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# Heterogenized water oxidation catalysts prepared by immobilizing Klaüi-type organometallic precursors

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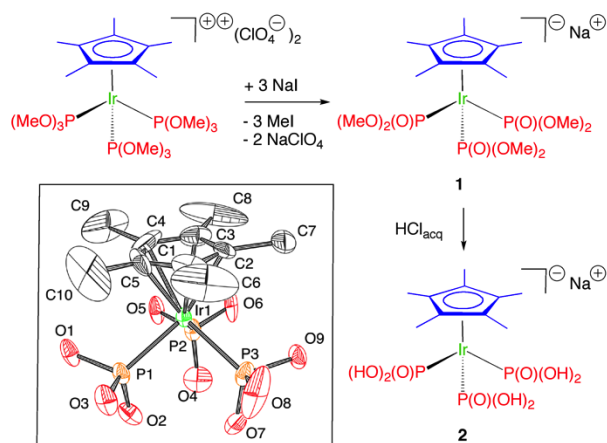
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**An efficient and stable heterogenized water oxidation catalyst (2\_TiO<sub>2</sub>) has been synthesized by immobilizing a novel organo-iridium Klaüi-type precursor onto rutile-TiO<sub>2</sub>. Iridium homogeneously distributes at the molecular and atomic/small cluster levels in 2\_TiO<sub>2</sub> and 2'\_TiO<sub>2</sub> (solid catalyst after a catalytic run), respectively, as indicated by STEM-HAADF studies. 2\_TiO<sub>2</sub> exhibits TOF values up to 49.5 min<sup>-1</sup> in water oxidation to O<sub>2</sub> driven by NaIO<sub>4</sub>, at pH close to the neutrality, and a TON limited only by the amount of NaIO<sub>4</sub> used. 2\_TiO<sub>2</sub> maintains its performances even when contacted for 24 h with water solutions at both pH 14 (by KOH) and pH 1 (by HNO<sub>3</sub>). NMR studies indicate that activation of 2\_TiO<sub>2</sub> likely occurs through the oxidative dissociation of PO<sub>4</sub><sup>3-</sup>.**

The development of an efficient catalytic system for the oxidation of water,<sup>[1-2]</sup> aimed at generating electrons and protons<sup>[3]</sup> for the photosynthesis of renewable fuels,<sup>[4]</sup> is one of the most difficult challenges that the scientific community is facing today. Molecular<sup>[1]</sup> and material<sup>[2]</sup> water oxidation catalysts (WOCs) with remarkable performances have been reported. Furthermore, it has been recently shown that anchoring a properly tailored homogeneous catalyst onto solid supports, thus obtaining heterogenized WOCs, is a promising strategy to combine the best of two worlds;<sup>[5-8]</sup> this allows to finely modulating electron density and geometry of WOCs, whereas grafting the latter on solid supports leads to enhanced stability and facilitates catalyst recovering.<sup>[5]</sup> At the same time, heterogenized WOCs allow the exploitation of metal to be minimized due to the elevated percentage of active centers, in principle, not so different than that in homogeneous catalysis.<sup>[5]</sup> Klaüi-type compounds (KTCs) [(C<sub>5</sub>R<sub>5</sub>)M{P(O)R'R''}<sub>3</sub>]<sup>-</sup> (R = H, Me; M = Co, Rh; R' and R'' = alkyl, aryl, or O-alkyl)<sup>[9]</sup> attracted our attention as precursors for fabricating heterogenized WOCs because their hydrolysis might generate three -P(O)(OH)<sub>2</sub> moieties, particularly suitable for immobilizing them onto properly selected functional materials. Generally speaking, KTCs have been widely used as monoanionic terdentate ligands to stabilize coordination complexes and organometallics of almost all metals of the periodic table.<sup>[10]</sup> The derived compounds have found application in several fields, including homogeneous catalysis, lithium selective transportation across membranes<sup>[11]</sup> and extraction of alkali metal ions, magnesium and calcium ions.<sup>[12]</sup> It has also been attempted to anchor KTCs onto solid supports with the main aim of generating novel exchange materials and heterogenized catalysts.<sup>[13]</sup> In all cases, KTCs have been used as ligands and no investigation has been carried out to explore the possible catalytic activity of the M-metal center. This could be related to the fact that, being 18-electrons saturated compounds, they are supposed to have little propensity to

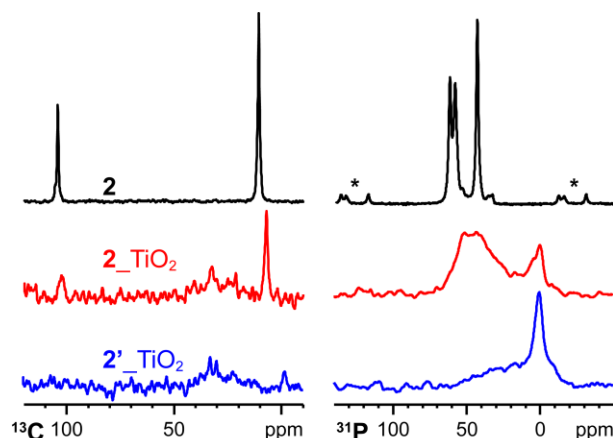
coordinate and activate a substrate. Nevertheless, we thought that such a possible drawback could be not so crucial in WO because a coordinative position might be generated by the oxidative elimination of meta phosphoric acid  $P(O)_2(OH)$  (see below) or by the oxidative transformation of the  $-C_5R_5$  ligand.<sup>[14]</sup>



**Scheme 1.** Synthesis and an ORTEP view of complex **2**. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Ir–P1 = 2.277, Ir–P2 = 2.276, Ir–P3 = 2.267, Ir–Cp\* = 1.935, P1–O1 = 1.564, P1–O2 = 1.581, P1–O3 = 1.564; P1–Ir–P2 = 74.88, P2–Ir–P3 = 90.72, P3–Ir–P1 = 93.76, Cp\*–Ir–P1 = 122.89, Cp\*–Ir–P2 = 123.84, Cp\*–Ir–P3 = 125.34. Cp\* is the centroid of the C1, C2, C3, C4 and C5 atoms.

Herein we report the synthesis and characterization of a novel KTC  $[Cp^*Ir\{P(O)(OH)_2\}_3]Na$  (**2**) and show that it is a competent WOC and, more importantly, a particularly suitable precursor to be anchored onto  $TiO_2$  providing a heterogenized WOC, which exhibits remarkable activity and robustness. Complex **1** was synthesized according to the literature,<sup>[15]</sup> reacting  $[Cp^*IrCl(\mu-Cl)]_2$  with  $P(OMe)_3$  in the presence of  $AgClO_4$  followed by the oxidative transformation of the three Ir– $P(OMe)_3$  moieties into Ir– $P(O)(OMe)_2$  by the Michaelis-Arbusov type reaction (Scheme 1).<sup>[16]</sup> **2** was obtained by the hydrolysis of **1** with 3M HCl (Scheme 1, SI) as a pale yellow solid that changes its color when scratched with a spatula, becoming red and, successively, dark brown. Interestingly, once dissolved in water, acetone, and other solvents, it provides yellow solutions that give-back a pale yellow powder once the solvent is removed. The latter undergoes the same change of color when manipulated with a spatula. This reversible behavior is typical of mechanochromic materials.<sup>[17]</sup> The solid structure of **2** was determined by X-Ray single crystal studies. The intramolecular structure (Scheme 1) does not reveal any particular feature with the exception of a rather long Ir–Cp\* distance (1.935 Å). This indicates that the three  $P(O)(OH)_2^-$  ligands provide high electron density at the metal center making the Cp\* coordination weaker than usual. Consistently, the C–Me quaternary carbons resonate at rather high chemical shift (101.9 ppm) in the  $^{13}C$  NMR spectrum.<sup>[18]</sup> The intermolecular structure exhibits an alternation of hydrophobic and hydrophilic layers constituted by Cp\* and Ir– $P(O)(OH)_2$  moieties, respectively, of different molecular units (SI). **2** was heterogenized by contacting ca. 5 ml of a water solution ( $3\text{--}4 \times 10^{-3}$  M) with dispersed rutile- $TiO_2$  (1 g) at room temperature for 24h, following the course of heterogenization by monitoring the intensity decrease of the  $^{31}P$  NMR resonance of **2**. The resulting **2**– $TiO_2$  material was washed with water, a 0.1 M  $HNO_3$  solution, acetonitrile and dichloromethane, before drying it under vacuum. The loading of iridium, as evaluated by ICP-OES analysis, was 8.54  $\mu M/g$ . **2**– $TiO_2$  was structurally characterized by solid-state NMR spectroscopy and STEM-HAADF (scanning transmission electron microscopy - high angle annular dark field) (SI). Figure 1 shows a comparison between the  $^{31}P$  and  $^{13}C$  CP MAS NMR spectra of precursor **2**, **2**– $TiO_2$  and a sample recovered after a catalytic run (**2'**– $TiO_2$ ). Consistently with the literature, heterogenization of **2** onto  $TiO_2$  causes a shift to lower frequencies of carbon and phosphorous resonances.<sup>[19]</sup> Furthermore, a remarkable broadening of  $^{31}P$  resonance is observed likely due to the different binding modalities of Ir– $P(O)(OH)_2$  moieties and typologies of  $TiO_2$  superficial sites. A sharper resonance is present at -0.8 ppm reasonably due to the oxidative detachment of a phosphate group that binds in a monodentate fashion to  $TiO_2$ .<sup>[20]</sup> Such a resonance is present in higher percentage in **2'**– $TiO_2$ , whereas the intensity of the broader resonances is substantially reduced. Also  $^{13}C$  NMR resonances due to Cp\* have a dramatic lower

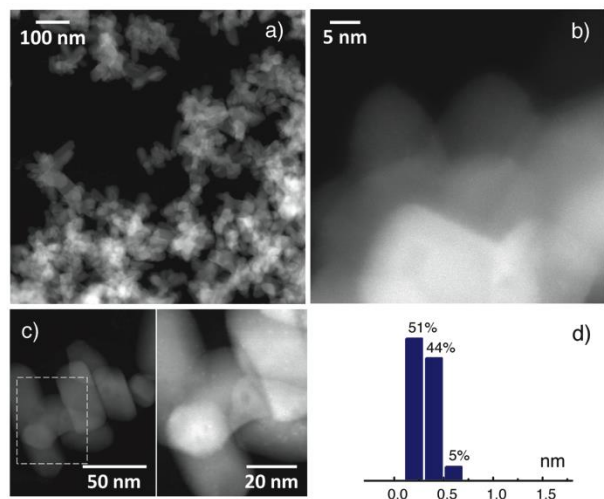
intensity in the spectrum of **2'**\_TiO<sub>2</sub> compared with that of **2**\_TiO<sub>2</sub>. The reasons of these observations are discussed below after having reported the catalytic results. STEM-HAADF studies of **2**\_TiO<sub>2</sub> indicate that the sample contains TiO<sub>2</sub> particles very well dispersed and quite homogeneous in size, about 20x40 nm. A general view of the sample is depicted in Figure 2. At high levels of magnification, besides the TiO<sub>2</sub> support crystallites, both **2**\_TiO<sub>2</sub> and **2'**\_TiO shows extremely small Ir clusters (at the limit of the microscope sensitivity), ranging from 0.2 to 0.4 nm (Figure 2). Assuming a Gaussian particle size distribution, even smaller clusters, which escape STEM detection, should be present. In the STEM-HAADF images the clusters are hardly seen, as brighter spots on the TiO<sub>2</sub> crystallites. All seems to indicate that Ir is atomically distributed or forms very small clusters in both **2**\_TiO<sub>2</sub> and **2'**\_TiO<sub>2</sub>. Given the small particle size no EDS analysis was reliable. It is important to note that these metallic clusters are not formed upon electron beam exposure, that is, they are not the result of electron damage on the sample. This has been carefully checked by using different electron dosage over the sample.



**Figure 1.** <sup>13</sup>C{<sup>1</sup>H} (left) and <sup>31</sup>P{<sup>1</sup>H} (right) CPMAS NMR spectra of **2** (black), **2**\_TiO<sub>2</sub> (red) and **2'**\_TiO<sub>2</sub> (blue). Asterisks denote spinning side bands.

**1**, **2** and **2**\_TiO<sub>2</sub> were tested as WOCs using cerium ammonium nitrate (CAN) and NaIO<sub>4</sub> as chemical sacrificial oxidants, monitoring the reaction by manometry and Clark electrode. Selected results are reported in Table 1 (complete data set is given in SI). Complex **1** is not active at all with CAN and exhibits just a poor catalytic activity with NaIO<sub>4</sub>, affording only 26 cycles with a TOF = 0.1 min<sup>-1</sup> (Tab. 1, entries 1-2). On the contrary complex **2** is an efficient WOC with both oxidants, capable of completing all cycles expected based on the concentration of the employed sacrificial oxidant with TOF up to 30 min<sup>-1</sup> and 50 min<sup>-1</sup> with CAN and NaIO<sub>4</sub>, respectively (Tab. 1, entries 3-6). The catalytic activity of **2** was strongly affected by the pH of the reaction medium. This was clearly demonstrated by adding an increased amount of KOH to the solution of **2** before the injection of a solution of NaIO<sub>4</sub> (SI). TOF of oxygen production remains substantially the same (about 6 min<sup>-1</sup>) when 1-4 equivalents of KOH were added (SI), but it markedly increases up to 49.5 min<sup>-1</sup> when 16 equivalents of KOH were added (Tab. 1, entry 6). Also **2**\_TiO<sub>2</sub> is an active WOC with both CAN and NaIO<sub>4</sub>; however an almost complete leaching of the catalyst occurs with CAN, already after the first catalytic run (Tab. 1, entries 7-9). This is likely due to the high tendency of KTCs to act as terdentate ligand for the oxophylic Ce<sup>4+</sup>.<sup>[21]</sup> For that reason we focused our attention on the catalytic activity of **2**\_TiO<sub>2</sub> with NaIO<sub>4</sub> as sacrificial oxidant. **2**\_TiO<sub>2</sub> exhibited a catalytic activity similar to **2** (compare entries 10 and 5 in Tab. 1) and did not undergo any leaching as demonstrated by the complete inactivity of the supernatant (Tab. 1, entry 11) and observation of comparable TOF and TON values for the second (Tab. 1, entry 12) and other consecutive runs (SI). Addition of 16 equivalents of KOH caused a remarkable increase of TOF, from 2.8 min<sup>-1</sup> to 19.8 min<sup>-1</sup> (entries 13-14, Tab. 1), analogously to what observed for **2**. Three successive runs were performed after having washed the solid catalyst with water (SI); all expected cycles were completed and the original TOF in absence of KOH is gradually restored. Two additional runs were carried out after having left the catalyst in contact with a water solution at pH 10 and pH 14 for 24h, respectively, and washed with water (SI); the catalyst maintains its performances both in terms of TON and TOF and the supernatant is not

active in both cases suggesting no leaching. Finally, in order to further explore the stability of the catalyst, three independent catalytic experiments were carried out (Tab. 1, entries 15-17), utilizing exactly the same concentration of **2**\_TiO<sub>2</sub> and NaIO<sub>4</sub>, with the standard protocol (Tab. 1, entry 15), contacting **2**\_TiO<sub>2</sub> with a water solution at pH 14 (by KOH) for 24h (Tab. 1, entry 16) and contacting **2**\_TiO<sub>2</sub> with a solution at pH 1 (by HNO<sub>3</sub>) (Tab. 1, entry 17). In all three runs, oxygen production was almost quantitative; TOF value after prolonged contact with the strongly basic solution was more than two times higher (6.8 min<sup>-1</sup> vs 2.4 min<sup>-1</sup>) consistently with what said above, whereas TOF value after contacting with the acidic one is substantially the same than the original TOF value (2.3 min<sup>-1</sup> vs 2.4 min<sup>-1</sup>).



**Figure 2.** a) and c) STEM-HAADF images of **2**\_TiO<sub>2</sub> at different levels of magnification; b) A STEM-HAADF image of **2**'\_TiO<sub>2</sub> at the maximum level of magnification; d) Size distribution of Ir-particles in **2**'\_TiO<sub>2</sub>.

pH was measured for all steps related to a catalytic experiment in which a suspension 19.1 mM of **2**\_TiO<sub>2</sub> was reacted with a solution of 9.1 mM of NaIO<sub>4</sub>, in the presence of 16 equivalents of KOH. Specifically, pH changed from 5.10 to 4.41 when **2**\_TiO<sub>2</sub> was dispersed in deionized water. The addition of KOH caused an increase of pH up to 9.60, whereas injection of NaIO<sub>4</sub> led to a pH = 6.32 that remained substantially unaltered until the end of catalysis. The observed acidification caused by NaIO<sub>4</sub> addition can be explained considering that IO<sub>4</sub><sup>-</sup> undergoes hydration with two water molecules leading to the weak acid H<sub>4</sub>IO<sub>6</sub><sup>-</sup>.<sup>[22]</sup>

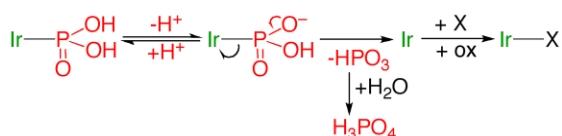
**Table 1.** Selected catalytic data for WOCs obtained by manometry.

| Entry                        | C <sub>Cat</sub><br>(μM) | C <sub>Ox</sub><br>(mM) | TOF<br>(min <sup>-1</sup> ) | TON                     | O <sub>2</sub> yield |     |     |
|------------------------------|--------------------------|-------------------------|-----------------------------|-------------------------|----------------------|-----|-----|
| <b>Cat 1</b>                 |                          |                         |                             |                         |                      |     |     |
| 1                            | 5.0                      | CAN/10.0                | –                           | –                       | –                    |     |     |
| 2                            | 1.0                      | NaIO <sub>4</sub> /10.0 | 0.1                         | 26                      | 5%                   |     |     |
| <b>Cat 2</b>                 |                          |                         |                             |                         |                      |     |     |
| 3                            | 5.0                      | CAN/10.0                | 29.9                        | 496                     | 99%                  |     |     |
| 4                            | 1.0                      | NaIO <sub>4</sub> /10.0 | 9.6                         | 3299                    | 66%                  |     |     |
| 5                            | 18.2                     | NaIO <sub>4</sub> /9.1  | 3.0                         | 230                     | 92%                  |     |     |
| 6                            | 16 <sup>eq</sup>         | KOH                     | 5.0                         | NaIO <sub>4</sub> /10.0 | 49.5                 | 980 | 98% |
| <b>Cat 2_TiO<sub>2</sub></b> |                          |                         |                             |                         |                      |     |     |
| 7                            | I <sub>solid</sub>       | 20.0                    | CAN/10.0                    | 63.8                    | 93                   | 77% |     |

|   |      |                        |      |      |     |
|---|------|------------------------|------|------|-----|
| 8 I <sub>supernatant</sub>                  | n.a. | CAN/10.0               | n.a. | 100  | 83% |
| 9 II <sub>solid</sub>                       | n.a. | CAN/10.0               | n.a. | 22   | 19% |
| 10 I <sub>solid</sub>                       | 19.3 | NaIO <sub>4</sub> /9.1 | 2.8  | 200  | 85% |
| 11 I <sub>supernatant</sub>                 | n.a. | NaIO <sub>4</sub> /9.1 | n.a. | n.a. | 0%  |
| 12 II <sub>solid</sub>                      | 19.3 | NaIO <sub>4</sub> /9.1 | 2.8  | 212  | 90% |
| 13 I <sub>solid</sub>                       | 19.3 | NaIO <sub>4</sub> /9.1 | 2.8  | 200  | 85% |
| 14 II <sub>solid</sub> 16 <sup>eq</sup> KOH | 19.3 | NaIO <sub>4</sub> /9.1 | 19.8 | 218  | 92% |
| 15  | 19.1 | NaIO <sub>4</sub> /9.1 | 2.4  | 210  | 88% |
| 16 <sup>a</sup>                             | 19.1 | NaIO <sub>4</sub> /9.1 | 6.8  | 220  | 92% |
| 17 <sup>b</sup>                             | 19.1 | NaIO <sub>4</sub> /9.1 | 2.3  | 206  | 86% |

<sup>a</sup>Run performed after having left the catalytic suspension at pH = 14 for 24h. <sup>b</sup>Run performed after having left the catalytic suspension at pH = 1 for 24h.

In order to understand the modality of activation of **2** and **2**·TiO<sub>2</sub> and the reason why **1**, contrary to **2**, exhibits poor catalytic activity, preliminary NMR studies were performed. <sup>1</sup>H and <sup>31</sup>P NMR spectra of a solution 1-5 mM of **1** were found to be substantially unaffected by the addition of up to 16 equivalents of KOH and several equivalents of NaIO<sub>4</sub>. On the contrary, <sup>1</sup>H and <sup>31</sup>P NMR spectra of **2** showed a shift of resonances to lower frequency as increasing amounts of KOH were added, consistent with the gradual deprotonation of acidic functionalities. More importantly, the multiple-addition of 0.25 equivalents of NaIO<sub>4</sub> nicely tracks with the quantitative appearance of a <sup>31</sup>P NMR resonance assigned to PO<sub>4</sub><sup>3-</sup> (SI). Contemporary, the intensity of the <sup>1</sup>H NMR Cp\* resonance of **2** (a quartet due the H-P scalar coupling with <sup>31</sup>P) decreases and singlet appears at 1.50 ppm, suggesting elimination of all P-moieties. Oxidative transformation of Cp\*, as indicated by the appearance of <sup>1</sup>H resonances due to acetic and formic acids,<sup>[23]</sup> starts successively to PO<sub>4</sub><sup>3-</sup> elimination. It can be concluded that **2** easily transforms into a Cp\*IrX<sub>3</sub><sup>-</sup> species (X = anionic species or water) by the oxidative elimination of PO<sub>4</sub><sup>3-</sup>, asking for the presence of a P–O–H functionality as illustrated in Scheme 2. This might explain why **1** is not an active WOC.



**Scheme 2.** Modality of activation of **2**.

Interestingly, a coordination vacancy appears to be necessary in order to initiate the oxidative transformation of Cp\* and this not the case in **2** which cannot undergo the expulsion of a –P(O)(OMe)<sub>2</sub> unit. Solid-state <sup>31</sup>P NMR spectrum shows that some PO<sub>4</sub><sup>3-</sup> is already present in **2**·TiO<sub>2</sub> before catalysis, likely derived from oxidative dissociation (photo)catalyzed by TiO<sub>2</sub>, and it substantially increases after a catalytic run (Figure 1). Nevertheless, a broad band centered at 24.7 ppm is still present. It can be speculated that the latter is due to some iridium centers missing the Cp\*, still bearing a bonded phosphate group. In conclusion, it has been demonstrated, for the first time, that KTCs, bearing –P(O)(OH)<sub>2</sub> functionalities, are excellent precursors for the fabrication of heterogenized catalysts for WO. The resulting iridium-TiO<sub>2</sub> hybrid material exhibits remarkable TOF and TON performances in WO driven by NaIO<sub>4</sub> and an extremely low propensity to leaching. This strategy appears to be rather general and many extensions can be envisioned. For example, the nature of KTC metal center, especially considering cheap metals, and support can be changed. At the same time, photochemical and electrochemical tests have to be performed. All these experiments are in progress in our laboratories and results will be reported in due time.

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**Keywords:** water oxidation • iridium • titania • Klaüi-type compounds • water splitting

- [1] a) *Molecular Water Oxidation* (Ed.: A. Llobet), Wiley-Interscience, New York, **2014**; b) M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark, *Chem. Rev.* **2014**, *114*, 11863-12001; c) J. D. Blakemore, R. H. Crabtree, G. W. Brudvig, *Chem. Rev.* **2015**, *115*, 12974-13005; d) F. Evangelisti, R. More, F. Hodel, S. Lubner, G. R. Patzke, *J. Am. Chem. Soc.* **2015**, *137*, 11076-11084.
- [2] F. E. Osterloh, *Chem. Mater.* **2008**, *20*, 35-54.
- [3] a) K. J. Young, L. A. Martini, R. L. Milot, R. C. Snoeberger III, V. S. Batista, C. A. Schmuttenmaer, R. H. Crabtree, G. W. Brudvig, *Coord. Chem. Rev.* **2012**, *256*, 2503-2520; b) A. Kudo, Y. Miseki *Chem. Soc. Rev.* **2009**, *38*, 253-278.
- [4] a) N. S. Lewis, D. G. Nocera, *Proc. Natl. Accad. Sci.* **2006**, *103*, 15729-15735; b) N. S. Lewis, *Nature* **2001**, *414*, 589-590; c) V. Balzani, A. Credi, M. Venturi, *ChemSusChem* **2008**, *1*, 26-58; d) T. J. Meyer, *Nature* **2008**, *451*, 778-779.
- [5] a) C. Coperet, M. Chabanas, R. P. Saint-Arroman, J. M. Basset, *Angew. Chem. Int. Ed.* **2003**, *42*, 156-181; b) *Heterogenized Homogeneous Catalysts for Fine Chemicals Production* Eds.: P. Barbaro and F. Liguori, Springer, Dordrecht, **2010**.
- [6] J.-M. Savéant, *Chem. Rev.* **2008**, *108*, 2348-2378.
- [7] A. Macchioni, *Proc. SPIE* **9176** **2014**, Solar Hydrogen and Nanotechnology IX, 917608; doi:10.1117/12.2060957.
- [8] a) C. Wang, J.-L. Wang, W. Lin, *J. Am. Chem. Soc.* **2012**, *134*, 19895-19908; b) A. Savini, A. Bucci, M. Nocchetti, R. Vivani, H. Idriss, A. Macchioni, *ACS Catal.* **2015**, *5*, 264-271; c) S. W. Sheehan, J. M. Thomsen, H. Hintermair, R. H. Crabtree, G. W. Brudvig, C. A. Schmuttenmaer, *Nat. Commun.* **2015**, DOI: 10.1038/ncomms7469; d) Y. Gao, X. Ding, J. Liu, L. Wang, Z. Lu, L. Li, L. Sun, *J. Am. Chem. Soc.* **2013**, *135*, 4219-4222; e) K. S. Joya, N. K. Subbaiyan, F. D'Souza, H. J. M. de Groot, *Angew. Chem. Int. Ed.* **2012**, *51*, 9601-9605.
- [9] W. Klaüi, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 627-637.
- [10] W.-H. Leung, Q.-F. Zhang, X.-Y. Yi, *Coord. Chem. Rev.* **2007**, *251*, 2266-2279.
- [11] H. Shinar, G. Navon, W. Klaüi, *J. Am. Chem. Soc.* **1986**, *108*, 5005-5006.
- [12] H. Bukowsky, E. Uhlemann, W. Klaüi, *Anal. Chim. Acta* **1996**, *319*, 271-274.
- [13] a) W. Klaüi, N. Mocigemba, A. Weber-Schuster, R. Bell, W. Frank, D. Mootz, W. Poll, H. Wunderlich, *Chem. Eur. J.* **2002**, *8*, 2335-2340; b) E. Bae, W. Choi, J. Park, H. S. Shin, S. B. Kim, J. S. Lee, *J. Phys. Chem. B* **2004**, *108*, 14093-14101.
- [14] C. Zuccaccia, G. Bellachioma, O. Bortolini, A. Bucci, A. Savini, A. Macchioni, *Chem. Eur. J.* **2014**, *20*, 3446-3456 and references therein.
- [15] M. Scotti, M. Valderrama, P. Campos, W. Klaüi, *Inorg. Chim. Acta* **1993**, *207*, 141-145.
- [16] T. B. Brill, S. J. Landon, *Chem. Rev.* **1984**, *84*, 577-585.
- [17] K. Ariga, T. Mori, J. P. Hill, *Adv. Mater.* **2012**, *24*, 158-176.
- [18] Typical <sup>13</sup>C chemical shift values for C-CH<sub>3</sub> quaternary carbon is about 80-90 ppm: A. Savini, A. Bucci, G. Bellachioma, S. Giancola, F. Palomba, L. Rocchigiani, A. Rossi, M. Suriani, C. Zuccaccia, A. Macchioni, *J. Organomet. Chem.* **2014**, *771*, 24-32.
- [19] G. Guerrero, P. H. Mutin, A. Vioux, *Chem. Mater.* **2001**, *13*, 4367-4373.
- [20] D. Lahcène, A. Arsal, B. Boury, R. M. Laine, *J. Colloid Interface Sci.* **2013**, *393*, 335-339.
- [21] X.-Y. Yi, T. C. H. Lam, I. D. Williams, W.-H. Leung, *Inorg. Chem.* **2010**, *49*, 2232-2238.
- [22] R. M. Kren, H. W. Dodgen, C. J. Nyman, *Inorg. Chem.* **1968**, *7*, 446-451.
- [23] a) A. Savini, P. Belanzoni, G. Bellachioma, C. Zuccaccia, D. Zuccaccia, A. Macchioni, *Green Chem.* **2011**, *13*, 3360-3374; b) D. B. Grotjahn, D. B. Brown, J. K. Martin, D. C. Marelus, M.-C. Abadjian, H. N. Tran, G. Kalyuzhny, K. S. Vecchio, Z. G. Specht, S. A. Cortes-Llamas, V. Miranda-Soto, C. van Niekerk, C. E. Moore, A. L. Rheingold, *J. Am. Chem. Soc.* **2011**, *133*, 19024-19027.