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VIP **Water Splitting**

Photoassisted Ti–O Activation in a Decamethyltitanocene Dihydroxido Complex: Insights into the Elemental Steps of Water Splitting**

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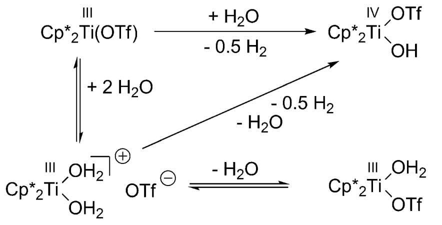
Dedicated to Professor Matthias Beller on the occasion of his 50th birthday

One of the major challenges for mankind concerns power supply. Renewable forms of energy are being investigated intensively as an alternative to the fossil resources commonly used nowadays.[1] As all types of such renewable energies (except geothermal and tidal power) originate in the solar radiation, direct utilization of this ubiquitous sustainable energy source appears to be most reasonable. Apart from photovoltaic electricity production, for example, by Grätzel cells,[2] the conversion of sunlight into chemical energy is a very promising research topic.

After the discovery of the Honda–Fujishima effect, which describes the photoassisted generation of dihydrogen and dioxygen from water using a TiO_2/Pt electrode array,[3] scientists have investigated dihydrogen and dioxygen evolution independently as well as in combined overall water splitting systems.[4] To obtain insights into this reaction, numerous homogeneous systems have been developed;[5,6] however, an understanding of the processes at the molecular level is still very difficult. This motivated us to study the reactions of well-defined early transition-metal complexes, especially titanocenes, with water as well as their behavior upon irradiation with light on the molecular level.

In this context, Milstein and co-workers have described a homogeneous process that leads to the stoichiometric liberation of dihydrogen and dioxygen in two consecutive thermally and light-driven steps that are mediated by mononuclear, well-defined ruthenium pincer-type complexes.[7] Moreover, very recently, Li and Yoshizawa theoretically studied the dihydrogen generation by reductive cleavage of water and α-H abstraction on a molybdenum complex, thus demonstrating that these reaction motifs are also applicable for early transition-metal complexes.[8]

We have investigated the reaction of the low-valent decamethyltitanocene alkyne complex $[Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) with water to give the corresponding dihydroxido complex $[Cp^*_2Ti(OH)_2]$ (**1**) and dihydrogen.[9] More recently, we have demonstrated that the decamethyltitanocene(III) species $[Cp^*_2TiOTf]$ (OTf = trifluoromethylsulfonate) reacts with water to give the titanium(IV) complex $[Cp^*_2Ti(OH)OTf]$ and dihydrogen in a redox reaction.[10] Furthermore, we have shown that the oxidation of the titanocene center proceeds stepwise by dissociation of the OTf group and coordination of two molecules of water, most likely followed by oxidation of the titanium(III) species and dissociation of one equivalent of water (Scheme 1). Of note, this reaction is thermally driven and also takes place in the complete absence of light. This reaction sequence can serve as a model for the first half-reaction of overall water splitting, that is, dihydrogen evolution.



Scheme 1. H_2 evolution by the reaction of a decamethyltitanocene(III) complex and water.

To extend our studies to the second half-reaction, namely water oxidation to dioxygen, we investigated the photoassisted degradation of the known decamethyltitanocene complex **1**. Bearing in mind that generation of dioxygen is known to take place at the TiO_2 site,[3] this approach appeared to be promising. The photoassisted reduction of titanium(IV) species is known in principle and was reported before by Robertson, Sadler, and co-workers for titanium(III/IV) citrate complexes.[11]

Irradiation of a solution of complex **1** in *n*-hexane at room temperature for 18 h results in a color change of the solution from yellow to green and formation of a yellow precipitate. Isolation of the solids and recrystallisation from THF yielded a yellow crystalline material, which was found to be a mixture of two tetranuclear μ-oxo-bridged titanium complexes: the previously unknown compound $[(Cp^*Ti)_4(OH)_2(\mu\text{-}O)_5]$ (**2**)

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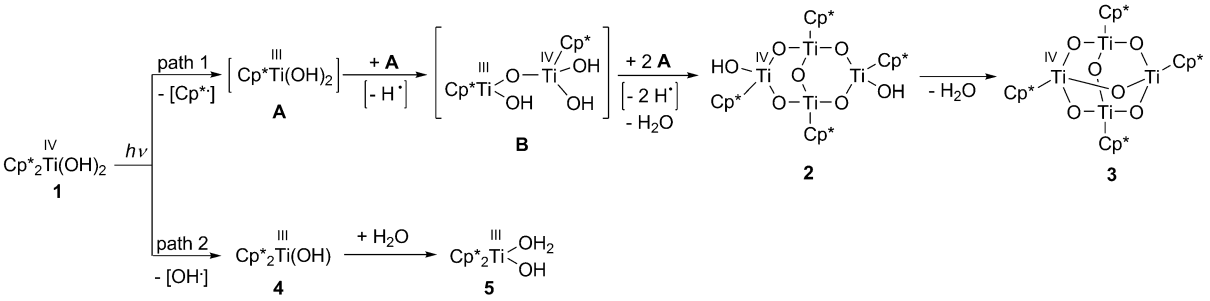

Scheme 2. Competing reaction pathways 1 and 2 during irradiation of complex **1**. Formal oxidation states for the complexes are given. Only the formal oxidation state of one Ti center is given in complexes **2** and **3** for clarity.

and the known species $[(\mathrm{Cp^*Ti})_4(\mu\text{-O})_6]$ (**3**), which was described before by Day and Klemperer (Scheme 2).[12]

The presence of complex **3** was confirmed by ^{1}H NMR ([D$_6$]benzene, $\delta = 2.08$ ppm) and mass spectroscopic analysis (M^+ at m/z 829); furthermore, X-ray analysis established the constitution of this species unequivocally. Interestingly, in the formation of both isolated complexes, one of the Cp* ligands was cleaved off from the decamethyltitanocene starting material **1**.

Such light-induced eliminations of cyclopentadienyl ligands are known in principle and were described by Vitz and Brubaker, for example.[13] It should be noted that even on exposure of a solution of complex **1** to daylight for several weeks, formation of these tetranuclear complexes readily takes place.

In the course of the irradiation of **1** in *n*-hexane, the tetranuclear complex **2** was formed and crystals suitable for an X-ray analysis were obtained from the reaction solution (Figure 1).[14] All four titanium centers display a slightly distorted tetrahedral coordination geometry, with each metal atom bearing a Cp* ligand. Two of the titanium atoms are connected to a terminal OH group and two μ-bridging oxygen atoms, whereas the other two are bound to three μ-bridging oxygen atoms. The mean Ti–O distance in **2** is 1.834 Å, which is in good agreement with the average value found before in complex **3** (1.837 Å).[12] In fact, all of the other characteristic distances and angles are in the same range and match well with values reported for other organotitanoxanes.[15] In the ^{1}H NMR spectrum ([D$_6$]benzene), characteristic signals are present at 5.21 ppm and at 2.07 and 2.05 ppm, corresponding to the OH and Cp* groups, respectively.

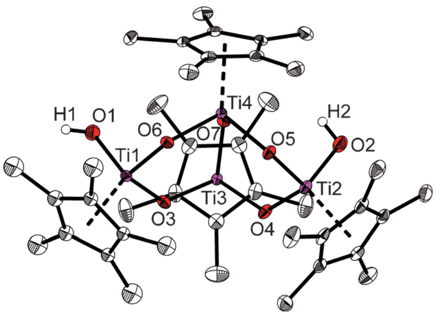

Figure 1. Molecular structure of complex **2**. Ellipsoids are set to 30% probability; hydrogen atoms (except H1 and H2) are omitted for clarity.

It is easy to understand that **2** should be an intermediate for the formation of **3**, as condensation of both terminal OH groups yields the fully condensed, sixfold μ-oxo-bridged species **3**. However, the formation of these complexes from complex **1** should follow a radical pathway, implying dissociation of a Cp*• radical with the elusive species $[\mathrm{Cp^*Ti(OH)_2}]$ (**A**) as the intermediate. The latter could then be coupled stepwise, accompanied by elimination of H• radicals, to give the Ti$^{\mathrm{IV}}$ complexes **2** and **3** (Scheme 2). This assumption is corroborated by the observation of dihydrogen formation (gas chromatography and ^{1}H NMR ([D$_6$]benzene), $\delta = 4.47$ ppm) as well as by detection of Cp*• radicals by EPR spectroscopy (see below).

A deeper insight into the formation mechanism of complexes **2** and **3** can be obtained from in situ EPR studies (see also the Supporting Information). This technique has proved to be very useful for the spectroscopic control of reactions involving organometallic radical species;[16] for example, a detailed study of the HAT (hydrogen atom transfer) reaction involving $[\mathrm{Cp_2TiCl}]$ and water was published very recently by Gansäuer et al.[17] Upon irradiation of the Ti$^{\mathrm{IV}}$ complex **1**, two Ti$^{\mathrm{III}}$ signals are immediately detected (Figure 2). Based on spectrum simulations (Supporting Information, Figure S2),[18] the signal at $g = 1.9773$ with superhyperfine structure (shfs) from coupling of the single Ti$^{\mathrm{III}}$ electron to two protons of OH groups ($2I = \frac{1}{2}$, $A_{\mathrm{H}} = 2.1$ G) is assigned to $[\mathrm{Cp^*Ti(OH)_2}]$ (**A**), which is formed from complex

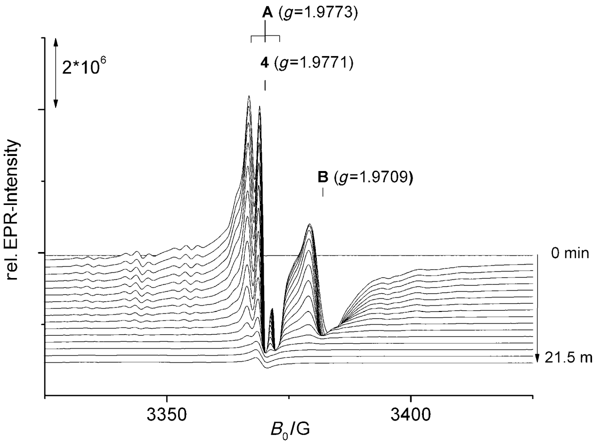

Figure 2. EPR spectra of the irradiation of complex **1** in *n*-hexane.

1 by dissociation of a Cp*• radical (Scheme 2). The weak signals in the low- and high-field range are due to hyperfine structure (hfs) coupling to the nuclear spin of the isotopes ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$; Supporting Information, Figure S2). The second Ti^{III} signal at $g = 1.9709$ (Figure 2; Supporting Information, Figure S2) is tentatively assigned to the degradation product **B** from the degradation of **A** (Scheme 2). A third Ti^{III} signal at $g = 1.9771$, superimposed on the hfs signal at 1.9773, has been discerned by spectra simulation (Supporting Information, Figure S3). Based on literature data, we assign this signal to [Cp*$_2$Ti(OH)] (**4**; Scheme 2).[19] Cp*• radicals are indicated by a weak shfs multiplet ($g = 2.0034$, $15\,A_H = 6.2$ G; Supporting Information, Figure S3).[20] Moreover, recombination of Cp*• and H• radicals gave pentamethylcyclopentadiene, which was detected by ^{1}H NMR spectroscopy (Supporting Information, Figure S1).[21]

While the signal of complex **4** is rather stable, declining only at the end of the experiment, the signals of compounds **A** and **B** vanish almost completely during the first 20 minutes (Supporting Information, Figure S4), which is due to conversion via the intermediate **2** to complex **3**. We suppose that water liberated during irradiation of **1** reacts with compound **4**, as can be assumed from the decay of the EPR signal at extended reaction time. The feasibility of such an oxidation reaction was demonstrated by us before for the case of a triflate-substituted titanocene(III) complex.[10]

Indeed, mixed crystals of complex **4**[19] containing its water adduct [Cp*$_2$Ti(H$_2$O)OH] (**5**) as minor product (30%) could also be isolated from a concentrated reaction solution in *n*-hexane (Supporting Information, Figure S5). Therefore, we can conclude that upon irradiation of complex **1**, two independent and competing reaction pathways (Scheme 2) take place:

- Pathway 1: Photoassisted dissociation of a Cp*• radical from **1** generates the elusive Ti^{III} species **A**, which recombines stepwise to give the tetranuclear Ti^{IV} complexes **2** and **3**.
- Pathway 2: Photoassisted dissociation of an OH• radical from **1** leads to the Ti^{III} complex **4**, which is stable under reaction conditions, until enough water is liberated by pathway 1 that converts **4** into **5**.

Unfortunately, the OH• radicals do not recombine to give hydrogen peroxide, which can be regarded as an source for dioxygen.[7] Instead, fast reaction with intermediate Cp*• radicals leads to pentamethylcyclopentadienol, C$_5$Me$_5$OH. The presence of this species was confirmed by mass spectroscopic analysis of the reaction mixture (M^+ at m/z 152).[22] From these observations, it could be assumed that bridging of the Cp* ligands at the metal center could prevent the dissociation in pathway **1**, which is unfavorable regarding the release of hydrogen peroxide from complex **1**.

Homolytic Ti–O bond cleavages are very rare, although predicted to be possible.[23] This rarity is presumably due to the high metal–oxygen bond energies[24] and the elusive nature of the formed oxygen radicals. To the best of our knowledge, only one example has been described: Waymouth and Huang reported thermally induced homolysis of a Ti–O bond in a titanocene(IV)-TEMPO complex (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) to give the free TEMPO radical and the corresponding titanocene(III) chloride.[25] In this case, the high stability of the dissociated TEMPO radical was assumed to be one of the driving forces for the homolytic bond cleavage.

To close the catalytic cycle and generate dihydrogen along with oxidation of the titanocene(III) center, reaction of complex **4** with water to form complex **1** in the absence of light would be necessary. However, contrary to the results from the reaction of triflate-substituted decamethyltitanocene(III) complexes with water,[10] in this case the reactivity is more diverse and no well-defined product could be isolated. Recent results imply that titanocene(III) species of the type [Cp'$_2$Ti(H$_2$O)L] (L = OH (**5**), Cl) are not responsible for the generation of H• radicals in HAT reactions.[17] Instead, it is more likely that formation of the latter takes place from cationic fragments [Cp'$_2$Ti(H$_2$O)$_2$]$^+$.

In summary, we have shown that irradiation of the decamethyltitanocene dihydroxido complex **1** results in the formation of several well-defined mono- and tetranuclear Ti^{III} and Ti^{IV} complexes. The overall reaction most likely takes place via two different reaction pathways, namely by Ti–O bond activation and Cp*• elimination. Despite the fact that we were not able to observe hydrogen peroxide formation, the reaction process described herein can be regarded as a model for the second half-reaction of overall water splitting.

Experimental Section

All operations were carried out under an argon atmosphere using standard Schlenk techniques or a glovebox. Nonhalogenated solvents (including [D$_6$]benzene) were freshly distilled from sodium/benzophenone prior to use and stored under argon. Complex **1** was synthesized according to a published procedure.[9] The following spectrometers were used: Mass spectra: MAT 95-XP; NMR spectra: Bruker AV 300. Chemical shifts (^{1}H, ^{13}C) are given in ppm relative to SiMe$_4$ and are referenced to signals of the solvent used: [D$_6$]benzene ($\delta_H = 7.16$, $\delta_C = 128.0$). In situ X-band EPR spectra were recorded with a Bruker EMX CW-micro spectrometer using an ER 4119HS-WI high-sensitivity optical resonator with a grid in the front side using the following parameters: microwave power 6.64 mW, modulation frequency 100 kHz, modulation amplitude 1 G. g values have been calculated with respect to the standard DPPH ($g = 2.0036$). Gas chromatography: Agilent Technologies 7890A, column: 60/80 Carboxen 1000 (Supelco), Detection: TCD. Elemental analyses: Leco CHNS-932 elemental analyzer. Photochemical experiments were carried out using a Xe arc lamp (LOT Oriel, LSB530, $P = 300$ W).[26]

Irradiation of complex **1** on a preparative scale: In a temperature-controlled double-walled reaction vessel, a solution of complex **1** (0.360 g, 1.02 mmol) was dissolved in *n*-hexane (20 mL) and kept at 25 °C. The yellow solution was placed in front of a Xe arc lamp, stirred and irradiated for 18 h. The color of the solution changed from yellow to dark green, and a yellow precipitate formed. The solution was filtered into a Schlenk tube and all volatiles were removed under vacuum to give a dark purple solid mixture of complexes **4** and **5** (0.170 g, ca. 0.51 mmol). Mixed crystals of complexes **4** and **5** were obtained from a reaction solution (*n*-hexane) and analyzed by X-ray crystallography. The yellow residue was washed with cold *n*-hexane, dried in vacuum, and analyzed by NMR spectroscopy and mass spectrometry. It was found to be a mixture of compounds **2** and **3** (varying ratios of **2** and **3**; 0.078 g); for this reason, no exact elemental analysis of **2** could be obtained. Crystals of **2** and **3** suitable for an X-ray analysis were obtained from a saturated reaction solution (*n*-hexane) at 25 °C and by recrystallization from THF, respectively.

Complex **2**: ^{1}H NMR ([D$_6$]benzene, 300 MHz, 297 K): $\delta = 2.05$ (s, 30 H, Cp*), 2.07 (s, 30 H, Cp*), 5.21 ppm (s, 2 H, OH). ^{13}C NMR ([D$_6$]benzene, 75 MHz, 297 K): $\delta = 11.7$ (C_5Me_5), 122.1 (C_5Me_5), 122.4 ppm (C_5Me_5). MS (CI, isobutane): *m/z* 829 $[M-H_2O]^+$. **3**: ^{1}H NMR ([D$_6$]benzene, 300 MHz, 297 K): $\delta = 2.08$ (s, Cp*). ^{13}C NMR ([D$_6$]benzene, 75 MHz, 297 K): $\delta = 11.5$ (C_5Me_5), 121.6 ppm (C_5Me_5). MS (CI, isobutane): *m/z* 829 $[M]^+$. **4**: MS (CI, isobutane): $m/z = 335$ $[M]^+$. **5**: MS (CI, isobutane): *m/z* 353 $[M]^+$.

Irradiation of complex **1** as an EPR experiment: A solution of **1** in *n*-hexane ($c = 1.0$ mg mL^{-1}, 0.10 mL) was filled into a J. Young EPR tube in a glove box, introduced into the EPR spectrometer and the sample was irradiated with a LOT Oriel 300 W Xe lamp. Spectra were recorded at given reaction/irradiation times.

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[1] M. I. Hoffert, K. Caldeira, A. K. Jain, E. F. Haites, L. D. D. Harvey, S. D. Potter, M. E. Schlesinger, S. H. Schneider, R. G. Watts, T. M. L. Wigley, D. J. Wuebbles, *Nature* **1998**, *395*, 881–884.

[2] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737–740.

[3] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38.

[4] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253–278.

[5] Selected reviews on water reduction: a) A. J. Esswein, D. Nocera, *Chem. Rev.* **2007**, *107*, 4022–4047; b) L. L. Tinker, N. D. McDaniel, S. Bernhard, *J. Mater. Chem.* **2009**, *19*, 3328–3337.

[6] Selected reviews on water oxidation: a) C. W. Cady, R. H. Crabtree, G. W. Brudvig, *Coord. Chem. Rev.* **2008**, *252*, 444–455; b) H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, *ChemCatChem* **2010**, *2*, 724–761.

[7] S. W. Kohl, L. Weiner, L. Schwartsburd, L. Konstaninovski, L. J. W. Shimon, Y. Ben-David, M. A. Iron, D. Milstein, *Science* **2009**, *324*, 74–77.

[8] J. Li, K. Yoshizawa, *Angew. Chem.* **2011**, *123*, 12178–12181; *Angew. Chem. Int. Ed.* **2011**, *50*, 11972–11975.

[9] P.-M. Pellny, V. V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, *Z. Anorg. Allg. Chem.* **1999**, *625*, 910–918.

[10] M. Kessler, S. Hansen, D. Hollmann, M. Klahn, T. Beweries, A. Spannenberg, A. Brückner, U. Rosenthal, *Eur. J. Inorg. Chem.* **2011**, 627–631.

[11] J. Paradies, J. Crudass, F. MacKay, L. J. Yellowlees, J. Montgomery, S. Parsons, I. Oswald, N. Robertson, P. J. Sadler, *J. Inorg. Biochem.* **2006**, *100*, 1260–1264.

[12] L. M. Babcock, V. W. Day, W. G. Klemperer, *J. Chem. Soc. Chem. Commun.* **1987**, 858–859.

[13] E. Vitz, C. H. Brubaker, Jr., *J. Organomet. Chem.* **1974**, *82*, C16–C18.

[14] CCDC 867777 (**2**) and 867778 (**4**/**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] Examples for titanoxanes: a) S. Garcia Blanco, M. P. Gomez Sal, S. Martinez Carreras, M. Mena, P. Royo, R. Serrano, *J. Chem. Soc. Chem. Commun.* **1986**, 1572–1573; b) O. Buitrago, M. E. G. Mosquera, G. Jimenez, T. Cuenca, *Inorg. Chem.* **2008**, *47*, 3940–3942.

[16] D. Hollmann, F. Gärtner, R. Ludwig, E. Barsch, H. Junge, M. Blug, S. Hoch, M. Beller, A. Brückner, *Angew. Chem.* **2011**, *123*, 10429–10433; *Angew. Chem. Int. Ed.* **2011**, *50*, 10246–10250.

[17] A. Gansäuer, M. Behlendorf, A. Cangönül, C. Kube, J. M. Cuerva, J. Friedrich, M. van Gastel, *Angew. Chem. Int. Ed.* **2012**, *51*, 3266–3270.

[18] EPRSim32: T. Spałek, P. Pietrzyk, Z. Sojka, *J. Chem. Inf. Model.* **2005**, *45*, 18–29; Subroutine diagonal + PT: F. E. Mabbs, D. Collison, *Mol. Phys. Rep.* **1999**, *26*, 39–59.

[19] M. Horáček, R. Gyepes, J. Kubišta, K. Mach, *Inorg. Chem. Commun.* **2004**, *7*, 155–159.

[20] J. Lusztyk, A. G. Davies, *J. Chem. Soc. Chem. Commun.* **1980**, 554–555.

[21] U. Burger, A. Delay, F. Mazenod, *Helv. Chim. Acta* **1974**, *57*, 2106–2111.

[22] J. B. Macaulay, A. G. Fallis, *J. Am. Chem. Soc.* **1990**, *112*, 1136–1144.

[23] A. Gansäuer, B. Rinker, M. Pierobon, S. Grimme, M. Gerenkamp, C. Mück-Lichtenfeld, *Angew. Chem.* **2003**, *115*, 3815–3818; *Angew. Chem. Int. Ed.* **2003**, *42*, 3687–3690.

[24] Dias and co-workers determined Ti–O bond enthalpies in titanocene(IV) complexes to be in the range from $340 \leq \Delta H^\circ \leq 461$ kJ mol^{-1}: M. J. Calhorda, M. A. A. F. de C. T. Carrondo, A. R. Dias, A. M. T. S. Domingos, J. A. M. Simoes, C. Teixeira, *Organometallics* **1986**, *5*, 660–667.

[25] a) K.-W. Huang, R. M. Waymouth, *J. Am. Chem. Soc.* **2002**, *124*, 8200–8201; b) K.-W. Huang, J. H. Han, A. P. Cole, C. B. Musgrave, R. M. Waymouth, *J. Am. Chem. Soc.* **2005**, *127*, 3807–3816; c) K.-W. Huang, J. H. Han, C. B. Musgrave, R. M. Waymouth, *Organometallics* **2006**, *25*, 3317–3323; d) S. DeBeer George, K.-W. Huang, R. M. Waymouth, E. I. Solomon, *Inorg. Chem.* **2006**, *45*, 4468–4477.

[26] For specifications of the light source (LOT-Oriel-300-W-Xe-lamp, LSB530), please see: http://www.lot-oriel.com.