Photochemistry

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Concerted Two-Electron Transfer and High Selectivity of TiO_2 in Photocatalyzed Deoxygenation of Epoxides**

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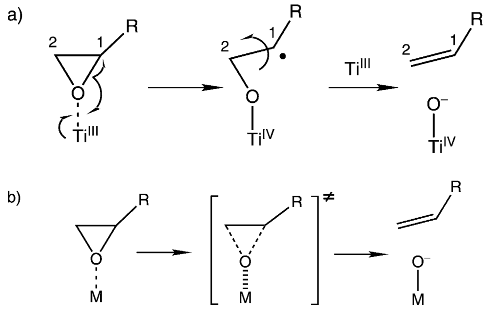
TiO_2 photocatalysis has shown promising potential in the degradation of pollutants, fixation of CO_2, and splitting of H_2O. In recent years, the selective conversions of organic compounds by TiO_2 photocatalysis have been explored actively.[1] Even though most of the photocatalytic reactions involve the total gain or loss of multiple equivalents of electrons, and the term multielectron reaction is frequently used in documents on TiO_2 photocatalysis, these redox processes are conventionally thought to proceed through sequential single-electron-transfer (SET) pathways.[2] For example, the photocatalytic oxidation of an alcohol to an aldehyde (or ketone) is a typical two-electron oxidation process through a SET mechanism.[2c] In this process, the alcohol first reacts with a valence band hole (h_{vb}^+) to generate a radical intermediate, which injects another electron into the conduction band to complete the two-electron reaction (the current amplification effect). According to the SET mechanisms radical intermediates are inevitably involved and is extremely unfavorable for the selective transformation of organic substrates.

The concerted multielectron-transfer (CMET) pathway, in which multiple (usually two) electrons are transferred from or to an adsorbed species in a single kinetic step, could avoid the formation and side reactions of radical intermediates. As a result of its high state density, TiO_2 particles can store multiple conduction band electrons (e_{cb}^-) and h_{vb}^+, and is a character of photocatalysis which distinguishes it from molecular redox systems. Principally, the storage of multiple e_{cb}^-/h_{vb}^+ paves the way for CMET. However, the occurrence of CMET has rarely been experimentally verified in the stoichiometric multielectron photocatalytic reactions of pristine TiO_2 systems.

The reduction of an epoxide to the corresponding alkene is an important reaction in organic synthesis[3] and biological chemistry.[4] Traditionally, the deoxygenation of epoxides is realized using the complexes of low-valent metals as stoichiometric reductants.[5] For the reduction of epoxides with *E*–*Z* isomerism, metal complexes which can offer single electron per molecule, such as [Cp_2TiCl] (Cp = cyclopentadienyl), give the alkene products with no stereoretention (that is, the yield distribution of stereoisomeric products is independent of substrate configuration) and low overall selectivity (see Table S1 in the Supporting Information for a literature survey), because of the formation of labile radical intermediates (Scheme 1 a).[5a,b] In contrast, for W and Mo complexes, predominant retention of substrate configuration was observed in their deoxygenation systems, and was explained by either the absence of a radical intermediate or by an O-atom-transfer mechanism (Scheme 1b).[5c,d] Thus, the stereochemistry of alkene products offers a great deal of information on the reduction pathway.[6]



Scheme 1. Sequential SET mechanism (a) and O-atom-transfer mechanism (b) for the reductive deoxygenation of an epoxide.

Herein, we show our compelling experimental evidence that CMET is the dominant pathway in the photocatalytic deoxygenation of epoxides on pristine TiO_2 surface. The CMET mechanism ensures the much higher alkene selectivity and higher stereoretention of this transformation. This study provides a clear example of the CMET characteristic of TiO_2 photocatalysis, as well as a cheap and green method for the selective deoxygenation of epoxides.

The photocatalytic reactions were carried out in isopropyl alcohol (*i*PrOH), which also serves as a reductive sacrifice to scavenge h_{vb}^+.[2c] Styrene oxide was consumed almost completely in 15 hours under UV irradiation, and nearly quantitatively deoxygenated to styrene (Table 1, entry 1). Control experiments showed that both TiO_2 and UV irradiation are necessary for the deoxygenation (see Table S2). Moreover, when 1-phenyl-1,2-ethanediol or 2-methoxy-2-phenylethanol was used as substrate, no alkene product was obtained, thus indicating that photocatalytic deoxygenation does not proceed via hydrolysis or alcoholysis intermediates. High alkene

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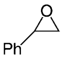
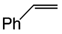
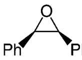
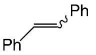
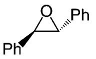
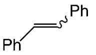
Table 1: Comparison of the alkene selectivity and stereochemistry between TiO_2 photocatalytic[a] and $[Cp_2TiCl]$[b] deoxygenation systems.

Entry	Substrate	Product	System	Conv. [%]	Sel. [%]	*E*/*Z*
1			TiO_2/UV	97	97	–
2			$[Cp_2TiCl]$	100	57	–
3			TiO_2/UV[c]	61	ca. 100	48:52
4			$[Cp_2TiCl]$	100	37	98:2
5			TiO_2/UV[d]	30	ca. 100	97:3
6			$[Cp_2TiCl]$	100	44	99:1

[a] 15 mg TiO_2 (P25), 0.1 mmol epoxide, 5 mL *i*PrOH, Ar atmosphere, 100 W Hg lamp cutoff below $\lambda = 300$ nm, irradiation time: 15 h. Conversion and selectivity determined by GC analysis. [b] 5 mL freshly prepared $[Cp_2TiCl]$ solution of THF (3.4 mmol) was mixed with 5 mL deaerated *i*PrOH solution containing 1 mmol epoxide at room temperature, reaction time: 10 min. [c] To avoid the photoisomerization of alkene products, light with $\lambda > 350$ nm was used, time: 35 h. [d] $\lambda > 350$ nm, time: 120 h.

selectivity was also observed in the photocatalytic reduction of (*E*)- and (*Z*)-stilbene oxides (Table 1, entries 3 and 5), although the rates were apparently slower, probably a result of steric effects. In contrast, the deoxygenation selectivities of $[Cp_2TiCl]$ systems were rather poor (30–60%), even though the reductive electron of $[Cp_2TiCl]$ is also distributed mainly around the Ti atom.

More intriguingly, in the photocatalytic deoxygenation of (*E*)-stilbene oxide, the ratio of the yield of *E* to *Z* alkene (*E*/*Z*) was 97:3, whereas a mixture of stilbene stereoisomers with an *E*/*Z* ratio of 48:52 was obtained when (*Z*)-stilbene oxide was used as the reactant (Table 1), thus indicating that a large fraction of the stereochemistry of the epoxide substrate is retained in photocatalytic deoxygenation. In control experiments, *Z* stilbene was dissolved in a TiO_2 suspension in *i*PrOH. After 35 hours of irradiation, only 2% of *Z* stilbene was converted into its *E* isomer. Therefore, the photoisomerization of alkene products cannot influence markedly the stereochemistry of products. In contrast, for the reduction system of $[Cp_2TiCl]$, the *E* alkene was always the main product ($E/Z = 99{:}1$ for (*E*)-stilbene oxide and 98:2 for its *Z* isomer), thus indicating that the stereochemistry of alkene products is independent on the configuration of the substrate.

It is well accepted that the deoxygenation of epoxides by $[Cp_2TiCl]$, which can offer only one electron per complex, proceeds by two consecutive SET processes (Scheme 1a). The first electron transfer causes the opening of oxirane ring and the formation of a β-metaloxy radical. This radical has enough time to rotate around the C1–C2 bond to realize configuration relaxation before its reduction by the second equivalent of the Ti^{III} complex. The partial retention of substrate stereochemistry in the photocatalytic deoxygenation indicates that the long-lived, open-ring radical intermediate is not involved in this reaction. To validate this argument, ethyl acrylate and methyl methacrylate (radical traps)[5b,6] were added to the photocatalytic system. No product of radical capture was detected (see Table S3), thus confirming the absence of radical intermediates. The partial retention of substrate configuration during epoxide deoxygenation was frequently observed for reductions system in which the reductant can offer more than one electron.[5c,d] The partial stereoretention of photocatalytic deoxygenation suggests that, instead of separate SETs, this reaction proceeds by a CMET pathway.

The difference between TiO_2 photocatalysis and Ti^{III} systems may be attributed to the ability of TiO_2 particles to store and simultaneously provide multiple e_{cb}^-,[7] and its high state density. Therefore, we analyzed the accumulation of e_{cb}^- using an in situ UV/Vis-DRS method. Under UV irradiation, the TiO_2 suspension in *i*PrOH showed a broad absorption band above $\lambda = 380$ nm (see Figure S1), which is the typical absorption of the e_{cb}^- of TiO_2.[8] By trapping the accumulated e_{cb}^- with Fe^{3+} and quantifying the formed Fe^{2+}, the total amount of stored e_{cb}^- at a photostationary state was estimated to be 123.8 μM. Assuming that TiO_2 (P25) nanoparticles are spherical with a diameter of 21 nm and their density is 4.0 g cm^{-3},[9] an average of 73 e_{cb}^- are stored in each TiO_2 particle (Figure 1a).

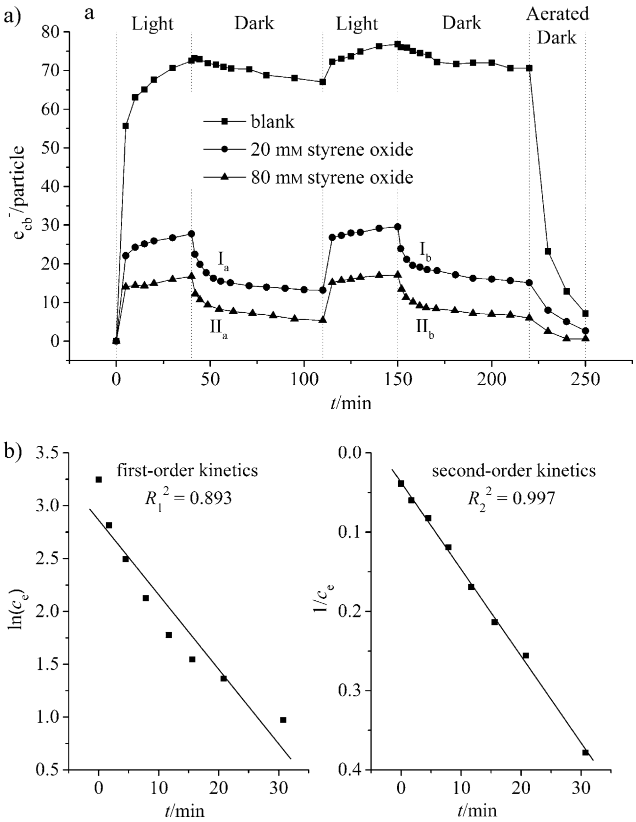


Figure 1. a) The accumulation and decay of e_{cb}^- in TiO_2 particles in the presence and absence of styrene oxide. b) The comparison between the fitting of the e_{cb}^- decay process I$_a$ according to first- and second-order kinetics, c_e: μM.

In the presence of styrene oxide, the accumulated amount of e_{cb}^- was significantly decreased because of its reaction with the epoxide. With 20 and 80 mM styrene oxide, an average of 29 and 17 e_{cb}^-, respectively, were stored in one TiO_2 particle at the photostationary state. These results mean that during the photocatalytic reduction of epoxides multiple e_{cb}^- are always available in the TiO_2 particle. After the termination of irradiation, the e_{cb}^- absorption band underwent a remarkable decrease in the presence of styrene oxide (Figure 1a). The decay of e_{cb}^- provides us an opportunity to study the electron-transfer mechanism of photocatalytic deoxygenation. The kinetic distinction between the sequential SET and CMET pathways originates from the number of electrons transferred in the rate-determining step. For the SET pathway, the overall reaction is controlled by the first electron reduction of the epoxide, so the decay of e_{cb}^- would exhibit first-order kinetics. However, in the CMET pathway, since two e_{cb}^- are simultaneously transferred, the decay of e_{cb}^- should obey second-order kinetics. Therefore, through the kinetic analysis of e_{cb}^- decay, these two pathways could be distinguished (the detailed kinetic derivation and more discussion are given in the Supporting Information). As shown in Figure 1b, for decay process I_a, the temporal change of e_{cb}^- concentration was much better described by second-order kinetics ($1/c_e \approx t$) with the correlation coefficient R_2^2 of 0.997, rather than by first-order kinetics ($\ln(c_e) \approx t$, $R_1^2 = 0.893$). The fitting of the other e_{cb}^- decay processes in Figure 1a (I_b, II_a, and II_b) gave similar results ($R_2^2 = 0.966$–0.997 versus $R_1^2 = 0.812$–0.905; see Figure S2). In another experiment, the e_{cb}^- was first stored in TiO_2 particles by irradiating a TiO_2 suspension in *i*PrOH under an Ar atmosphere, and then the absorption at $\lambda = 800$ nm was chronometrically recorded after the addition of deaerated styrene oxide. Again, second-order kinetics ($R_2^2 = 0.997$–0.998) were superior to the first-order kinetics ($R_1^2 = 0.962$–0.969) for the e_{cb}^- decay (see Figure S3). The second-order kinetic decay of e_{cb}^- is an indication of the concerted two-electron-transfer pathway. However, for the SET-based photocatalytic reduction of benzaldehyde and acetophenone,[10] first-order kinetics was more suitable for the e_{cb}^- decay than second-order kinetics (see Figure S4).

We also noted the O-atom-transfer mechanism (Scheme 1b), in which the O atom of the epoxide is transferred directly to the TiO_2 surface in a single step,[5c] would also give the second-order decay of e_{cb}^- because two e_{cb}^- are involved in this process. However, according to this mechanism, the configuration of the epoxide substrate should be predominantly retained in alkene products, and is in conflict with the partial stereoretention (52%) observed in the photocatalytic reduction of (*Z*)-stilbene oxide. Therefore, we do not consider O-atom-transfer as the dominant pathway.

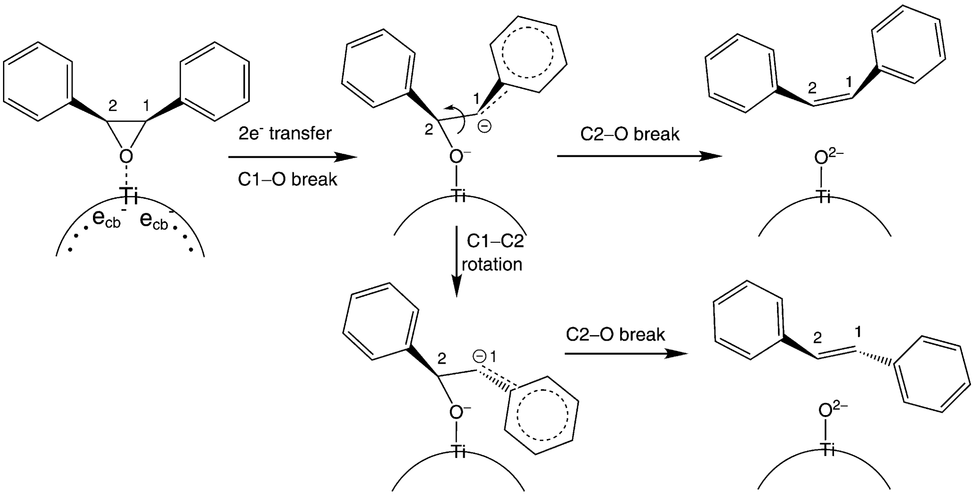
Careful study of the effect of light intensity on the stereochemistry of the photocatalytic deoxygenation of (*Z*)-stilbene oxide provides another line of evidence for the CMET pathway. When the reduction of (*Z*)-stilbene oxide was carried out under a Hg lamp, stilbene products with the *E*/*Z* ratio of 48:52 were obtained (Table 2, entry 1). When using a stronger Xe lamp (3.95 mW cm^{-2}) as the light source, the stereochemistry of the products was nearly unchanged, even though the overall deoxygenation was accelerated by 4.3 times (entry 2). Further enhancement of irradiation intensity with a laser (250 mW cm^{-2}) also had little effect on the isomer distribution of alkene products (*E*/*Z* = 48:52, entry 3). Light intensity is known to be able to greatly affect the accumulation and reductive ability of e_{cb}^-,[2b,11] and consequently, the e_{cb}^--transfer rate from TiO_2 to the epoxide (or radical intermediate if formed) would also be influenced, as proven by the accelerated deoxygenation rate at enhanced light intensity. If the loss of substrate stereochemistry were caused by the rotation of the C1–C2 bond of the radical intermediate formed in the SET pathway, the enhancement of irradiation intensity would exaggerate the accumulation of e_{cb}^-, and consequently accelerate the transfer of the second e_{cb}^-. As a result, the lifetime of the radical intermediate would be shortened, and thus higher retention of the configuration would be obtained at an enhanced intensity of irradiation, all of which is in conflict with our experimental observations. More reasonably, the independence of stereochemisty on light intensity suggests that the transfer of the second e_{cb}^- occurs prior to the rotation of C1–C2 bond, and is consistent with the CMET pathway evidenced by the fitting of e_{cb}^- decay. According to this mechanism, the photocatalytic deoxygenation is initiated by the two-electron reduction of the substrate to a carbanion intermediate, which also has C1–C2 bond that can rotate (Scheme 2). The stereochemistry of alkene products is determined by the competition between C1–C2 bond rotation and C2–O bond cleavage of the formed carbanion intermediate. Neither of these two processes involves the redox of the intermediate, so e_{cb}^--influencing factors, such as light intensity, cannot have an effect on the stereochemistry of the reaction, but can markedly affect the overall deoxygenation rate. In addition, the *E*-configured carbanion intermediate is thermodynamically more favorable than the *Z*-configured carbanion. As a result, the loss of substrate stereochemistry would not happen in the reduction of (*E*)-stilbene oxide (Table 1, entry 5).

Table 2: The effect of light intensity (*I*) on the reduction of (*Z*)-stilbene oxide.[a]

Entry	Light source	*I* [mW cm^{-2}]	*t* [h]	Conv. [%][b]	*E*/*Z*
1	Hg lamp	0.166	35	61	48:52
2	Xe lamp	3.95	4	30	49:51
3	Laser (355 nm)	250	1	21	48:52

[a] 3 g L^{-1} TiO_2, 20 mM (*Z*)-stilbene oxide, 5 mL *i*PrOH, Ar atmosphere, light with $\lambda > 350$ nm was used. [b] Conversion determined by GC analysis.

The CMET character of epoxide deoxygenation is reminiscent of a platinum cocatalyst, which is able to trap e_{cb}^- and catalyze multielectron redox reactions on its surface.[7c,12] However, in our experiments, the platinization of TiO_2 was found to significantly suppress the deoxygentation rate of (*Z*)-stilbene oxide ($k_{TiO2}/k_{Pt\text{-}TiO2} = 1{:}0.48$, see Figure S5), while the *E*/*Z* ratio of the formed stilbene isomers was nearly unaffected (47:53). Obviously, the deposited platinum is inert to the deoxygenation of epoxide. Otherwise, the overall reaction rate would be accelerated and the stereochemistry would be altered. The reaction should predominantly occur on pristine TiO_2 surface, and the supression is due to the competition of platinum with surface Ti sites for e_{cb}^-. This experiment implies that the surface Ti sites of TiO_2 are essential for the deoxygenation. The strong affinity of Ti^{4+} to oxygen[13] would facilitate CMET by providing additional thermodynamic drive with the formation of surface Ti–O bond.



Scheme 2. Concerted two-electron-transfer pathway for the photocatalytic deoxygenation of epoxides.

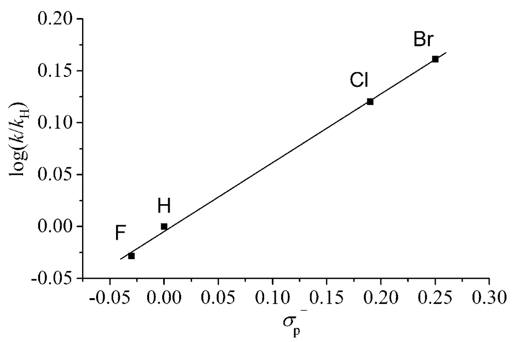
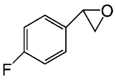
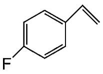
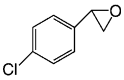
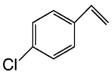
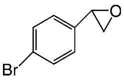
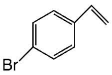
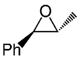
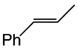
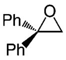
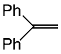
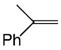
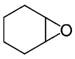
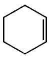


Figure 2. Hammett plots of log (k/k_H) versus the substituent constant $\sigma^-_p{}^-$ for the photocatalytic deoxygenation of *para*-substituted styrene oxide.

The formation of a carbanion intermediate is supported by the linear free energy relationship of photocatalytic deoxygenation. It was observed that *para* substitution with F, Cl, and Br all facilitated the photocatalytic deoxygenation (the selectivities were all $> 90\%$; see Table 3). Hammett plots of the logarithm of relative rates ($\log(k/k_H)$) against corresponding σ_p^- substituent constants gave good correlation ($R^2 = 0.998$, Figure 2), while the correlation with σ_p was poor ($R^2 = 0.791$, see Figure S6), thus illustrating that an electronegative reaction center is formed and the aromatic ring stabilizes it through conjugation.[14] The Hammett constant (ρ) obtained was 0.66. The better correlation with σ_p^- and a positive value of ρ imply that the reductive dissociation of the C–O bond is involved in the rate-determining step.[15] In our mechanism, the charge accumulation in the carbanion intermediate would be weakened by the C1–O bond cleavage, and the formation of surface Ti–O bond also has an effect of charge compensation, and makes the CMET pathway more feasible. These effects make the ρ value for photocatalytic deoxygenation a relatively small absolute value.

Inspired by the CMET nature of photocatalytic deoxygenation, we extended the scope of substrates to test the applicability of this reaction. As shown in Table 3, similar to styrene oxide, the alkene yields of the *para*-halogen-substituted derivatives of styrene oxide were all greater than 90% (entries 1–3). The photocatalytic deoxygenation of *E*-β-methylstyrene oxide, a 1,2-disubstituted oxirane, was also nearly quantitative. However, the deoxygenation of 1,1-disubstituted aromatic oxiranes exhibited lower selectivities (entries 5 and 6). The poor selectivities could be explained by the competing hydrolysis and alcoholysis reactions, since such substrates are highly acid sensitive.[5e] This argument was supported by the GC-MS analysis of the reaction solution. For example, the hydrolysis product, 2-phenyl-1,2-propanediol, was the main byproduct in the photocatalytic reduction of α-methylstyrene oxide (see Figure S7). Aliphatic epoxides were inert to photocatalytic reduction (entries 7 and 8), and may result from the absence of the stabilizing effect of the aromatic ring on the carbanion intermediate.

Table 3: Photocatalytic deoxygenation of epoxides.[a]

Entry	Substrate	Product	t [h]	Conv. [%][b]	Sel. [%][b]
1			15	100	99
2			15	100	96
3			15	100	91
4			60	68	ca. 100
5			80	46	65
6			15	72	21
7			25	8	0
8			25	<1	–

[a] Reaction conditions: 15 mg TiO_2 (P25), 0.1 mmol epoxide, 5 mL *i*PrOH, 100 W Hg lamp cutoff below $\lambda = 300$ nm, Ar atmosphere.
[b] Conversion and selectivity determined by GC analysis.

In summary, we have achieved selective deoxygenation of epoxides on TiO_2. The high selectivity of this reaction is attributed to a CMET pathway. Through this pathway, highly reactive radical intermediates are avoided, and is beneficial to the selectivity of organic transformation. Our work also suggests that CMET might also proceed in other photocatalytic reactions, such as the reduction of CO_2 and O_2, as a result of the high state density of the semiconductor.

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Keywords: alkenes · electron transfer · photochemistry · small ring systems · titanium

[1] a) M. Zhang, C. Chen, W. Ma, J. Zhao, *Angew. Chem.* **2008**, *120*, 9876–9879; *Angew. Chem. Int. Ed.* **2008**, *47*, 9730–9733; b) G. Palmisano, E. Garcia-Lopez, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro, L. Palmisano, *Chem. Commun.* **2010**, *46*, 7074–7089; c) X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao, *Angew. Chem.* **2011**, *123*, 4020–4023; *Angew. Chem. Int. Ed.* **2011**, *50*, 3934–3937; d) H. Kisch, *Angew. Chem.* **2013**, *125*, 842–879; *Angew. Chem. Int. Ed.* **2013**, *52*, 812–847.

[2] a) S. O. Obare, T. Ito, G. J. Meyer, *J. Am. Chem. Soc.* **2006**, *128*, 712–713; b) W. Choi, M. R. Hoffmann, *J. Phys. Chem.* **1996**, *100*, 2161–2169; c) M. Miyake, H. Yoneyama, H. Tamura, *Chem. Lett.* **1976**, 635–640.

[3] W. S. Johnson, M. S. Plummer, S. P. Reddy, W. R. Bartlett, *J. Am. Chem. Soc.* **1993**, *115*, 515–521.

[4] R. Teufel, T. Friedrich, G. Fuchs, *Nature* **2012**, *483*, 359–362.

[5] a) T. V. RajanBabu, W. A. Nugent, M. S. Beattie, *J. Am. Chem. Soc.* **1990**, *112*, 6408–6409; b) T. V. RajanBabu, W. A. Nugent, *J. Am. Chem. Soc.* **1994**, *116*, 986–997; c) L. M. Atagi, D. E. Over, D. R. McAlister, J. M. Mayer, *J. Am. Chem. Soc.* **1991**, *113*, 870–874; d) K. G. Moloy, *Inorg. Chem.* **1988**, *27*, 677–681; e) J. E. McMurry, M. G. Silvestri, M. P. Fleming, T. Hoz, M. W. Grayston, *J. Org. Chem.* **1978**, *43*, 3249–3255.

[6] T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem.* **2010**, *122*, 5677–5680; *Angew. Chem. Int. Ed.* **2010**, *49*, 5545–5548.

[7] a) J. Tang, J. R. Durrant, D. R. Klug, *J. Am. Chem. Soc.* **2008**, *130*, 13885–13891; b) N. M. Dimitrijevic, B. K. Vijayan, O. G. Poluektov, T. Rajh, K. A. Gray, H. He, P. Zapol, *J. Am. Chem. Soc.* **2011**, *133*, 3964–3971; c) C. M. Sánchez-Sánchez, A. J. Bard, *Anal. Chem.* **2009**, *81*, 8094–8100.

[8] T. Yoshihara, R. Katoh, A. Furube, Y. Tamaki, M. Murai, K. Hara, S. Murata, H. Arakawa, M. Tachiya, *J. Phys. Chem. B* **2004**, *108*, 3817–3823.

[9] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69–96.

[10] a) C. Joyce-Pruden, J. K. Pross, Y. Li, *J. Org. Chem.* **1992**, *57*, 5087–5091; b) S. Kohtani, E. Yoshioka, K. Saito, A. Kudo, H. Miyabe, *J. Phys. Chem. C* **2012**, *116*, 17705–17713.

[11] J. N. Schrauben, R. Hayoun, C. N. Valdez, M. Braten, L. Fridley, J. M. Mayer, *Science* **2012**, *336*, 1298–1301.

[12] a) R. Abe, H. Takami, N. Murakami, B. Ohtani, *J. Am. Chem. Soc.* **2008**, *130*, 7780–7781; b) W. Zhao, C. C. Chen, X. Z. Li, J. C. Zhao, H. Hidaka, N. Serpone, *J. Phys. Chem. B* **2002**, *106*, 5022–5028.

[13] P. M. Burkinshaw, C. T. Mortimer, *Coord. Chem. Rev.* **1983**, *48*, 101–155.

[14] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195.

[15] a) D. D. Tanner, J. A. Plambeck, D. W. Reed, T. W. Mojelsky, *J. Org. Chem.* **1980**, *45*, 5177–5183; b) E. V. Blackburn, D. D. Tanner, *J. Am. Chem. Soc.* **1980**, *102*, 692–697.