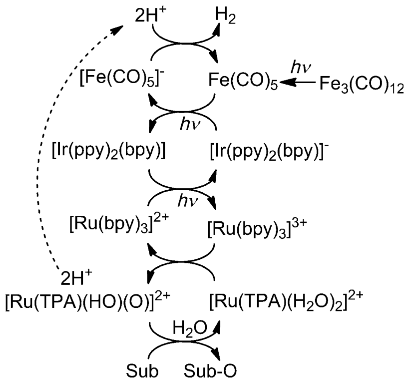
The effects of different light sources on the activity of water splitting were investigated using a visible light source and natural sunlight. Although H_2 formation was observed when a 500 W halogen lamp was used, a much longer time is needed for the reaction to be complete and a smaller turnover number (see Figure S6 in the Supporting Information) is obtained. Oxidation of styrene under ambient sunlight was also carried out. Although we observed similar conversion yields to the yields obtained with the halogen lamp, a higher amount of CO was detected from GC-TCD analysis, probably because of faster decomposition of iron carbonyl compounds under UV irradiation of sunlight. The decomposition of iron carbonyls under UV light irradiaton is well-known, and CO has been observed during photocatalytic H_2 formation by iron carbonyls.[14]

To optimize the conditions for H_2 production, the concentration of each component was varied to investigate their effects on H_2 evolution. Among the conditions listed in Table S1 in the Supporting Information, the best activity for

H_2 production was observed for entry 1, where the ratio of **1**/Ru PS/Ir/PS/**2** is 1:4:1:4. From Table S1 in the Supporting Information, the concentration of Ru PS has a greater effect on the amount of H_2 produced (entries 2 and 3), while the amout of Ir PS seems to have less effect on the amount of H_2 formation (entries 1 and 2).

We also investigated the photooxidation of sodium *p*-styrene sulfonate (NaSS) under the same conditions as that of the styrene oxidation. 4-Formylbenzenesulfonate was detected from ^{1}H NMR spectroscopy and GC-MS analysis, and a TON of 55 was observed for H_2 production (Table 1 and Figure S7 in the Supporting Information). Oxidation of 4-methyl benzylalcohol was conducted under the same conditions as described above, 4-methyl benzaldehyde was found to be the only product from GC-MS analysis with concomitant production of H_2. The amount of H_2 produced corresponds to a TON of 28 (Table 1 and Figure S8 in the Supporting Information). In the absence of water, H_2 production was also observed from GC-TCD analysis (TON = 9), suggesting that benzyl alcohol could be the source of H_2. However, in the presence of H_2O, a higher turnover number (28) for H_2 production was observed, implying water may facilitate the oxidation of alcohol and hydrogen production.

At present, the exact reaction mechanism for alkene oxidation and H_2 production by the above-described multi-component system remains to be determined. Based on the mechanisms proposed for the photocatalytic oxidation of hydrocarbons and the reduction of water by iron carbonyls and Ir PS, we propose a reaction mechanism that involves possible electron transfer from Ru PS to Ir PS as the key step for coupling hydrocarbon oxidation to hydrogen formation from photocatalytic splitting of water (Scheme 2).[6b,14] Upon light irradiation, the excited states of Ru PS (Ru^{II*}) can act as both an oxidant with a redox potential of 0.68 V ($Ru^{II*/I}$) and a reductant with a potential of −0.78 V ($Ru^{III/II*}$). The excited state of Ir PS (Ir^{III*}) has redox potentials of −0.85 V and 0.68 V (vs. SCE), assignable to $Ir^{IV/III*}$ and $Ir^{III*/II}$, respectively.[15] Beller et al. suggested that the reduced Ir PS$^-$ is responsible for reducing iron carbonyl compounds to produce H_2.[14] A comparison of the redox couples between $Ru^{III/II*}$ (−0.78 V) and $Ir^{III*/II}$ (0.68 V) indicated that there could be a 1.46 V driving force to yield the reduced Ir PS$^-$ (Ir^{II}) and the oxidized Ru PS (Ru^{III}) from electron transfer between Ru^{II*} and Ir^{III*} [Eq. (4)]. Therefore, light-induced sequential electron transfer from Ru PS to Ir PS could result in the generation of a $[Ru(bpy)_3]^{3+}$ (Scheme 2), which can oxidize **1** to produce a high-valent Ru^{IV}=O species, a possible active intermediate for the oxygenation of hydrocarbons. The resulting Ir PS$^-$ can transfer electrons to an iron carbonyl compound which catalyzes the proton reduction to H_2.



Scheme 2. Proposed mechanism for light-induced hydrocarbon oxygenation and H_2 production from water splitting.

$$Ru^{II*} + Ir^{III*} \longrightarrow Ru^{III} + Ir^{II} \qquad (\Delta E = 1.46\text{ V}, \Delta G^\circ = -141\text{ kJ mol}^{-1}) \tag{4}$$

In summary, we have reported a homogeneous multi-component system for photocatalytic oxygenation of hydrocarbons and the production of H_2. The use of two photosensitizers allows the coupling of the hydrocarbon oxygenation reaction to the H_2 production process from photocatalytic water splitting, where water is the source of both oxygen and hydrogen. Ongoing photophysical and mechanistic studies will provide detailed information about the photocatalytic cycle of alkene and alcohol oxidation, and offer guidelines towards the design of photocatalytic systems for the oxidation of water and organic substances, as well as the splitting of water to O_2 and H_2.

Experimental Section

All catalytic reactions were carried out under an Ar atmosphere. For photoinduced hydrogen evolution, each sample was prepared in a 30 mL rectangular flask with 10 mL THF/H_2O (9:1) solution containing $[Ru(bpy)_3](BPh_4)_2$ (8 μmol), $[Ru(TPA)(H_2O)_2)](BPh_4)_2$ (2 μmol), $[Ir(ppy)_2(bpy)](PF_6)$ (2 μmol), $Fe_3(CO)_{12}$ (8 μmol), and the corresponding substrate (1 mmol). The samples were sealed with a septum, degassed under vacuum, and flushed with Ar gas three times to remove any oxygen. The samples were stirred constantly at room temperature and irradiated by LED (Cree 3-Up XP-E) light at 450 nm. The amount of H_2 produced was determined using a HP 5890 series II gas chromatograph with a TCD detector (molecular sieve 5 Å column). ^{1}H NMR spectroscopy and GC-MS analysis were used to confirm and quantify the oxygenation products. Detailed procedures were provided in the Supporting Information.

Received: September 14, 2011

Keywords: hydrocarbons · hydrogen production · photocatalysis · water splitting

---

[1] a) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729–15735; b) V. Balzani, A. Credi, M. Venturi, *ChemSusChem* **2008**, *1*, 26–58; c) J. Barber, *Biochem. Soc. Trans.* **2006**, *34*, 619–631; d) O. Kruse, J. Rupprecht, J. H. Mussgnug, G. C. Dismukes, B. Hankamer, *Photochem. Photobiol. Sci.* **2005**, *4*, 957–970.
[2] a) G. Renger, *Biochim. Biophys. Acta Bioenerg.* **2001**, *1503*, 210–228; b) K. N. Ferreira, T. M. Iverson, K. Maghlaoui, J. Barber, S. Iwata, *Science* **2004**, *303*, 1831–1838; c) J. Yano, J. Kern, K.

Sauer, M. J. Latimer, Y. Pushkar, J. Biesiadka, B. Loll, W. Saenger, J. Messinger, A. Zouni, V. K. Yachandra, *Science* **2006**, *314*, 821–825; d) B. Loll, J. Kern, W. Saenger, A. Zouni, J. Biesiadka, *Nature* **2005**, *438*, 1040–1044; e) Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature* **2011**, *473*, 55–60.

[3] a) J. T. Groves, Y.-z. Han in *Cytochrome P450, Structure, Mechanism, and Biochemistry* 2nd ed. (Ed.: P. R. Ortiz de Montellano), Prenum, New York, **1995**, pp. 3–48; b) B. Meunier, S. P. de Visser, S. Shaik, *Chem. Rev.* **2004**, *104*, 3947–3980.

[4] a) J. T. Groves, Y. Watanabe, *J. Am. Chem. Soc.* **1988**, *110*, 8443–8452; b) L. Que, *Acc. Chem. Res.* **2007**, *40*, 493–500; c) W. Nam, *Acc. Chem. Res.* **2007**, *40*, 522–531; d) J. R. Carey, S. K. Ma, T. D. Pfister, D. K. Garner, H. K. Kim, J. A. Abramite, Z. Wang, Z. Guo, Y. Lu, *J. Am. Chem. Soc.* **2004**, *126*, 10812–10813.

[5] a) J. Hansen, H. M. L. Davies, *Coord. Chem. Rev.* **2008**, *252*, 545–555; b) X. Chen, K. M. Engle, D. H. Wang, J. Q. Yu, *Angew. Chem.* **2009**, *121*, 5196–5217; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115; c) K. W. Fiori, C. G. Espino, B. H. Brodsky, J. DuBois, *Tetrahedron* **2009**, *65*, 3042–3051; d) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417–424; e) M. S. Chen, M. C. White, *Science* **2007**, *318*, 783–787; f) D. Quiñonero, D. G. Musaev, K. Morokuma, *J. Mol. Struct. Theochem.* **2009**, *903*, 115–122; g) A. H. Stoll, S. B. Blakey, *J. Am. Chem. Soc.* **2010**, *132*, 2108–2109.

[6] a) M. Zhang, Q. Wang, C. Chen, L. Zang, W. Ma, J. Zhao, *Angew. Chem.* **2009**, *121*, 6197–6200; *Angew. Chem. Int. Ed.* **2009**, *48*, 6081–6084; b) D. Kalita, B. Radaram, B. Brooks, P. P. Kannam, X. Zhao, *ChemCatChem* **2011**, *3*, 571–573; c) W. Chen, F. N. Rein, R. C. Rocha, *Angew. Chem.* **2009**, *121*, 9852–9855; *Angew. Chem. Int. Ed.* **2009**, *48*, 9672–9675; d) S. Fukuzumi, T. Kishi, H. Kotani, Y.-M. Lee, W. Nam, *Nat. Chem.* **2011**, *3*, 38–41.

[7] a) A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38; b) K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, *Nature* **2006**, *440*, 295; c) A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253–278; d) K. Maeda, K. Domen, *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.

[8] a) M. Wang, Y. Na, M. Gorlov, L. C. Sun, *Dalton Trans.* **2009**, 6458–6467; b) L. L. Tinker, N. D. McDaniel, S. Bernhard, *J. Mater. Chem.* **2009**, *19*, 3328–3337; c) X. Sala, I. Romero, M. Rodriguez, L. Escriche, A. Llobet, *Angew. Chem.* **2009**, *121*, 2882–2893; *Angew. Chem. Int. Ed.* **2009**, *48*, 2842–2852.

[9] a) P. V. Bernhardt, L. A. Jones, *Inorg. Chem.* **1999**, *38*, 5086–5090; b) X. Hu, B. S. Brunschwig, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 8988–8998; c) C. Baffert, V. Artero, M. Fontecave, *Inorg. Chem.* **2007**, *46*, 1817–1824; d) J. P. Bigi, T. E. Hanna, W. H. Harman, A. Chang, C. J. Chang, *Chem. Commun.* **2010**, *46*, 958–960; e) Y. Sun, J. P. Bigi, N. A. Piro, M. L. Tang, J. R. Long, C. J. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 9212–9215; f) P.-A. Jacques, V. Artero, J. Pécaut, M. Fontecave, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 20627–20632; g) J. L. Dempsey, B. S. Brunschwig, J. R. Winkler, H. B. Gray, *Acc. Chem. Res.* **2009**, *42*, 1995–2004; h) W. R. McNamara, Z. Han, P. J. Alperin, W. W. Brennessel, P. L. Holland, R. Eisenberg, *J. Am. Chem. Soc.* **2011**, *133*, 15368–15371.

[10] a) J. P. Collin, A. Jouaiti, J. P. Sauvage, *Inorg. Chem.* **1988**, *27*, 1986–1990; b) M. Rakowski DuBois, D. L. DuBois, *Acc. Chem. Res.* **2009**, *42*, 1974–1982; c) A. Le Goff, V. Artero, B. Jousselme, P. D. Tran, N. Guillet, R. Métayé, A. Fihri, S. Palacin, M. Fontecave, *Science* **2009**, *326*, 1384–1387; d) U. J. Kilgore, J. A. S. Roberts, D. H. Pool, A. M. Appel, M. P. Stewart, M. R. DuBois, W. G. Dougherty, W. S. Kassel, R. M. Bullock, D. L. DuBois, *J. Am. Chem. Soc.* **2011**, *133*, 5861–5872; e) M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois, D. L. DuBois, *Science* **2011**, *333*, 863–866.

[11] a) G. A. N. Felton, A. K. Vannucci, J. Chen, L. T. Lockett, N. Okumura, B. J. Petro, U. I. Zakai, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Am. Chem. Soc.* **2007**, *129*, 12521–12530; b) M. Y. Darensbourg, E. J. Lyon, X. Zhao, I. P. Georgakaki, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3683–3688; c) C. Tard, X. Liu, S. K. Ibrahim, M. Bruschi, L. D. Gioia, S. C. Davies, X. Yang, L.-S. Wang, G. Sawers, C. J. Pickett, *Nature* **2005**, *433*, 610–613; d) L. Sun, B. Åkermark, S. Ott, *Coord. Chem. Rev.* **2005**, *249*, 1653–1663; e) S. Kaur-Ghumaan, L. Schwartz, R. Lomoth, M. Stein, S. Ott, *Angew. Chem.* **2010**, *122*, 8207–8211; *Angew. Chem. Int. Ed.* **2010**, *49*, 8033–8036; f) R. Mejia-Rodriguez, D. Chong, J. H. Reibenspies, M. P. Soriaga, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2004**, *126*, 12004–12014; g) F. Gloaguen, J. D. Lawrence, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2001**, *123*, 9476–9477; h) F. Wang, W.-G. Wang, X.-J. Wang, H.-Y. Wang, C.-H. Tung, L.-Z. Wu, *Angew. Chem.* **2011**, *123*, 3251–3255; *Angew. Chem. Int. Ed.* **2011**, *50*, 3193–3197.

[12] a) A. M. Appel, D. L. DuBois, M. R. DuBois, *J. Am. Chem. Soc.* **2005**, *127*, 12717–12726; b) H. I. Karunadasa, C. J. Chang, J. R. Long, *Nature* **2010**, *464*, 1329–1333.

[13] a) H. Ozawa, M. Haga, K. Sakai, *J. Am. Chem. Soc.* **2006**, *128*, 4926–4927; b) T. Lazarides, T. McCormick, P. Du, G. Luo, B. Lindley, R. Eisenberg, *J. Am. Chem. Soc.* **2009**, *131*, 9192–9194; c) P. Zhang, M. Wang, J. Dong, X. Li, F. Wang, L. Wu, L. Sun, *J. Phys. Chem. C* **2010**, *114*, 15868–15874; d) A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, *Angew. Chem.* **2008**, *120*, 574–577; *Angew. Chem. Int. Ed.* **2008**, *47*, 564–567; e) D. Streich, Y. Astuti, M. Orlandi, L. Schwartz, R. Lomoth, L. Hammarström, S. Ott, *Chem. Eur. J.* **2010**, *16*, 60–63; f) J. L. Dempsey, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2010**, *132*, 1060–1065; g) T. M. McCormick, B. D. Calitree, A. Orchard, N. D. Kraut, F. V. Bright, M. R. Detty, R. Eisenberg, *J. Am. Chem. Soc.* **2010**, *132*, 15480–15483; h) B. Probst, A. Rodenberg, M. Guttentag, P. Hamm, R. Alberto, *Inorg. Chem.* **2010**, *49*, 6453–6460.

[14] F. Gärtner, B. Sundararaju, A.-E. Surkus, A. Boddien, B. Loges, H. Junge, P. H. Dixneuf, M. Beller, *Angew. Chem.* **2009**, *121*, 10147–10150; *Angew. Chem. Int. Ed.* **2009**, *48*, 9962–9965.

[15] J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502–7510.

[16] C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, J. K. Nagle, *J. Am. Chem. Soc.* **1979**, *101*, 4815–4824.