

Electronic Supplementary Information for

Light-Driven Oxidation of CH₄ to C₁ Chemicals

Catalysed by an Organometallic Ru Complex with O₂

Tatsuya Nakano, Tsukasa Abe, Takahiro Matsumoto, Kento Kimura, Genta Nakamura,*

Shinya Hayami, Yoshihito Shiota, Kazunari Yoshizawa* and Seiji Ogo**

*Corresponding author. E-mail: matsumoto.takahiro.236@m.kyushu-u.ac.jp

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Experimental Section

Materials and Methods. All experiments were carried out under a N₂ atmosphere by using standard Schlenk techniques and a glovebox. CH₄ (99.9999%) was purchased from OSAKA GAS LIQUID Co., Ltd. C₂H₆ (>99.9%) and O₂ gases (99.9%) were purchased from Sumitomo Seika Chemical Co., Ltd. D₂O (99.9%) was purchased from Sigma-Aldrich. ¹⁸O₂ (98 atm%) was purchased from SI Science Co., Ltd. H₂¹⁸O (98 atm%) was purchased from Taiyo Nippon Sanso Co. H₂O was purchased from Hayashi Pure Chemical Ind., Ltd. A ruthenium complex [Ru^{II}(η⁵-C₅Me₅)(CH₃CN)₃](NO₃) was prepared by the methods described in the literature.¹

¹H NMR spectra were recorded on a JEOL JNM-AL400 spectrometer. ¹H NMR experiments in D₂O were measured at 25 °C using 3-(trimethylsilyl)-propionic-2,2,3,3-*d*₄ acid sodium salt (TSP) as an internal standard. ESI-MS data were obtained on a JEOL JMS-T100LC AccuTOF. UV-vis spectra were recorded on an Agilent Technologies Cary 8454 at room temperature (light path length: 0.10 cm). GC-MS data were recorded on a SHIMADZU GCMS-QP 2010. The magnetic susceptibilities were measured with a SQUID magnetometer (Quantum Design MPMS-5S). UV and visible light irradiation were carried out using Asahi Spectra MAX 303. Light power was measured by a Newport 843-R power meter. High pressure device with sapphire window transmitting UV light was made by Syn Corporation Ltd.

[Ru^{II}(η⁵-C₅Me₅)(H₂O)₃](NO₃) **{[1](NO₃)}**. [Ru^{II}(η⁵-C₅Me₅)(CH₃CN)₃](NO₃) was dissolved in H₂O, resulting in replacement of the CH₃CN ligands with H₂O to form a Ru aqua complex, [Ru^{II}(η⁵-C₅Me₅)(H₂O)₃](NO₃) **{[1](NO₃)}**, which was confirmed by ¹H NMR spectroscopy (Fig. S10). ¹H NMR (400 MHz, in D₂O): δ 1.62 (s, 15H, H of η⁵-C₅Me₅).

[Ru^{IV}(η⁵-C₅Me₅)₂(μ-O)₂](NO₃)₂ **{[2](NO₃)₂}**. O₂ was bubbled through a H₂O solution (30 mL) of [1](NO₃) (381 μmol) at 0–5 °C for 30 min to form [2](NO₃)₂. The pH of the resulting solution was adjusted to 7.2 by addition of one equivalent of NaOH (0.10 M NaOH aqueous solution, 1.88 mL, 188 μmol) to **2** because this complex is stable at neutral pH. Then the solvent was removed under reduced pressure and a brown powder was obtained (126 mg, 188 μmol, yield: 99%). ESI-MS (in H₂O): *m/z* 521.9 **{[2 + OH]⁺}**, relative intensity (*I*) = 100% in the range of *m/z* 200–2000}. Anal. Calcd for C₂₀H₃₀N₂O₈Ru₂·NaOH·H₂O: C, 34.99; H, 4.84; N, 4.08. Found: C, 34.98; H, 4.50; N,

4.43. SQUID: diamagnetic.

Isotope Labelling Experiment with $^{16}\text{O}_2$ in H_2^{18}O . $^{16}\text{O}_2$ was bubbled through a H_2^{18}O solution (500 μL) of [1](NO_3) (2.4 μmol) at 0–5 $^\circ\text{C}$ to form $[\text{Ru}_2^{\text{IV}}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-}^{18}\text{O})_2](\text{NO}_3)_2$ {[^{18}O -labeled 2](NO_3) $_2$ }. ESI-MS (in H_2^{18}O): m/z 527.9 ([^{18}O -labeled 2 + ^{18}OH] $^+$, $I = 100\%$ in the range of m/z 200–2000). This result indicates that oxido ligands of 2 can be exchanged for external H_2^{18}O .

Isotope Labelling Experiment with $^{18}\text{O}_2$ in H_2^{16}O . $^{18}\text{O}_2$ was bubbled through a H_2O solution (500 μL) of [1](NO_3) (2.4 μmol) at 0–5 $^\circ\text{C}$ to form $[\text{Ru}_2^{\text{IV}}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-O})_2](\text{NO}_3)_2$ {[2](NO_3) $_2$ }. ESI-MS (in H_2O): m/z 521.9 ([2 + OH] $^+$, $I = 100\%$ in the range of m/z 200–2000). This result indicates that oxido ligands of ^{18}O -labeled 2 can be exchanged for external H_2O .

Catalytic Oxidation of CH_4 by O_2 with Complex 2 in H_2O under UV Light Irradiation. A H_2O solution (2.0 mL) of [2](NO_3) $_2$ (1.0 mM) under CH_4 (4 MPa) and O_2 (2 MPa) atmospheres was irradiated by UV light (250–385 nm, 15 mW/cm^2) for 5 h. After the reaction, 1.0 mL of the resulting solution was passed through a silica gel column (300 mg) to remove the Ru complex(es). The metal-free aqueous solution was adjusted to 2.0 mL by addition of H_2O , then analysed by GC-MS. The amounts of CH_3OH and HCHO were determined by calibration curves. The turnover numbers (TONs) of CH_3OH and HCHO were estimated as follows: (mol of CH_3OH)/(mol of 2) for CH_3OH and (mol of HCHO) $\times 2$ /(mol of 2) for HCHO . The TONs of CH_3OH and HCHO were determined as 1.1 and 3.0, respectively. Thus, the total TON was calculated as 4.1. No HCOOH was observed by GC-MS whose limit of detection was less than 0.02 mM, corresponding to a TON of 0.06. The yields of CH_3OH and HCHO based on CH_4 were determined to be 0.12 and 0.17%, respectively. After more than 5 h irradiation of UV light, complex 2 was decomposed, which was confirmed by ESI-MS (Fig. S8). Control experiments were conducted without 2, UV light (250–385 nm), CH_4 , or O_2 , showing no product formation. When visible light (385–740 nm, 15 mW/cm^2) was used instead of UV light, no reaction occurred.

Isotope Labelling Experiment for Catalytic Oxidation of CH_4 by O_2 with Complex 2 in H_2^{18}O under UV Light Irradiation. A H_2^{18}O solution (300 μL) of [2](NO_3) $_2$ (1.0 mM) under CH_4 (4 MPa) and $^{16}\text{O}_2$ (2 MPa) atmospheres was irradiated by UV light (250–385 nm) for 5 h. After the reaction, the resulting solution was passed

through a silica gel column (60 mg) to remove the Ru complex(es), and the metal-free aqueous solution was analysed by GC-MS, showing $\text{CH}_3^{16}\text{OH}$ formation without $\text{CH}_3^{18}\text{OH}$.

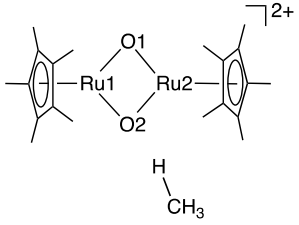
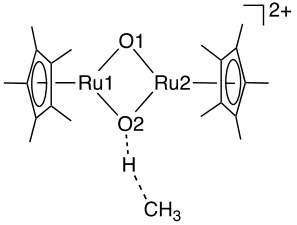
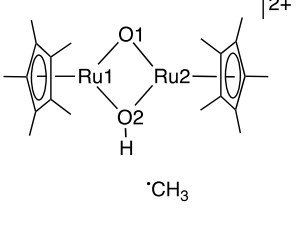
Catalytic Oxidation of CH_3OH by O_2 with Complex **2 in H_2O under UV Light Irradiation.** A H_2O solution (2.0 mL) of $[\mathbf{2}](\text{NO}_3)_2$ (1.0 mM) and CH_3OH (2.0 mM) was irradiated by UV light (250–385 nm, 15 mW/cm²) for 5 h. After the reaction, 1.0 mL of the resulting solution was passed through a silica gel column (300 mg) to remove the Ru complex(es). The metal-free aqueous solution was adjusted to 2.0 mL by addition of H_2O , then analysed by GC-MS. The amounts of CH_3OH and HCHO were determined by calibration curves. The TON of HCHO was determined as 1.1 and it was confirmed that the unreacted CH_3OH remained as is. No HCOOH was observed by GC-MS whose limit of detection was less than 0.02 mM, corresponding to a TON of 0.04. Control experiments were conducted without **2**, UV light (250–385 nm), CH_3OH , or O_2 , showing no product formation. When visible light (385–740 nm, 15 mW/cm²) was used instead of UV light, no reaction occurred.

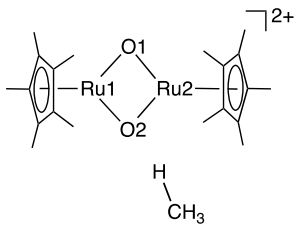
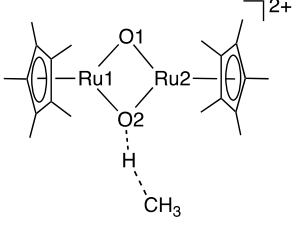
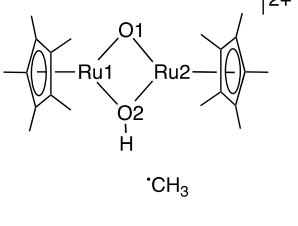
Catalytic Oxidation of C_2H_6 by O_2 with Complex **2 in H_2O under UV Light Irradiation.** A H_2O solution (2.0 mL) of $[\mathbf{2}](\text{NO}_3)_2$ (1.0 mM) under C_2H_6 (2 MPa) and O_2 (1 MPa) atmospheres was irradiated by UV light (250–385 nm, 15 mW/cm²) for 5 h. After the reaction, 1.0 mL of the resulting solution was passed through a silica gel column (300 mg) to remove the Ru complex(es). The metal-free aqueous solution was adjusted to 2.0 mL by addition of H_2O , then analysed by GC-MS. The amounts of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO were determined by calibration curves. The TONs of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO were estimated as follows: (mol of $\text{C}_2\text{H}_5\text{OH}$)/(mol of **2**) for $\text{C}_2\text{H}_5\text{OH}$ and (mol of CH_3CHO) \times 2/(mol of **2**) for CH_3CHO . The TONs of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO were determined as 0.31 and 0.46, respectively. Thus, the total TON was calculated as 0.77. A trace amount of CH_3COOH was observed. Control experiments were conducted without **2**, UV light (250–385 nm), CH_4 , or O_2 , showing no product formation. When visible light (385–740 nm, 15 mW/cm²) was used instead of UV light, no reaction occurred. Because the maximum pressure of C_2H_6 is 2 MPa in technical aspects, C_2H_6 oxidation was not conducted at the same pressure as CH_4 oxidation (4 MPa).

Computational Method. All full-optimized structures were obtained by using the UB3LYP functional^{2,3} as implemented in the Gaussian 16 packages.⁴ The SDD basis set⁵

was used for the Ru atom, and the D95** basis set⁶ was used for the C, O, and H atoms. By calculating the analytical harmonic vibration frequencies, we confirmed that the obtained local minima and transition states have none and one imaginary frequency, respectively. The contribution of zero-point energy corrections and the Grimme-D3 dispersion energy corrections⁷ were included to predict reliable energetics. To obtain UV spectra and excited states, TD-DFT⁸ calculations were carried out.

Table S1 Calculated Mulliken spin densities for the H atom abstraction of CH₄ in the excited triplet state (**T₂₇**) and the ground singlet state (**S₀**).

excited triplet (T₂₇)			
	3R*	3TS*	3P*
Ru1	0.63	0.70	0.91
Ru2	0.56	0.13	-0.07
O1	0.23	0.35	0.23
O2	0.24	0.32	0.06
C	0.00	0.52	1.00

ground singlet (S₀)			
	1R	1TS	1P
Ru1	-0.79	-0.57	-0.68
Ru2	0.77	-0.07	-0.07
O1	0.01	-0.28	-0.30
O2	0.03	0.25	0.03
C	0.00	0.61	0.94

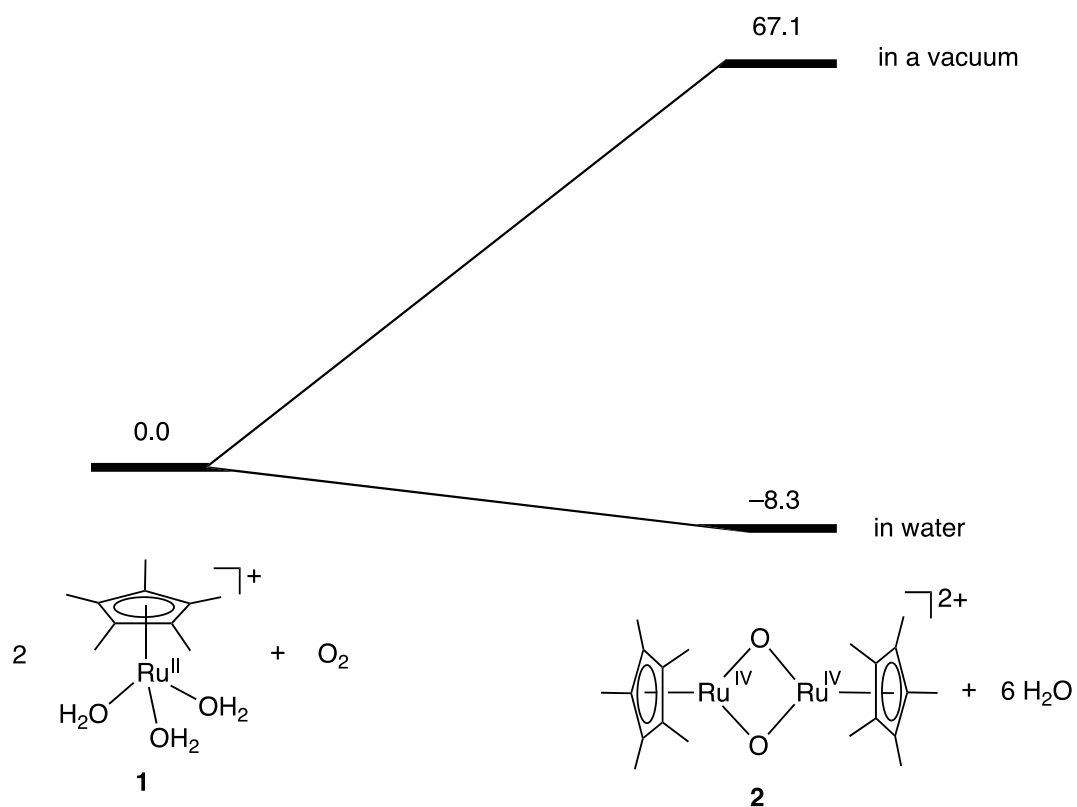


Fig. S1 Energy profiles for the formation of the bis(μ -oxido)Ru₂^{IV} complex **2** starting from the Ru^{II} triaqua complex **1** in the ground states in vacuum and water using the polarizable continuous model (PCM). The relative energies calculated from the dissociation limit of the bimolecular **1** and O_2 are given in units of kcal/mol.

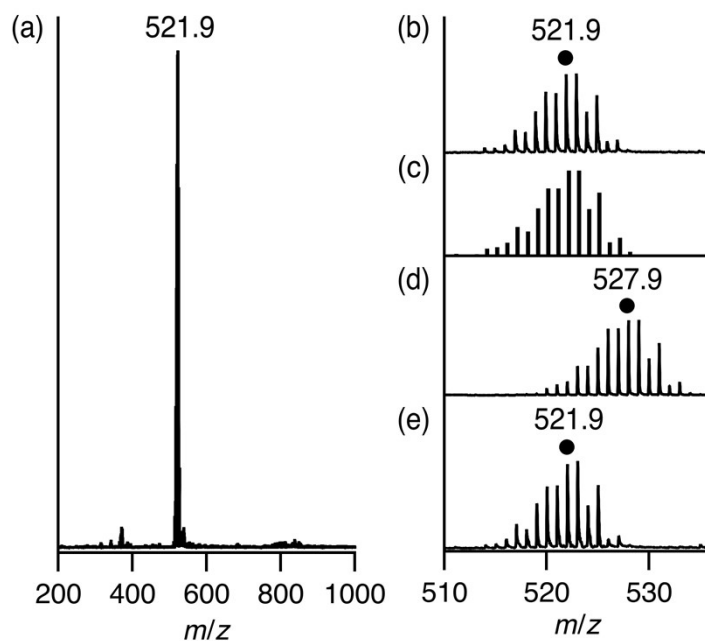


Fig. S2 (a) A positive-ion ESI mass spectrum of **2** in H₂O. (b) A signal at m/z 521.9 for [2 + OH]⁺. (c) A calculated isotopic distribution for [2 + OH]⁺. (d) A positive-ion ESI mass spectrum of ¹⁸O-labeled **2** in H₂¹⁸O, which is obtained from the reaction of **1** with O₂ in H₂¹⁸O. (e) A positive-ion ESI mass spectrum of **2** in H₂O, which is obtained from the reaction of **1** with ¹⁸O₂ in H₂O.

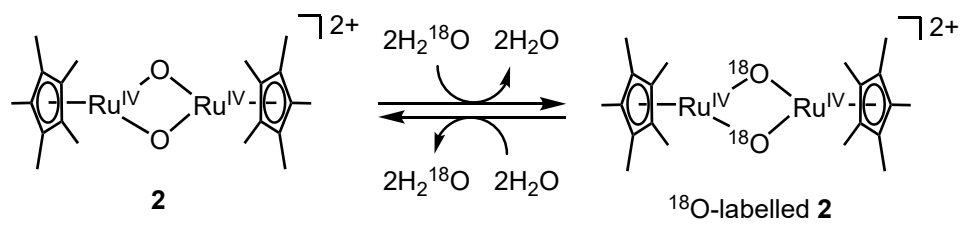


Fig. S3 Exchange of H_2^{18}O with oxido ligands in a bis(μ -oxido) Ru^{IV}_2 complex, and *vice versa*.

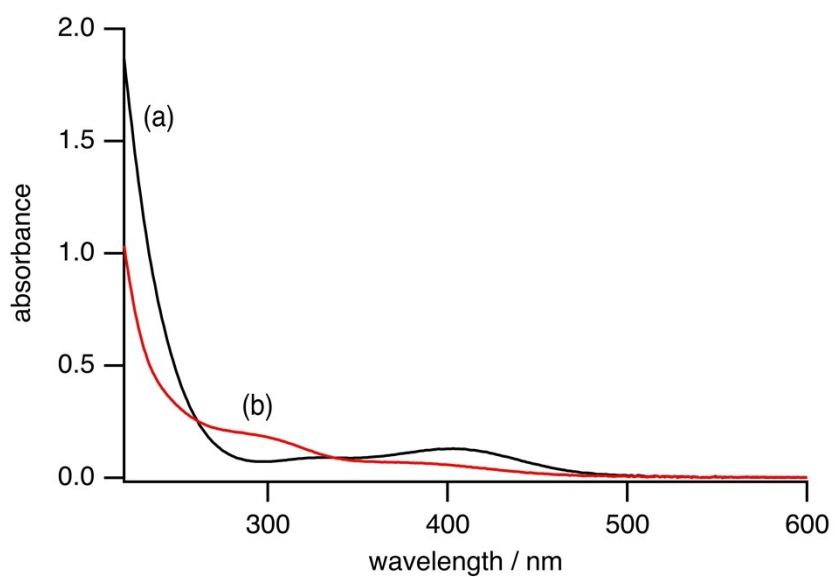


Fig. S4 UV-vis spectra of (a) $[\text{Ru}^{\text{II}}(\eta^5\text{-C}_5\text{Me}_5)(\text{H}_2\text{O})_3]^+$ (**1**) in H_2O (1.0 mM) (black line) under a N_2 atmosphere and (b) $[\text{Ru}_2^{\text{IV}}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-O})_2]^{2+}$ (**2**) in H_2O (0.50 mM) (red line) under an O_2 atmosphere.

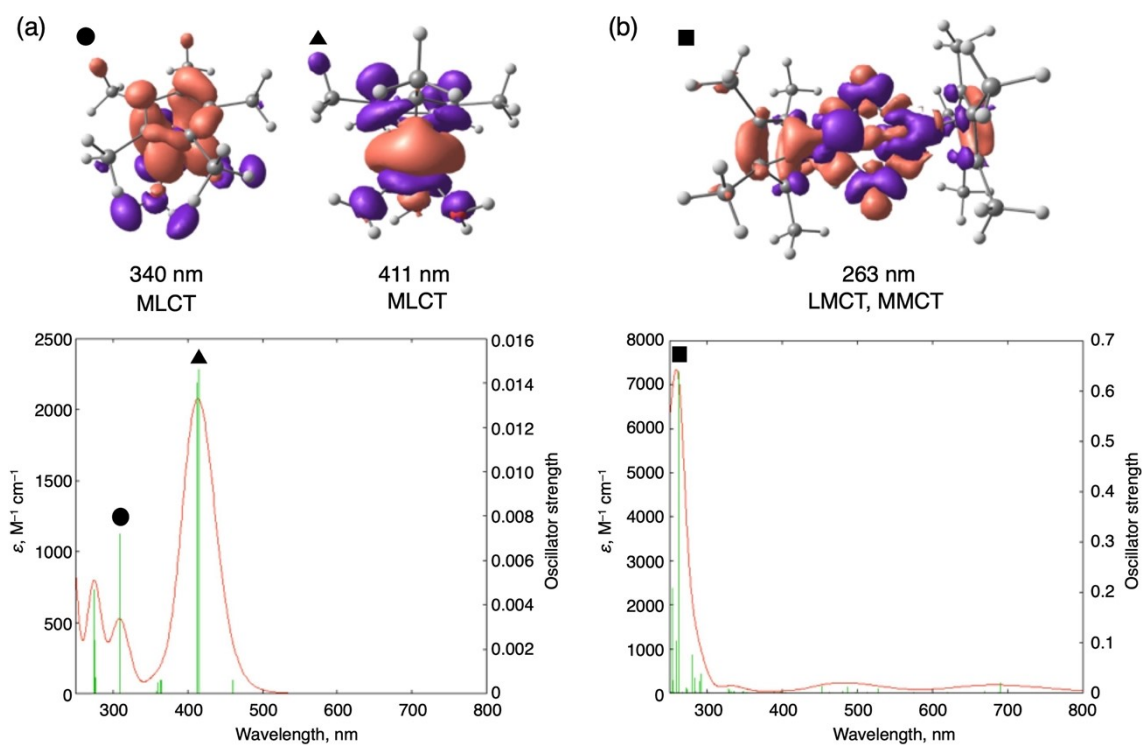


Fig. S5 Computed UV-vis spectra of (a) complex 1 and (b) complex 2 with electron-density difference pictures. Orange: electron-density decrease; purple: electron-density increase. As a result of the charge transfer, the electron density in the orange region is decreased while that in the purple region is increased. Absorptions shown in the calculated spectra as the circle, triangle, and rectangle were assigned to respective transitions depicted as orbital distributions above. MLCT: metal-to-ligand charge-transfer. LMCT: ligand-to-metal charge-transfer. MMCT: metal-to-metal charge transfer.

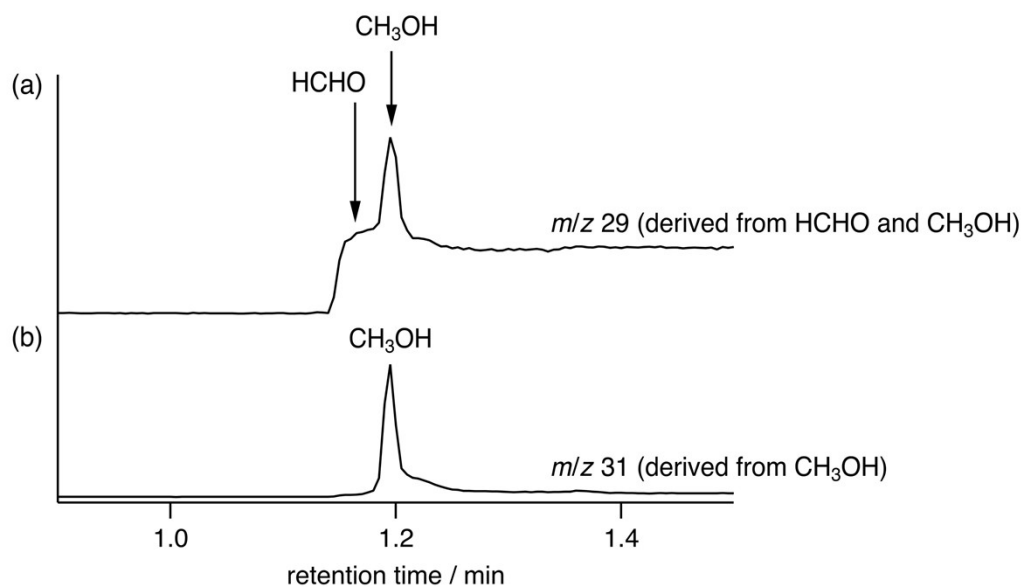


Fig. S6 GC-MS data of CH₃OH and HCHO obtained from the photo-induced oxidation of CH₄ by [Ru₂^{IV}(η⁵-C₅Me₅)₂(μ-O)₂]²⁺ (**2**) in H₂O. GC-MS analysis for (a) m/z 29 derived from HCHO and CH₃OH and (b) m/z 31 derived from CH₃OH.

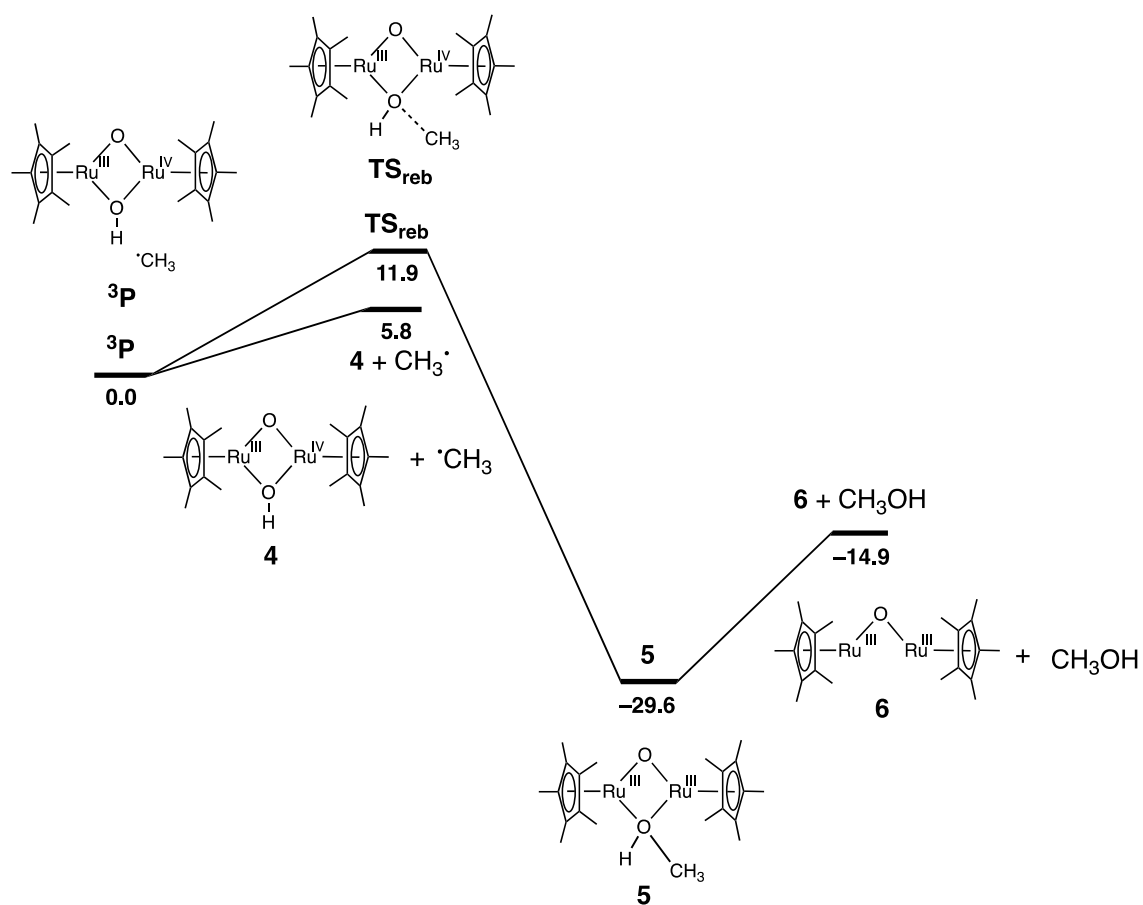


Fig. S7 Energy profile for the reaction of the $(\mu\text{-hydroxido})(\mu\text{-oxido})\text{Ru}_2^{\text{III,IV}}$ complex **4** and methyl radical (CH_3^\bullet) in the triplet state. The relative energies calculated from the complex **3P** are given in units of kcal/mol.

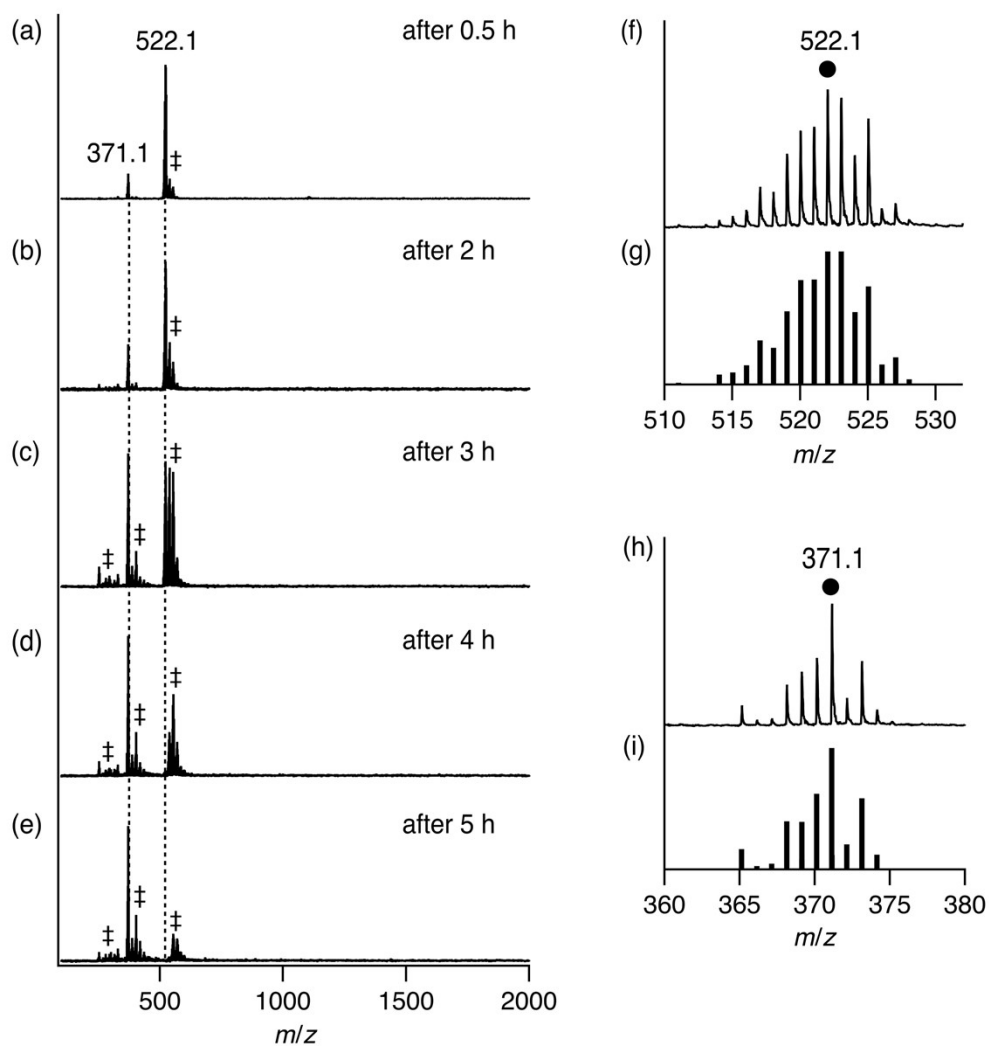


Fig. S8 Positive-ion ESI mass spectra obtained from the reaction of $[\text{Ru}_2^{\text{IV}}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-O})_2]^{2+}$ (**2**) with CH_4 and O_2 in H_2O under light irradiation for (a) 0.5 h, (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h. (f) A signal at m/z 522.1 for $[\mathbf{2} + \text{OH}]^+$. (g) A calculated isotopic distribution for $[\mathbf{2} + \text{OH}]^+$. (h) A signal at m/z 371.1 for $[\text{Ru}^{\text{II}}(\text{tetramethylfulvene})(\eta^5\text{-C}_5\text{Me}_5)]^+$. (i) A calculated isotopic distribution for $[\text{Ru}^{\text{II}}(\text{tetramethylfulvene})(\eta^5\text{-C}_5\text{Me}_5)]^+$. ‡: Unidentified species.

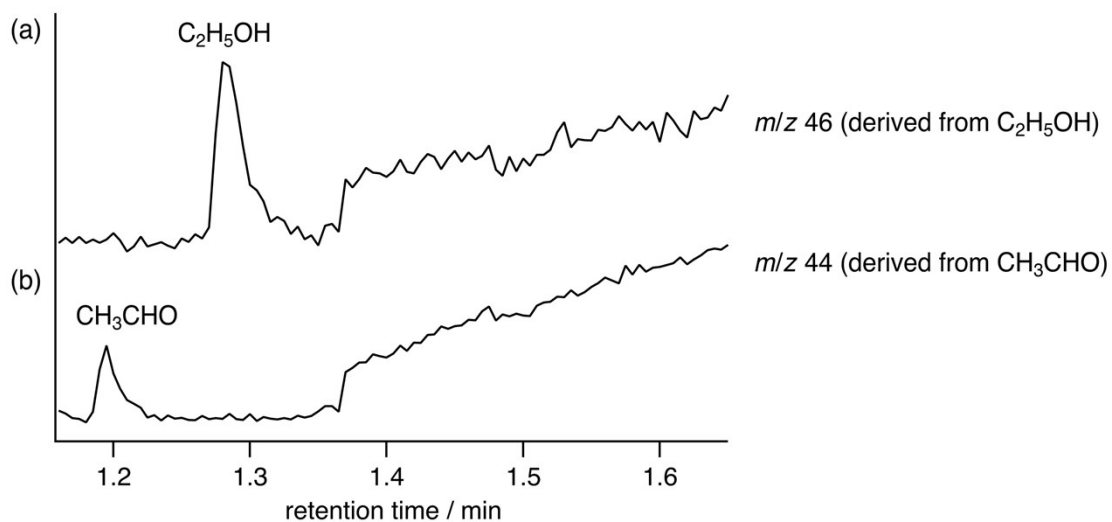


Fig. S9 GC-MS data of C_2H_5OH and CH_3CHO obtained from the photo-induced oxidation of C_2H_6 by $[Ru_2^{IV}(\eta^5-C_5Me_5)_2(\mu-O)_2]^{2+}$ (**2**) in H_2O . GC-MS analysis for (a) m/z 46 derived from C_2H_5OH and (b) m/z 44 derived from CH_3CHO .

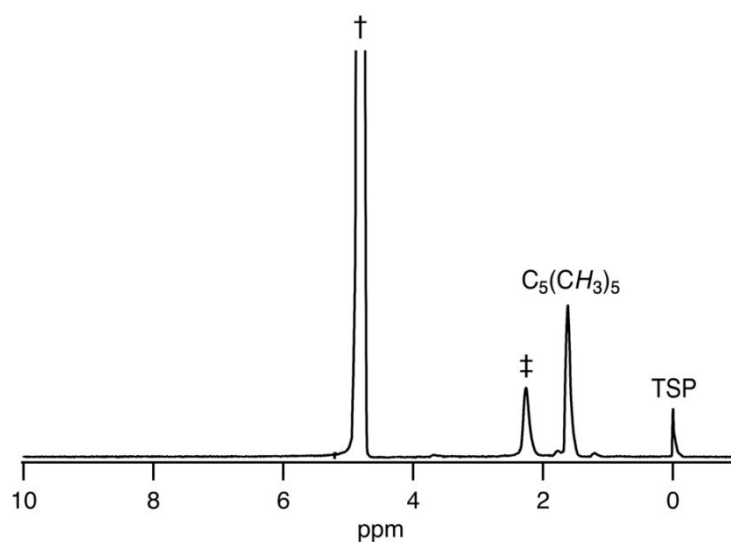


Fig. S10 ^1H NMR spectrum of $[\text{Ru}^{\text{II}}(\eta^5\text{-C}_5\text{Me}_5)(\text{H}_2\text{O})_3](\text{NO}_3)$ $\{[\mathbf{1}](\text{NO}_3)\}$ in D_2O under a N_2 atmosphere, in which H_2O ligands should be D_2O ligands because of the use of D_2O as a solvent. 3-(Trimethylsilyl)-propionic-2,2,3,3- d_4 acid sodium salt (TSP), referenced with the methyl proton resonance set at 0.00 ppm. †: water. ‡: free acetonitrile released from Ru center, which was confirmed by comparison with free acetonitrile.

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