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

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Supporting Information

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Figure S1. $^1$H NMR spectrum (297 K, 300 MHz, benzene-$d_6$) recorded after irradiation of complex 1 ($t = 18\,\text{h}$, Xe light, full spectrum).
EPR spectra

**Figure S2.** Experimental EPR Spectra and simulated EPR Spectra using EPRSim32. a) After 990 s (Slide 11). b) Corresponding simulated EPR Spectra. c) Compound [Cp*Ti(OH)₂] (A). d) Compound 4. e) Compound B. – contribution A/4/B: 1/0.39/0.23.

Simulation parameters:
- [Cp*Ti(OH)₂] (A) \( g = 1.9773 \), \( A_{\text{Ti}} = 10 \text{G} \), \( 2\times A_{\text{H}} = 2.1 \text{ G} \), \( \Delta B = 1.7 \text{ G} \),
- [Cp*₂Ti(OH)] (4) \( g = 1.9771 \), \( A_{\text{Ti}} = 7.5 \text{ G} \), \( \Delta B = 1.8 \text{ G} \),
- B \( g = 1.9709 \), \( A_{\text{Ti}} = 9.6 \text{ G} \), \( \Delta B = 3.5 \text{ G} \).

Due to a large line width of compound B, no coupling constant to hydrogen was determined. For compound 4 also no coupling to hydrogen is observed.
**Figure S3.** EPR spectra indicating the presence of Cp* radicals. a) EPR spectrum recorded during irradiation of a solution of complex 1 in n-hexane. b) EPR spectrum recorded during irradiation of C₅Me₃H in n-hexane. c) Simulated EPR spectrum of the Cp* radical.

Simulation parameters: [Cp* radical] (g = 2.0034, 15xAₜ = 6.2 G, ΔB = 0.9 G).
**Figure S4.** Area (double integral) of the EPR signals in Figure S3 normalised against time. The ratio of complexes A, B and 4 was analysed by spectra deconvolution using EPRSim32 (black line: complex A, blue line: complex B, red line: complex 4).
X-ray crystallography

Crystallographic details: Diffraction data were collected on a STOE-IPDS II diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods (SHELXS-97[1]) and refined by full-matrix least-squares techniques on F² (SHELXL-97).[1] Diamond was used for graphical representations.[2]

Complex 2: C₄₀H₆₂O₇Ti₄, Mr = 846.50, triclinic, space group P̅1, a = 11.0328(5) Å, b = 11.7506(5) Å, c = 17.7441(7) Å, α = 84.415(3)°, β = 84.561(3)°, γ = 64.963(3)°, V = 2070.66(15) Å³, Z = 2, ρcalc = 1.358 g·cm⁻³, T = 150 K, µ = 0.789 mm⁻¹, numerical absorption correction (max. and min. transmission: 0.9478 and 0.8377), 29033 reflections measured, 9496 independent (Rint = 0.0502) and 5830 observed reflections [I > 2σ(I)], final R values [I > 2σ(I)]: R₁ = 0.0462, wR₂ = 0.0968, final R values (all data): R₁ = 0.0864, wR₂ = 0.1047, 415 refined parameters.

Mixed crystals of complex 4 and 5: C₂₀H₃₁₆O₁₃Ti, Mr = 340.75, monoclinic, space group P2₁/c, a = 8.4304(3), b = 12.0623(4), c = 19.2228(8) Å, β = 107.710(3)°, V = 1862.13(12) Å³, Z = 4, ρcalcd = 1.215 g·cm⁻³, T = 150 K, µ = 0.462 mm⁻¹, numerical absorption correction (max. and min. transmission: 0.9014 and 0.8442), 27025 reflections measured, 4262 independent (Rint = 0.0324) and 3219 observed reflections [I > 2σ(I)], final R values [I > 2σ(I)]: R₁ = 0.0356, wR₂ = 0.0909, final R values (all data): R₁ = 0.0504, wR₂ = 0.0940, 227 refined parameters.
**Figure S5.** Molecular structure of complex 4 (black) and its water adduct Cp*-Ti(H₂O)OH (5) (greyscale) in the mixed crystal. Occupations are set at 70% for complex 4 and 30% for 5. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms (except H1A for complex 4 and H1B for 5) are omitted for clarity. Hydrogen atoms at O2 could not be located from difference Fourier map, however, from the Ti–O bond length we assign this as group as coordinated H₂O.

**References**
