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1. Supplementary Methods

I. General Techniques

a. General manipulations

All experiments were performed under an inert atmosphere of argon using standard Schlenk and vacuum-line techniques or in an MBraun glove box. Glassware was flame dried under high vacuum or dried at 120 °C overnight and cooled under HV prior to use. All reagents were used as received from commercial suppliers unless stated otherwise. *N*,*N'*-dimethylethylenediamine was purified by vacuum distillation. Dry solvents were obtained from an Innovative Technology solvent purification system and stored under argon. Deuterated solvents were purchased from Eurisotope and Cambridge Isotope Laboratories Inc., distilled with the proper drying agent and stored under argon with 3 Å (acetonitrile, ethanol[D6]) 4 Å (other solvents) molecular sieves.

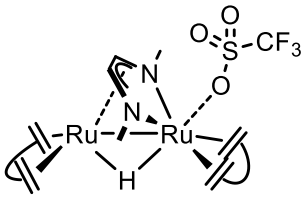
Solution NMR spectra were recorded on Bruker Avance 500, 400, and 300 spectrometers. The chemical shifts (δ) are expressed in ppm relative to TMS for ^{1}H and ^{13}C. Coupling constants *J* are given in Hz as absolute values. Where a first order analysis is appropriate, the multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets. The abbreviation br. is given for broadened signals. Aromatic units are indicated as H^{ar} or C^{ar} when not noted otherwise. Quaternary ^{13}C are indicated as C^{quat}. The olefinic protons and ^{13}C atoms of the two coordinated C=C moieties in dbcot (dibenzo[a,e]cyclooctatetraene) are indicated as H^{olef} and C^{olef}, respectively. The protons and carbon atoms of the diazabutadiene moiety are denoted as H^{dad} and C^{dad}, respectively. [Ru_2 H(μ-H)(Me_2(dad))($dbcot)_2$], [Ru(μ-H)(Me_2(dad))($dbcot)_2$]PF_6, and [Ru(OTf)(μ-H)(Me_2(dad))($dbcot)_2$] were synthesized as reported elsewhere.[S1]

The ICP-OES analysis was performed using a Varian 720 ES ICP-OES with SPS-3 Autosampler. Exhaust solutions were directly injected in the instrument. For calculating the ruthenium content in the **2@C^{k}** catalyst, 5 mg of the sample were dissolved in a PTFE vessel in 8 mL of aqua regia (6 mL of HCl 37% a and 2 mL of HNO_3 conc.). The resulting mixture was then digested in a microwawe oven and diluted to 50 mL adding bidistilled water.

GC-TCD was measured on an Agilent Technology 7890A GC System on a HP-Molsieve (19091P) column.

The scanning transmission electron microscopy (STEM) investigations were performed on the aberration-corrected HD-2700CS (Hitachi; cold-field emitter) or a Jeol F200 equipped with a cold field emission gun and a 16 MPixel camera, both operated at an acceleration potential of 200 kV. On the HD-2700CS, a probe corrector (CEOS) is incorporated in the microscope column between the condenser lens and the probe-forming objective lens providing excellent high-resolution capability (beam diameter ca. 0.1 nm in the selected ultra-high resolution mode). Images (1024 x 1024 pixels) were recorded with a high-angle annular dark field (HAADF) detector with frame times of ca 15 s. These imaging conditions give rise to atomic number (Z) contrast, a highly sensitive method to detect even atoms of strongly scattering elements (high Z) on light supports.

b. Synthesis of [Ru(OTf)(μ-H)(Me$_2$(dad))(dbcot)$_2$] (**2**)



2

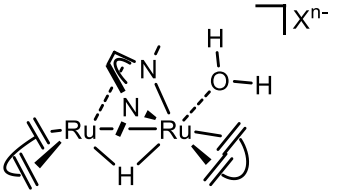
Route 1 (adapted from ref. [S1]): [RuH(μ-H)(Me$_2$(dad))(dbcot)$_2$] **1** (200 mg, 287 μmol) was mixed with tetrahydrofuran (10 mL). A solution of ferrocenium triflate (106 mg in 6 mL THF, 315 μmol) was added dropwise which caused a color change from a yellow dispersion to a brown solution. The mixture was stirred at room temperature for 30 minutes before the solvent was evaporated at reduced pressure. The obtained brown solid was washed with diethylether:dimethoxyethane 9:1 (3x 3 mL). The leftover solid was dissolved in acetonitrile, filtered through a syringe filter (pore size 0.2 μM) and precipitated by layering with diisopropyl ether to obtain a red-brown powder.

Route 2: [RuH(μ-H)(Me$_2$(dad))(dbcot)$_2$] **1** (100 mg, 143 μmol) was mixed with 1,2-difluorobenzene (20 mL). At -10 °C, triflic acid (1.43 mL of a 0.1 M solution in 1,2-difluorobenzene, 143 μmol) was added dropwise over 30 minutes which caused a color change from a yellow to an orange dispersion. The mixture was stirred for additional 15 minutes allowing it to warm to room temperature which caused a further color change to a red-brown solution, before the solvent was evaporated at reduced pressure. The obtained red-brown solid was washed with toluene (3x 2 mL) and 1,2-difluorobenzene (1x 2 mL). Subsequently, the solid was dissolved in acetonitrile and layered with diisopropyl ether. After 24 hours, the product was obtained as a red-brown powder. Yield: 167 mg, 69 %.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.45 (s, 2H, CH^{dad}), 7.08 – 7.04 (m, 2H, H^{ar}), 7.04 – 6.99 (m, 2H, H^{ar}), 6.88 (dddd, J = 16.7, 6.2, 5.3, 3.3 Hz, 6H, H^{ar}), 6.81 – 6.73 (m, 6H, H^{ar}), 4.84 (d, J = 9.1 Hz, 2H, CH^{olef}), 4.47 (d, J = 9.1 Hz, 2H, CH^{olef}), 4.06 (d, J = 8.6 Hz, 2H, CH^{olef}), 4.00 (d, J = 8.6 Hz, 2H, CH^{olef}), 2.02 (d, J = 0.9 Hz, 6H, CH$_3^{dad}$), -7.39 (s, 1H).^{13}C NMR (101 MHz, CD_3CN) δ 147.9 (s, 2C, C^{quat}), 147.5 (s, 2C, C^{quat}), 145.6 (s, 2C, C^{quat}), 143.5 (s, 2C, C^{quat}), 128.6 (2 CH, C^{ar}), 128.3 (2 CH, C^{ar}), 127.3 (2 CH, C^{ar}), 127.3 (2 CH, C^{ar}), 127.0 (2 CH, C^{ar}), 126.8 (2 CH, C^{ar}), 126.7 (2 CH, C^{ar}), 126.2 (2 CH, C^{ar}), 121.0 (s, 2C, CH^{dad}), 84.8 (s, 2C, CH^{olef}), 81.2 (s, 2C, CH^{olef}), 75.9

(s, 2C, CH^{olef}), 69.2 (s, 2C, CH^{olef}), 40.6 (2 CH_3, CH_3^{dad}). ^{19}F NMR (376 MHz, CD_3CN) δ -79.2 (s, OTf). MALDI HRMS (m/z): $\{Ru_2(Me_2dad)(dbcot)_2H\}^+$ calcd. For $C_{36}H_{33}N_2Ru_2$ 697.0725; found: 697.0732.

c. Synthesis of $[Ru(OH_2)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]^+{}_3(HSO_4^-)(SO_4^{2-})$ (**3a**)



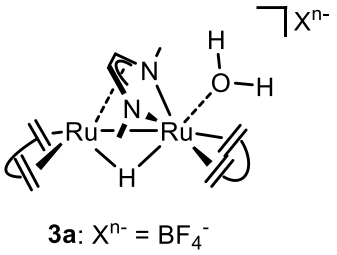
3a: X^{n-} = $^1/_2$ SO_4^{2-}, HSO_4^-

A 50% solution of sulfuric acid in water was degassed by bubbling argon through for 2 minutes. The acid solution (52 µl, 373 µmol) was dropwise added to a stirred dispersion of $[RuH(\mu\text{-}H)(Me_2(dad))(dbcot)_2]$ **1** (130 mg, 187 µmol) in THF (5 mL, 35 mM). The mixture was heated to 60 °C for 1 hour whereby it turned deeply red. The mixture was cooled to r.t. overnight whereby a red solid precipitated. The solid was washed with THF (3x1mL) and hexanes (3x1mL). After drying at HV overnight, a brightly red solid of the composition $[Ru(OH_2)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]HSO_4 \cdot 0.34\ THF \cdot 1.25\ H_2SO_4$ was obtained. Yield: 110 mg, 62 %.

^1H NMR (500 MHz, Acetonitrile-d_3) δ 7.48 (s, 2H, NCH), 7.46 – 7.32 (s (br), 4H, H_2O/H_3O^+), 7.06 (dd, J_{HH} = 5.6, 3.4 Hz, 2H, H^{ar}), 7.04 – 6.98 (m, 2H, H^{ar}), 6.94 – 6.84 (m, 6H, H^{ar}), 6.84 – 6.72 (m, 6H, H^{ar}), 4.84 (d, J_{HH} = 9.1 Hz, 2H, H^{olef}), 4.47 (d, J_{HH} = 9.1 Hz, 2H, H^{olef}), 4.06 (d, J_{HH} = 8.6 Hz, 2H, H^{olef}), 4.00 (dd, J_{HH} = 8.6, 1.0 Hz, 2H, H^{olef}), 2.02 (d, J_{HH} = 0.9 Hz, 6H, CH_3), -7.39 (s, 1H, H_b). ^{13}C NMR (126 MHz, CD_3CN) δ 147.9 (s, 2C, C^{quat}), 147.5 (s, 2C, C^{quat}), 145.6 (s, 2C, C^{quat}), 143.5 (s, 2C, C^{quat}), 128.6 (s, 2C, C^{ar}), 128.3 (s, 2C, C^{ar}), 127.3 (s, 2C, C^{ar}), 127.3 (s, 2C, C^{ar}), 127.0 (s, 2C, C^{ar}), 126.8 (s, 2C, C^{ar}), 126.7 (s, 2C, C^{ar}), 126.2 (s, 2C, C^{ar}), 120.9 (s, 2C, NCH), 84.8 (s, 2C, C^{olef}), 81.2 (s, 2C, C^{olef}), 75.9 (s, 2C, C^{olef}), 69.2(s, 2C, C^{olef}), 40.6 (2, 2C, CH_3^{dad}). IR (ATR-IR): 3171 (br, H_{acidic}), 2966 (m, C-H), 1580 (w, C=C), 1489 (m, C-H), 1406 (m, O-H), 1139 (s, br, Ru-O), 1028 (s, S-O). MALDI HRMS (m/z): $\{Ru_2(Me_2dad)(dbcot)_2H\}^+$ calcd. For $C_{36}H_{33}N_2Ru_2$ 697.0725; found: 697.0729. Elemental analysis calcd for $C_{36}H_{36}N_2O_5Ru_2S \cdot 0.34\ C_4H_8O \cdot 1.25\ H_2SO_4$ was: C 46.84, H 4.34, found: C 46.85, H 4.43.

Crystals suitable for qualitative X-ray diffraction experiments were obtained by heating a 50 mM THF solution to boiling and slowly cooling it down to room temperature over the course of 4 hours. The crystals revealed a composition of three $[Ru(\mu\text{-}H)(OH_2)(Me_2(dad))(dbcot)_2]$ molecules and two SO_4 molecules, but the crystal quality was not sufficient to assign a proton to HSO_4^-. Hence, tetrafluoroborate was chosen as a counterion for crystallization (*vide infra*).

d. Synthesis of [Ru(OH$_2$)(μ-H)(Me$_2$(dad))(dbcot)$_2$]$^+$BF$_4^-$ (**3a**)



3a: $X^{n-} = BF_4^-$

A 50% solution of HBF_4 in water was degassed by bubbling argon through for 2 minutes. The acid solution (36 µl, 287 µmol) was dropwise added to a stirred solution of [RuH(μ-H)(Me$_2$(dad))(dbcot)$_2$] **1** (100 mg, 144 µmol) in 1,2-difluorobenzene (2.9 mL, 50 mM). The mixture was heated to 65 °C for 10 minutes whereby it turned deeply red and a red solid started precipitating from the solution. (Note that the reaction with HBF_4 proceeds faster than with H_2SO_4.) The mixture was left at room temperature overnight which caused more solid to precipitate. The mother liquors removed by aspiration and the obtained solid was dried at HV overnight at 80 °C. The obtained crude product (119 mg, 104 %) was washed with 1,2-difluorobenzene (2x2 mL) and diethyl ether (2x2 mL), before being dried at HV overnight. A brightly red solid of the composition [Ru(OH$_2$)(μ-H) (Me$_2$(dad))(dbcot)$_2$]BF_4 was obtained. Yield: 73 mg, 64 %.

Crystals suitable for X-ray diffraction experiments were obtained by heating a 50 mM THF solution to boiling and slowly cooling it down to room temperature over the course of 4 hours. The title compound precipitated as red crystals from a yellow solution.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.45 (s, 2H, NCH), 7.09 – 7.03 (m, 2H, H^{ar}), 7.05 – 6.98 (m, 2H, H^{ar}), 6.93 – 6.84 (m, 6H, H^{ar}), 6.81 – 6.73 (m, 6H, H^{ar}), 4.84 (d, J_{HH} = 9.1 Hz, 2H, H^{olef}), 4.47 (d, J_{HH} = 9.1 Hz, 2H, H^{olef}), 4.06 (d, J_{HH} = 8.6 Hz, 2H, H^{olef}), 4.00 (dd, J_{HH} = 8.6, 1.0 Hz, 2H, H^{olef}), 2.84 (s, br, 2H, H2O) 2.02 (d, J_{HH} = 0.9 Hz, 6H, CH_3), -7.40 (s, 1H, H_b).

^{13}C NMR (126 MHz, CD_3CN) δ 147.9 (s, 2C, C^{quat}), 147.5 (s, 2C, C^{quat}), 145.6 (s, 2C, C^{quat}), 143.5 (s, 2C, C^{quat}), 128.6 (s, 2C, C^{ar}), 128.3 (s, 2C, C^{ar}), 127.3 (s, 2C, C^{ar}), 127.3 (s, 2C, C^{ar}), 127.0 (s, 2C, C^{ar}), 126.8 (s, 2C, C^{ar}), 126.7 (s, 2C, C^{ar}), 126.2 (s, 2C, C^{ar}), 120.9 (s, 2C, NCH), 84.8 (s, 2C, C^{olef}), 81.2 (s, 2C, C^{olef}), 75.9 (s, 2C, C^{olef}), 69.2 (s, 2C, C^{olef}), 40.6 (2, 2C, CH_3^{dad}). Elemental analysis calcd (%) for $C_{36}H_{35}BF_4N_2ORu_2$ was: C 54.01, H 4.41, N 3.50 found: C 53.90, H 4.44, N 3,53.

e. Synthesis of IrO_2

The IrO_2 anode for the complete electrolysis cell was synthetized as described in [S2]. In brief, 247 mg of $IrCl_3$*$3H_2O$ (0.7 mmol) were dissolved in 50 mL of ethylene glycol in presence of 700 mg of polyvinyl-pirrolidone (PVP). The solution was heated at 120°C for one hour to evaporate residual water and then was refluxed for 60 minutes under magnetic stirring. The solution was concentrated, cooled down and poured in a crucible, which was placed in a muffle furnace heated at 400°C for one hour (heating ramp: 7°C min^{-1}). The resulting solid was milled in an agate mortar.

f. Crystallographic structures

X-ray diffraction experiments were performed on a XtaLAB SynergyDualflex diffractometer, equipped with a Pilatus 300K hybrid pixel detector and a copper (1.5406 Å) microfocus tube and a Bruker D8 Venture Dual source diffractometer equipped with a PhotonII detector, respectively. Suitable crystals were selected, protected by polybutene oil and mounted under a cold nitrogen stream. The crystals were kept at 100 K during data collection. The data reduction was performed using CrysAlisPro and Apex3, respectively.. Using Olex2[S3], the structures were solved with SHELXT[S4], followed by least-squares refinement against full matrix (versus F2) with SHELXL.[S5] All non-hydrogen atoms were refined anisotropically. The crystal structures of [Ru(OH_2)(μ-H) (Me_2(dad))(dbcot)$_2$]BF_4 and [Ru($NCCH_3$)(μ-H) (Me_2(dad))(dbcot)$_2$]PF_6 are reported in figure 1 in the main text, crystal data and further crystallographic details are reported in table S1 and S2.

g. DFT caluclations

All calculations were carried out with ORCA 4.2.0.[S6,S7] Geometry optimizations were performed at the PBE0-D3BJ/def2-SVP/def2-TZVP(Ru) level of theory.[S7-S13] Solvent effects were taken into account implicitly by using the cpcm model with water as solvent and a gaussian charge scheme.[S14,S15] Numerical frequency calculations were carried out to confirm the nature of stationary points found by geometry optimizations. The RIJCOSX approximation was used for density functional theory (DFT) calculations. [S16,S17] Approximate transition states were generated using the nudged elastic band (NEB) method implemented in ORCA, followed by a saddle-point optimization. Cartesian coordinates of optimized molecular structures are reported in table S4.

h. XPS

XPS experiments were carried out in an UHV chamber with a base pressure lower than 10^{-10} mbar. The chamber was equipped with non-monochromatized Al (hν = 1486.6 eV) radiation and with a hemispherical electron/ion energy analyser (VSW mounting a 16-channel detector). The operating power of the X-ray source was 150 W (15 kV and 10 mA). Photoelectrons were collected normal to the sample surface and the analyser maintaining as well the angle between the analyser axis and the X-ray source fixed at 54.5°. All the samples were drop cats on gold on mica and all the XPS spectra were measured in fixed analyser transmission mode with pass energy of 44 eV. The binding energy (BE) was calibrated setting the Au*4f7/2* peak at 83.9 eV.

II. Complex impregnation on carbon black

The impregnation procedure was adapted from previous works.[S18-S20] In a 100 mL Schlenk round bottom flask purged with N_2 and vacuum, 36.0 mg (0.04 mmol) of $[Ru_2(OTf)(\mu\text{-}H)(Me_2dad)(dbcot)_2]$ were dissolved at room temperature in 15 mL of distilled acetonitrile. 214 mg of carbon black Ketjen Black EC-600-JD (C^k) (Akzo-Nobel) were milled in an agate mortar and suspended at room temperature in 60 mL of acetonitrile in a 100 mL round bottom Schlenk tube by 30 min of magnetic stirring. The two solutions were mixed together under nitrogen flow and the resulting suspension was homogenized at room temperature by 1 hour of magnetic stirring.

The solvent was slowly evaporated under vacuum at 50 °C keeping on the magnetic stirring, in order to obtain homogeneous complex dispersion on carbon. The so obtained catalytic powder was then vacuum dried at 50 °C for 1 hour. Table S5 summarizes the reagent amounts used in the synthesis.

The dry catalyst has a 12.4 wt% complex content (3.06 wt% Ru) and was stored under nitrogen atmosphere prior to use in electrochemical experiments.

A diluted catalyst was synthetized with the same impregnation procedure just adapting the reactants amounts, as described in table S6. The dry catalyst has a 1.86 wt% complex content (0.44 wt% Ru content) with a dilution of seven time respect the concentrated one.

III. Experimental apparatus used in the catalyst electrochemical characterization in half cell

a. General techniques

All the glassware was cleaned with a H_2O_2/H_2SO_4 conc. solution overnight and rinsed several times with Milli-Q water prior to use. The working electrode, a glassy carbon disk (0.1963 cm^2) embedded in a PTFE jacket (PINE™) was cleaned by stirring overnight in a 0.05 µm alumina aqueous suspension. After the treatment, the electrode was washed in sequence, in acetone, 2-propanol and Milli-Q water. All the solutions were prepared with Milli-Q water (18.5 MΩ*cm at 25°C) provided with a Millipore Milli-Q^3 apparatus (Nihon Millipore Ltd.). Chemicals were used as purchased from Sigma-Aldrich/Merk unless as differently mentioned. All electrochemical studies were carried out at room temperature (20-25°C) using a Parstat 2273 potentiostat–galvanostat (Princeton Applied Research) equipped with a Model 616 Rotating Disk Electrode (PAR/Ametek).

Polarization and chronoamperometric experiemts in aqueous environment were acquired in a standard pyrex® three-electrode cell experiments (Princeton Applied Research). The reference electrode was a commercial $Ag/AgCl/KCl_{sat}$ (Princeton Applied Research) and the counter electrode was a gold gauze enclosed in a glass tube with porous bottom. The working electrode WE was coated

with a drop of the catalyst ink (c.a. 9 µL) by means of a micropipette. The catalyst layer was then dried under air and the final catalyst amount in the deposit was determined using an analytical balance; the resulting metal loading onto the WE spans from 6.3 to 7.5 μg_{Ru} cm^{-2}. All the potentials were reported versus the Reference Hydrogen Electrode RHE without compensating the resistance.

b. Polarization experiments

Polarization (LSV) experiments were performed in a 1 M $H_2PO_4^-/HPO_4^{2-}$ buffer solution (pH 7.4) or 0.25 M $HClO_4$ aqueous solution (pH 0.6) saturated with hydrogen (30 minutes of pure hydrogen bubbling) with 1 mV s^{-1} scan rate, rotating the WE at 1600 rpm. The hydrogen evolution reaction was investigated performing the scans between 0.1 and -0.5 V vs RHE.

c. Chronoamperometric experiments

Chronoamperometries (potentiostatic experiments) were carried out in a 1 M $H_2PO_4^-/HPO_4^{2-}$ buffer solution (pH 7.4) or 0.25 M $HClO_4$ aqueous solution (pH 0.6) purged with nitrogen. The experiments were performed at the constant potential of 300 mV vs RHE rotating the working electrode at 1600 rpm for one hour.

d. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measures were carried out in a 0.25 M H_2SO_4 solution, under N_2 atmosphere (30 minutes of pure nitrogen bubbling), with frequency range spanning from 100 KHz to 0.01 Hz. Measures were acquired at OCP condition and at – 300 mV vs RHE, with a DC amplitude of 10 mV. Data were analyzed with Z-view software.

e. Ink preparation

The ink was prepared in a 5 mL glass vial suspending the milled catalyst in 600 mg of Milli-Q water, 600 mg of ethanol (purity 99%) and 12 mg of a 5% wt Nafion® solution in 2-propanol. The mixture was treated for 30 minutes with ultrasounds (59 Hz, 100 W) and then was stored under magnetic stirring. A fresh ink was prepared before each set of measurements.

Table S7 describe the $[Ru_2(OTf)(\mu\text{-}H)(Me_2dad)(dbcot)_2]/C^k$ ink preparation; catalysts concentration in the ink is c.a. 0.53 wt%.

IV. Experimental apparatus used in electrolysis experiments.

a. General techniques

Electrolysis experiments were performed in a Scribner cell (Scribner ass.) modified in our laboratory with stainless steel collector plates stable in acidic environment at potentials higher than 1.2 V. Cell

temperature was controlled with a Scribner 850c testing station (Scribenr ass.) and the anodic and cathodic compartments were fed respectively with 50 mL of Milli-Q water and 50 mL of a 0.1 M H_2SO_4 solution or H_2O by means of a multichannel peristaltic pump (Gilson minipulse 3) with 1 mL min^{-1} flow rate; exhaust fuels were collected in a closed vessel and recirculated in the cell. The cathodic vessel head was equipped with a flow meter to quantify the hydrogen produced during the electrolysis experiments.

The electrochemical measurements were performed with an Arbin LBT21084 multichannel potentiostat-galvanostat and the hydrogen amount produced during electrolysis was quantified with a Brockhorst El-Flow (3 mL min^{-1} or 1 L min^{-1}) flow meter.

b. MEA (Membrane Electrode Assembly) fabrication

The Membrane Electrode Assembly was obtained sandwiching a Nafion 117 membrane between the anode and the cathode in a 5 cm^2 Scribner cell fixture using a 4 Nm screwing torque.

The anode was realized mixing in an agate mortar 40 mg of IrO_2 with 20 mg of C^k and 100 mg of a Nafion 5%wt ionomer solution in low aliphatic alcohols; the resulting paste was spread onto a woven-non-woven titanium web conductive support (5 cm^2, Beakert). The electrode has the 66.6% wt IrO_2 loading (c.a. 7 $mg_{catalyst}$ cm^{-2}) and the 3% wt of pure Nafion amount.

Cathodes were obtained mixing 200 mg of the Nafion 5% wt. ionomer with 60 mg of $[Ru_2(OTf)(\mu\text{-}H)(Me_2dad)(dbcot)_2]$ /C^k catalyst (3.06% wt. Ru or 0.445% wt. Ru); the so obtained dense paste was spread onto a 5 cm^2 carbon cloth gas diffusion layer (CeTech). The resulting cathode has a total Nafion content of ca. 3.9 wt% and a Ru content of ca. 1 mg_{Ru} cm^{-2} **2@C^k** or 0.04 mg_{Ru} cm^{-2} for the seven time diluted catalyst **2$_{dil}$@C^k**.

V. Hydrogen and energy consumption quantification

The electrolysis efficiency in hydrogen production was calculated evaluating the hydrogen evolution reaction faradic efficiency FE as described in Eq.1.

$$FE\ (\%) = \frac{mol_{H_2}^{real}}{mol_{H_2}^{theoretic}} * 100 \qquad \text{Eq.1}$$

The real hydrogen amount produced during the electrolysis was calculated with the flow meter placed at the cell outlet while the theoretic amount was calculated electrochemically applying the Faraday's law (Eq.2) assuming 100% of coulombic efficiency for hydrogen evolution reaction (HER): I is the

current load applied to the cell during the experiment, F is the Faraday's constant (96485.3 C mol^{-1}) and 2 is the number of electrons moles involved in HER.

$$mol_{H_2}^{theoretic} = 2F \int I(t)\, d(t) \qquad \text{Eq.2}$$

The cell energy consumption required for electrolysis was calculated integrating over time the charging energy and dividing this value with the total hydrogen amount produced (expressed in kg_{H_2}) as described in Eq.3.

$$Energy\ consuption\ (kWh\ kg_{H_2}^{-1}) = \frac{\int V(t)I(t)\, d(t)}{kg_{H_2}^{real}} \qquad \text{Eq.3}$$

VI. Model reactions

a. In situ catalytic turnover

In a J-Young NMR tube with a Teflon screw-cap, [Ru(μ-H)(Me_2(dad))(dbcot)$_2$]PF_6 (6 mg, 7.1 μmol, 1 eq.) was mixed with THF-*d*8 (0.4 mL). After recording a ^{1}H-NMR spectrum, KC_8 (1.9 mg, 14 μmol, 2.0 eq.) was added to the top of the tube, which was closed and shaken. A ^{1}H-NMR spectrum was acquired and D_2O (0.15 μL, 7.5 μmol, 1.1 eq.) was added to the tube. After measuring ^{1}H-NMR, H_2SO_4 (50%, 1 drop) was added and the tube heated to 80 °C for 2 hours during which red crystals formed. NMR shows the formation of a new complex and the crystals were found to be of composition [Ru(OH_2)(μ-H)(Me_2(dad))(dbcot)$_2$]$_3$(SO_4^{2-})(HSO_4^-).

b. Verification of Stoichiometric H_2 Production by GC-TCD

In a 10 mL Schlenk tube capped with a rubber septum, [RuH(μ-H)(Me_2(dad))(dbcot)$_2$] (30 mg, 43 μmol, 1 eq.) was dissolved in THF (3 mL). Degassed sulfuric acid (50%, 0.2 mL, 10 eq.) was added and the stopcock closed. The mixture was heated to 80 °C for 1 hour, before a sample was taken from the headspace via syringe. The sample was subjected to GC-TCD, which allowed the identification of H_2 by its retention time.

c. Recovery of the exhaust cathode after electrolysis experiments

The exhaust catalyst **2@C^k** was recovered after the electrolysis experiments scratching the catalytic powder with a spatula from the electrode; the recovered amount was washed three times with

bidistilled water and dried under vacuum at room temperature. The powder was suspended in dry CD_3CN (c.a. 2 mL) by one hour of magnetic stirring under nitrogen atmosphere and the suspension was filtered over a celite plug. The brown filtrate was collected into a 5 mm NMR tube (under nitrogen) and subjected to ^{1}H-NMR analysis (figure S2). The spectrum shows the characteristic (**3c**) signals: (δ 7.46 (s, 2H, CH^{dad}), 7.35-7.18 (m, 2H, CH^{ar}), 7.13-7.02 (m, 2H, CH^{ar}), 6.92-6.85 (m, 8H, CH^{ar}), 6.84-6.74 (m, 2H, CH^{ar}), 6.75-6.61 (m, 2H, CH^{ar}), 4.86 (d, J_{HH} = 9.1 Hz, 2H, CH^{olef}), 4.78 (d, JHH = 9.3 Hz, 2H, CH^{olef}), 4.08 (d, J_{HH} = 8.7 Hz, 2H, CH^{olef}), 4.02 (d, J_{HH} = 8.5 Hz, 2H, CH^{olef}), 2.07 (s, 6H, CH_3), -7.37 (s, 1H, Ru-H)).

Supplementary figures

*Figures S1-S3: NMR spectra of compounds **3a** and **3c***

In less coordinating solvents like THF, the terminal coordination site is partially occupied by solvent and partially by triflate (**2** and **3b** in equilibrium) or water (**3a**and **3b** in equilibrium), as described in the literature for **3b**.[S1] Acetonitrile replaces the triflat anion or water molecule from the terminal coordination site. The NMR spectra in acetonitrile show only one species which is the same for **2**, **3a** and **3b** and thus is assumed to be $[Ru(\mu\text{-}H)(NCCD_3)(Me_2(dad))(dbcot)_2]^+$ (**3c**).

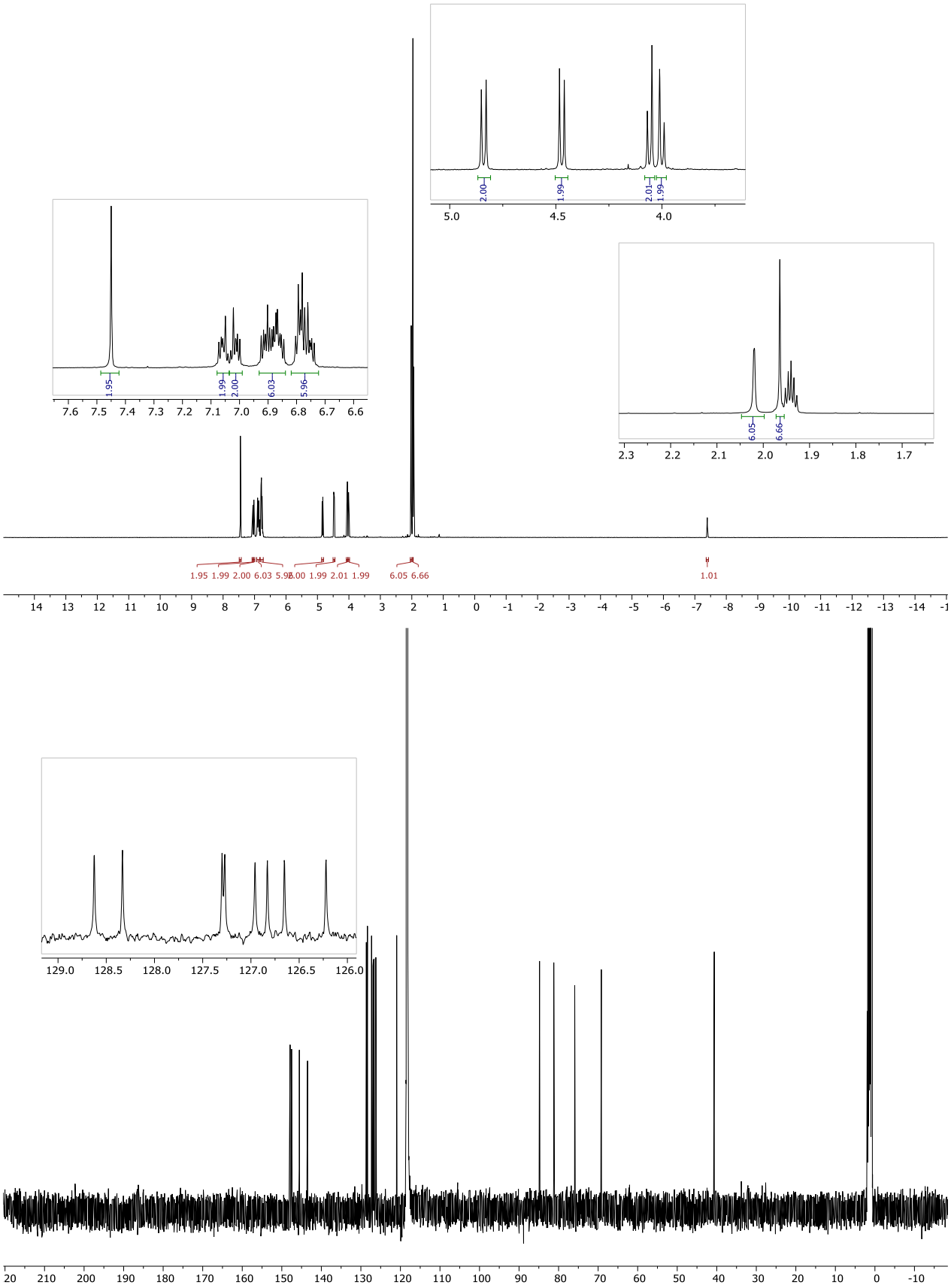


Figure S1: ^{1}H- (top) and ^{13}C- (bottom) NMR spectra of [Ru(NCCH$_3$)(μ-H)Me$_2$(dad))(dbcot)$_2$]OTf·2CH$_3$CN (**3c**, formed from **2** recrystallized in CH$_3$CN).

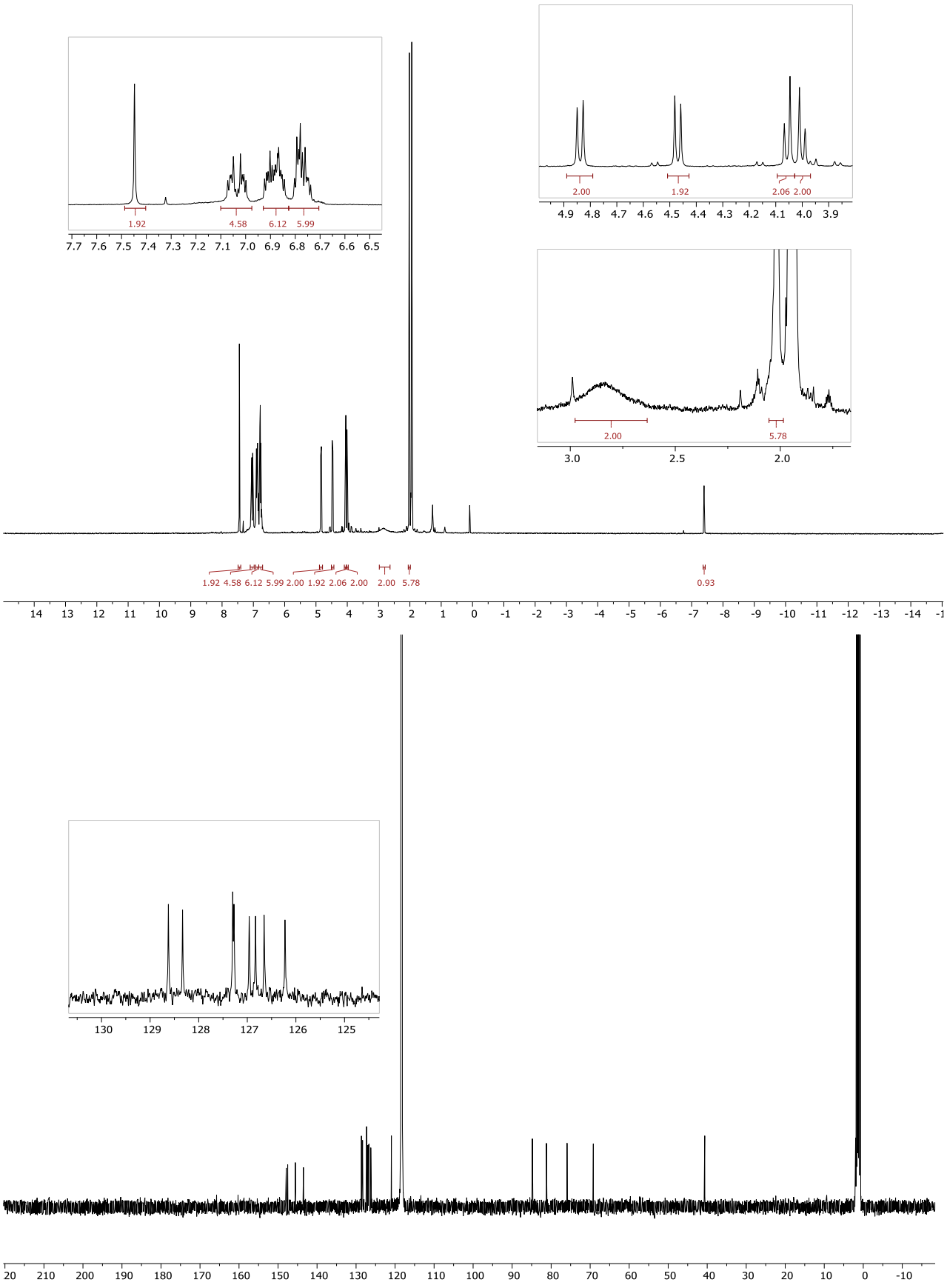


Figure S2: ^{1}H- (top) and ^{13}C- (bottom) NMR spectra of $[Ru(OH_2)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]_3BF_4$ (**3a**) in CD3CN (in-situ forms **3c** and free H_2O).

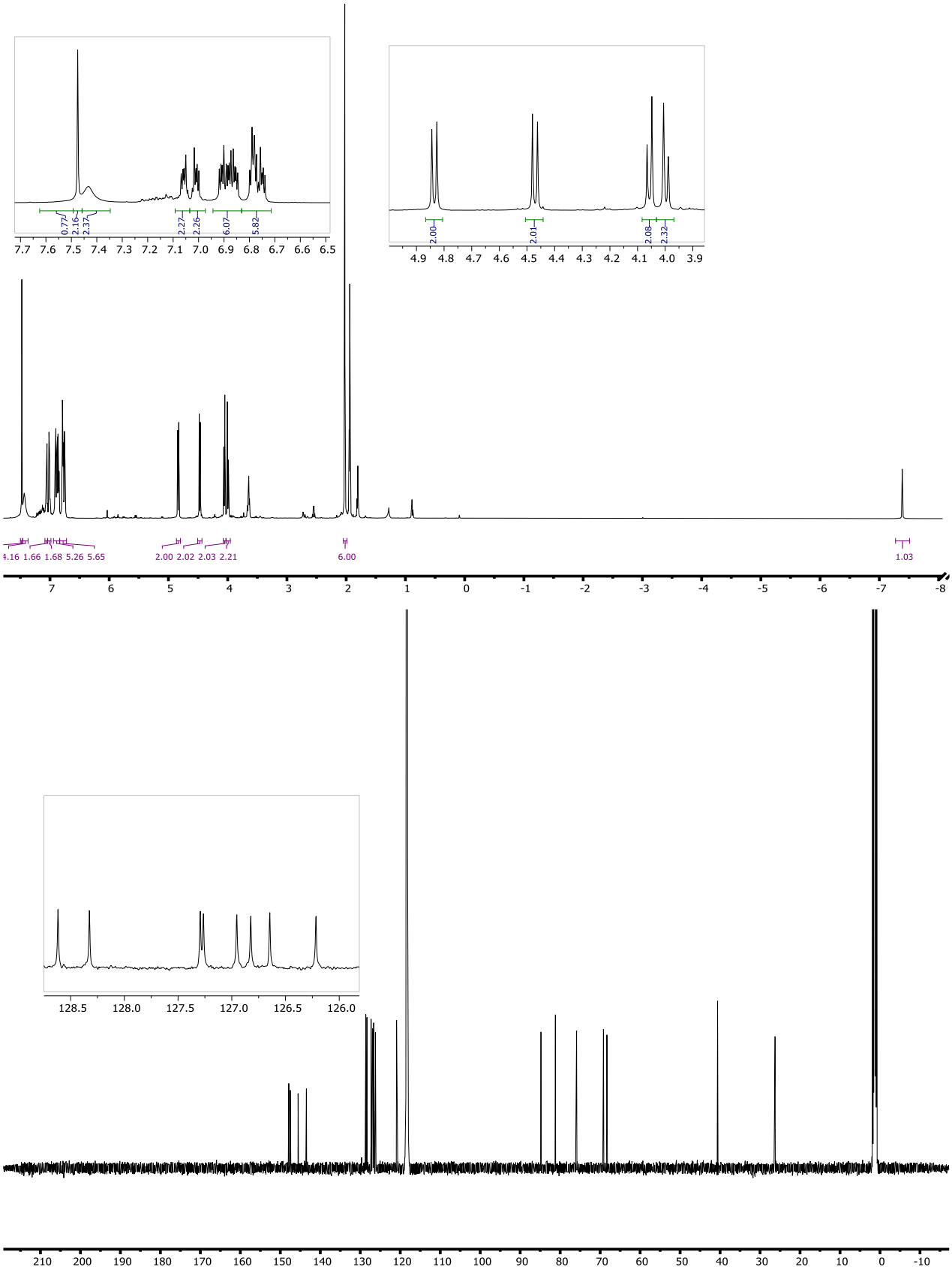


Figure S3: ^{1}H- (top) and ^{13}C- (bottom) NMR spectra of $[Ru(OH_2)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]_3(HSO_4)(SO_4)\cdot 0.34\ THF\cdot H_2SO_4$ (**3a**).

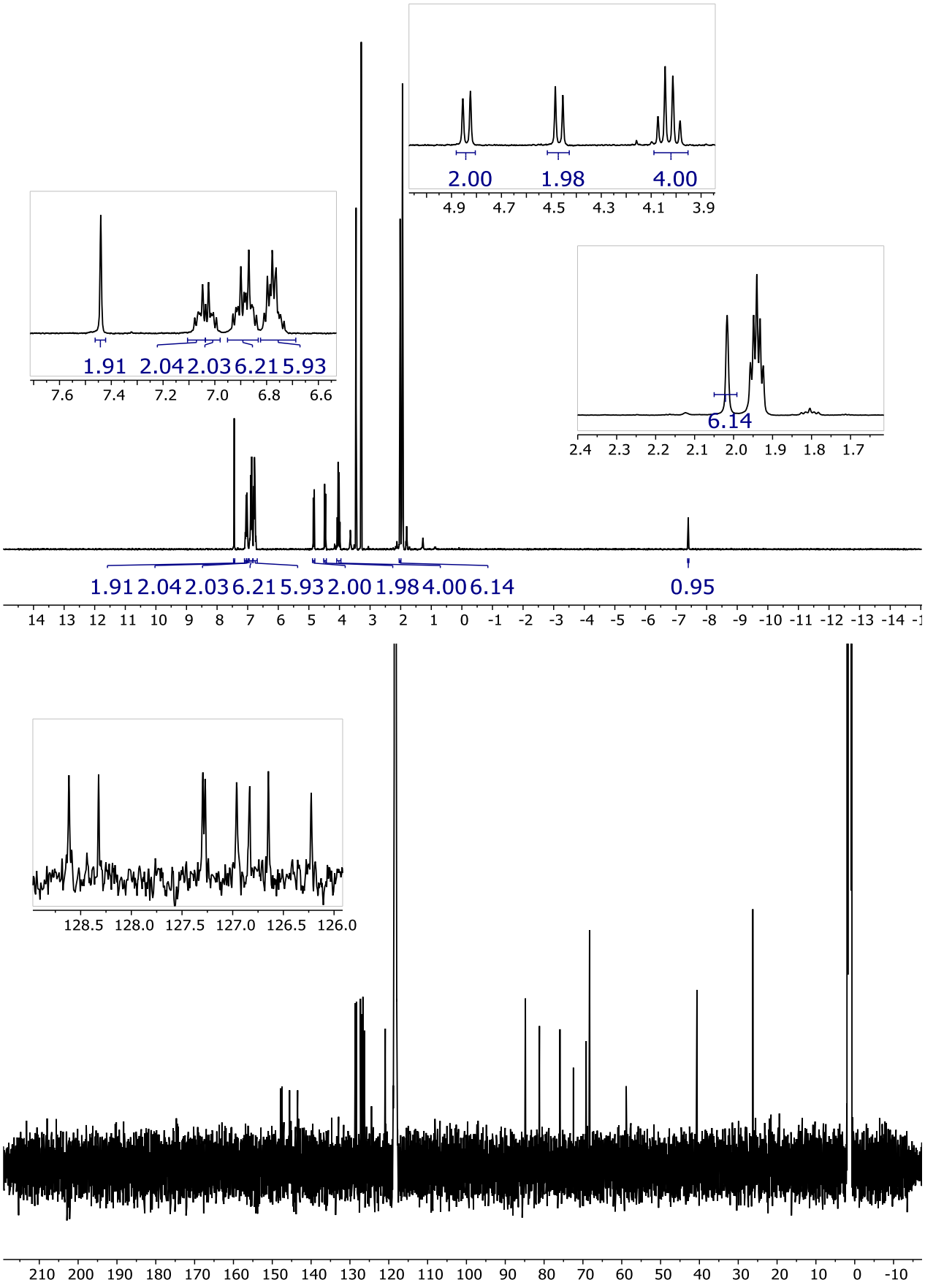


Figure S4: ^{1}H- (top) and ^{13}C- (bottom) NMR spectra of $[Ru(OH_2)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]_3(HSO_4)(SO_4)\cdot 0.34\ THF\cdot H_2SO_4$ (**3a**).

Figures S5-S7: Thermal Gravimetry Analysis

The TGA data suggest that in the solid, H_2O is indeed coordinated to the complex and not just co-crystallised (*vide infra*).

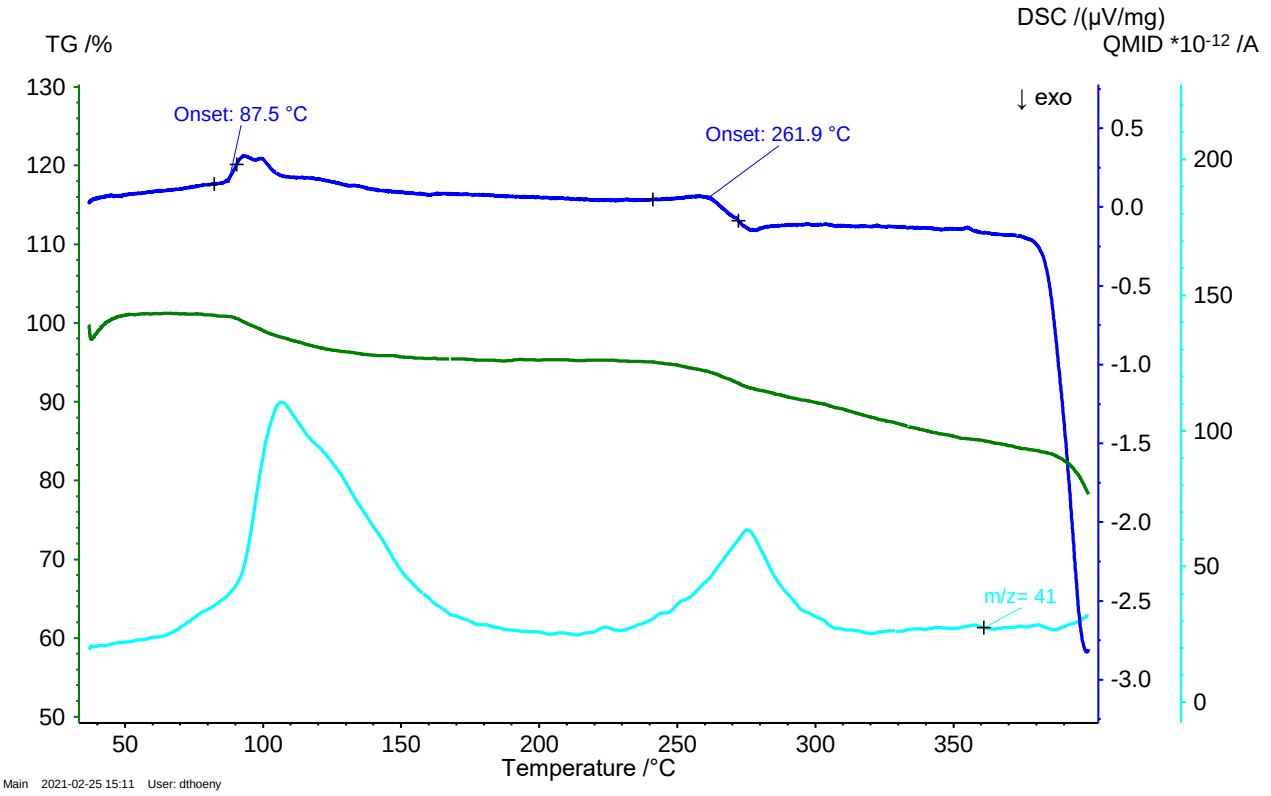


Figure S5: Thermal gravimetric analysis (green) and differential scanning calorimetry (deep blue) experiment of $[Ru(NCCH_3)(\mu\text{-}H)Me_2(dad))(dbcot)_2]OTf{\cdot}NCCH_3$ (**3c**) at a heating rate of 7 K/min. Mass trace of acetonitrile (m/z = 41, light blue). At an onset temperature of 87.5 °C, the co-precipitate acetonitrile evaporates. At an onset temperature of 262 °C, the coordinated acetonitrile is lost and the complex decomposes.

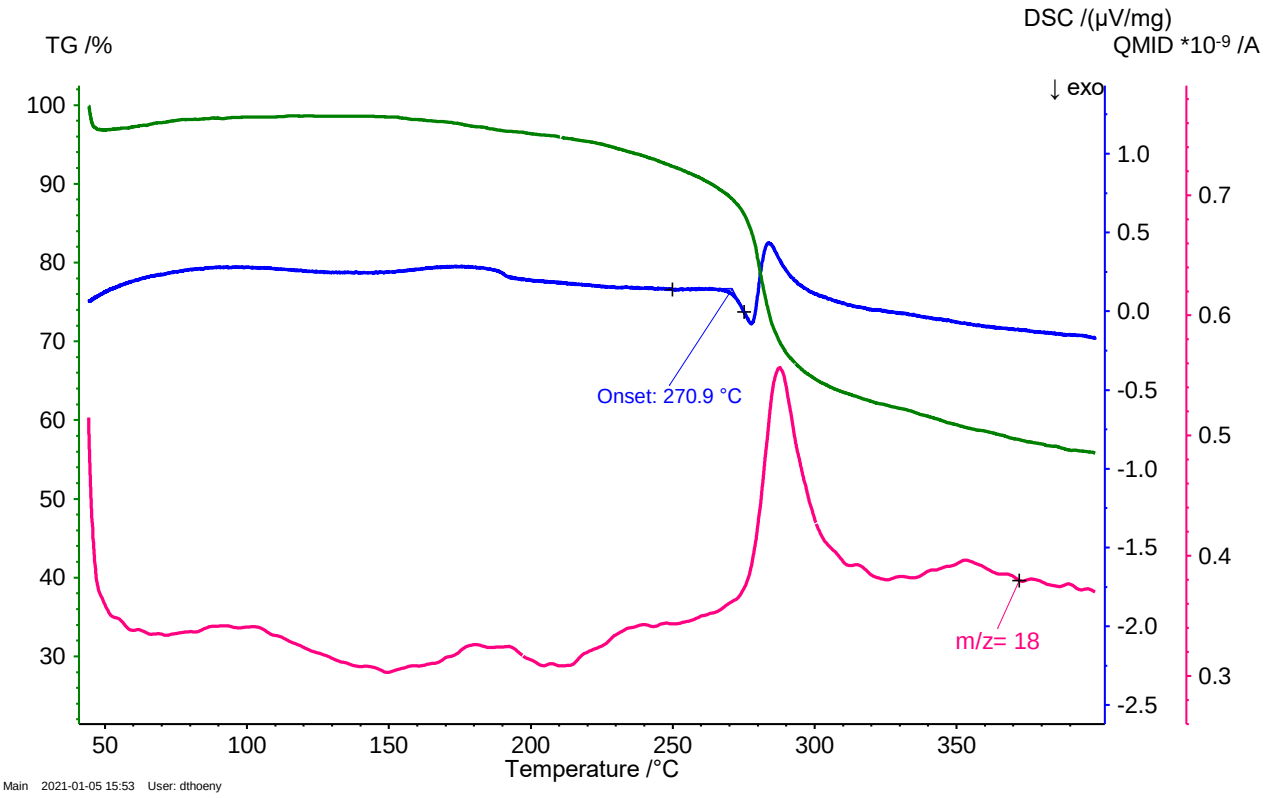


Figure S6: Thermal gravimetric analysis (green) and differential scanning calorimetry (blue) experiment of $[Ru(OH_2)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]_3(HSO_4)(SO_4)$ (**3a**) at a heating rate of 7 K/min. Mass trace of water (m/z = 18, pink). At an onset temperature of 271 °C, the coordinated water is lost and the complex decomposes.

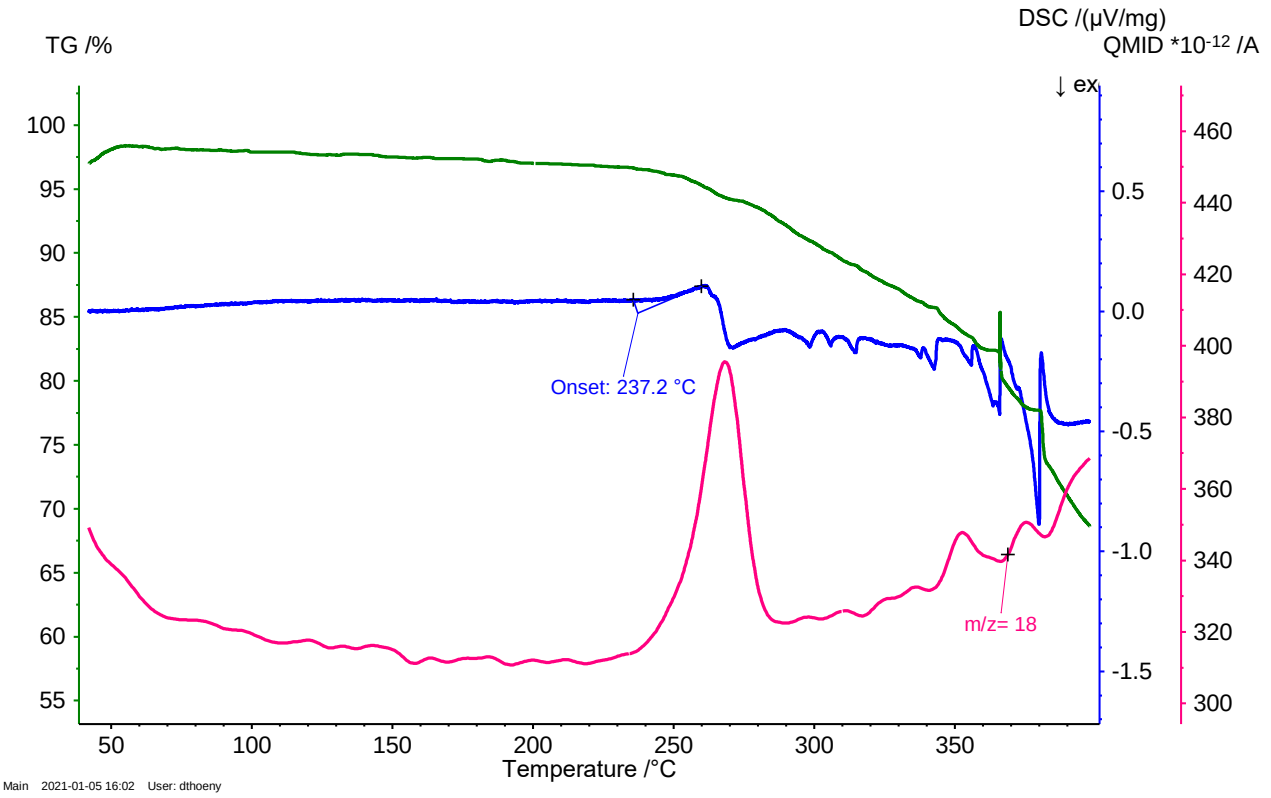


Figure S7: Thermal gravimetric analysis (green) and differential scanning calorimetry (blue) experiment of $[Ru(OH_2)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]BF_4$ (**3a**) at a heating rate of 7 K/min. Mass trace of water (m/z = 18, pink). At an onset temperature of 237 °C, the coordinated water is lost and the complex decomposes.

Figures S8: EIS measuremets

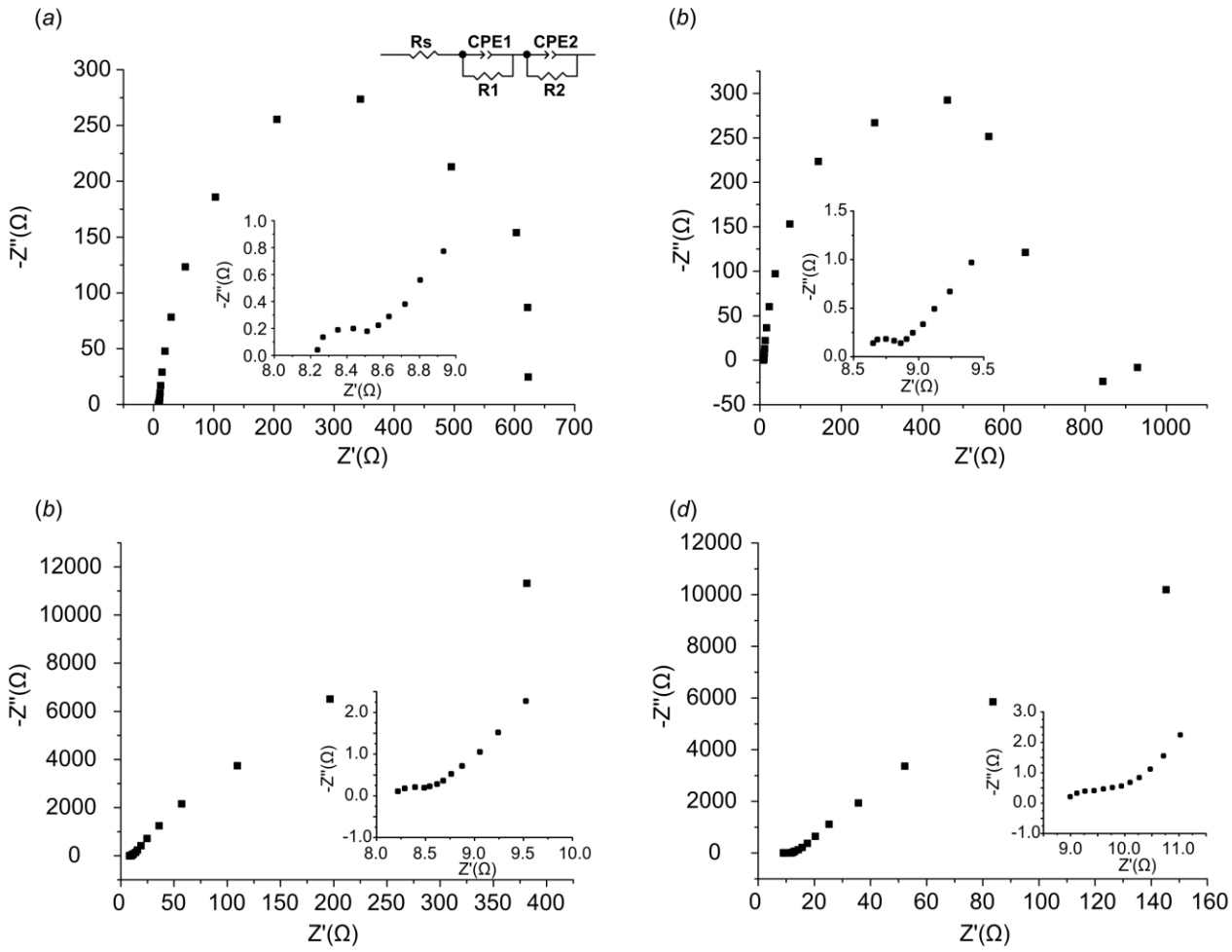


Figure S8: Nyquist plot of (a) **2@C^{k}** and (b) **C^{k}** t -300 mV vs RHE. (c) Nyquist plot of **2@C^{k}** and (d) of **C^{k}** at open circuit potential.

Figures S9: Cell set up

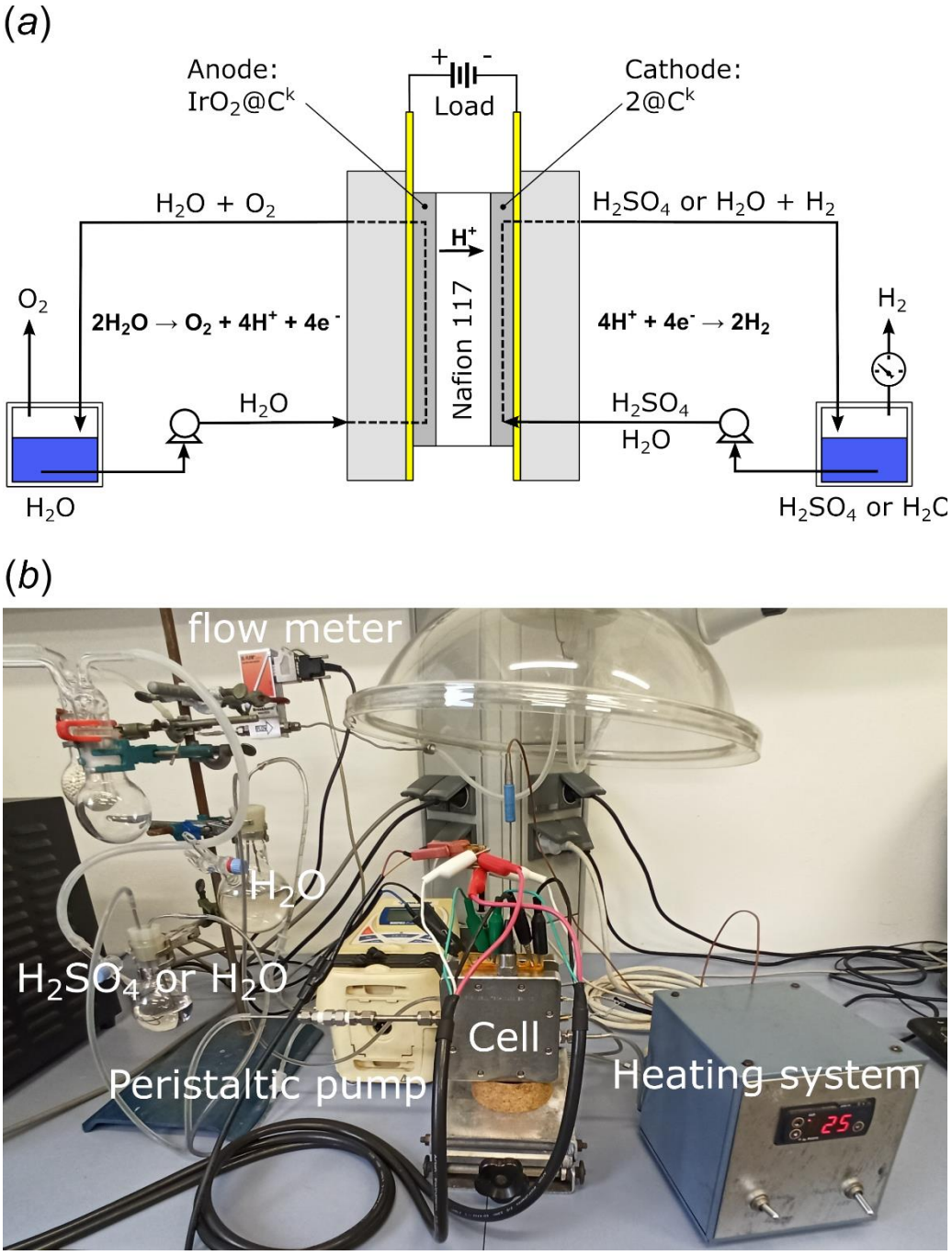


Figure S9: (a) Scheme of the electrolysis test cell experimental set up. (b) Picture of the electrolysis test station.

Figures S10-S18: Other figures

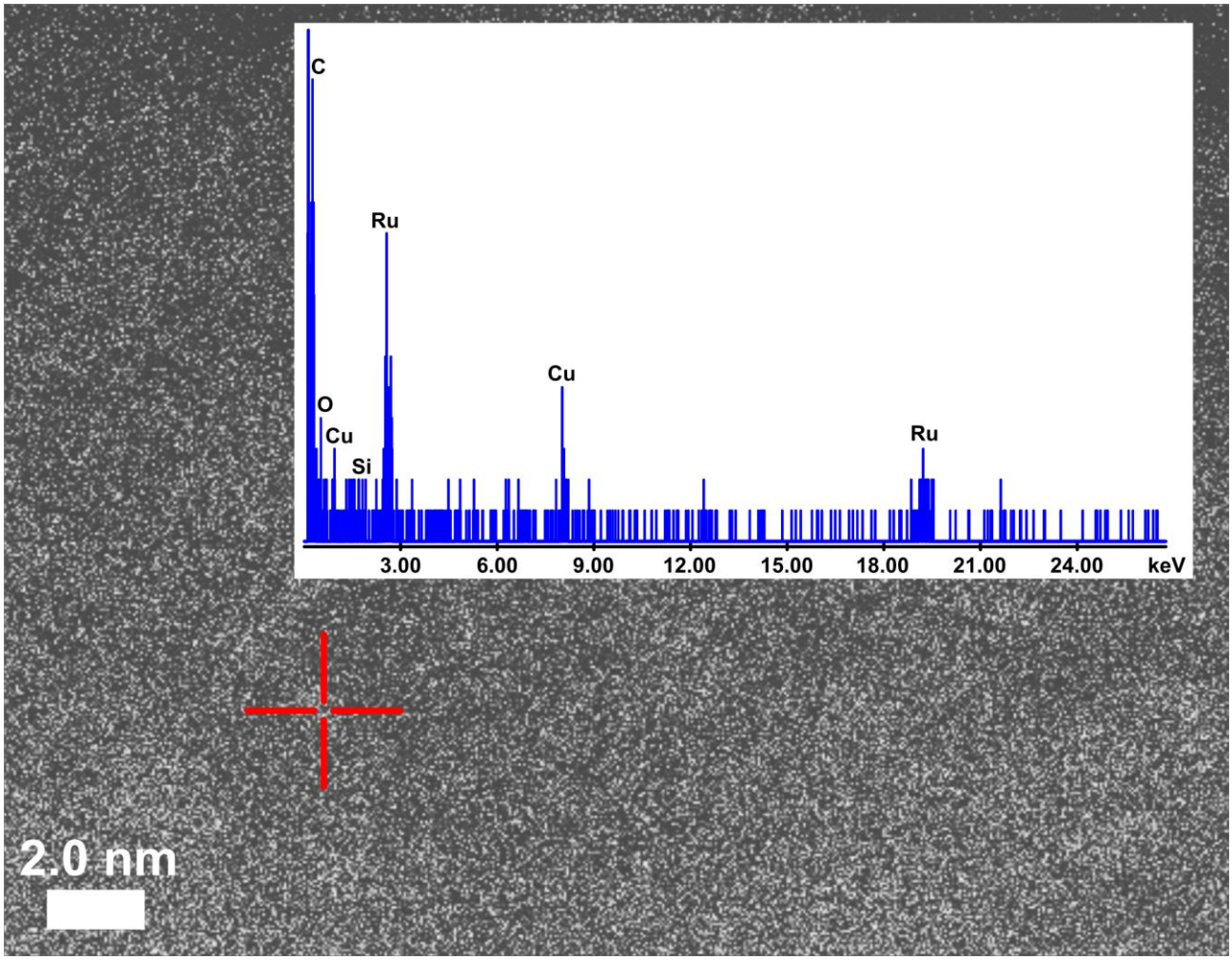


Figure S10: High magnification HAADF-STEM (*Z* contrast) image of **2$_{dil}$@C^{k}** exhaust cathode, 0.04 mg_{Ru} cm^{-2}. The insert shows the EDXS analysis of the marked spot (red cross) ascribable to the presence of Ru complex molecules.

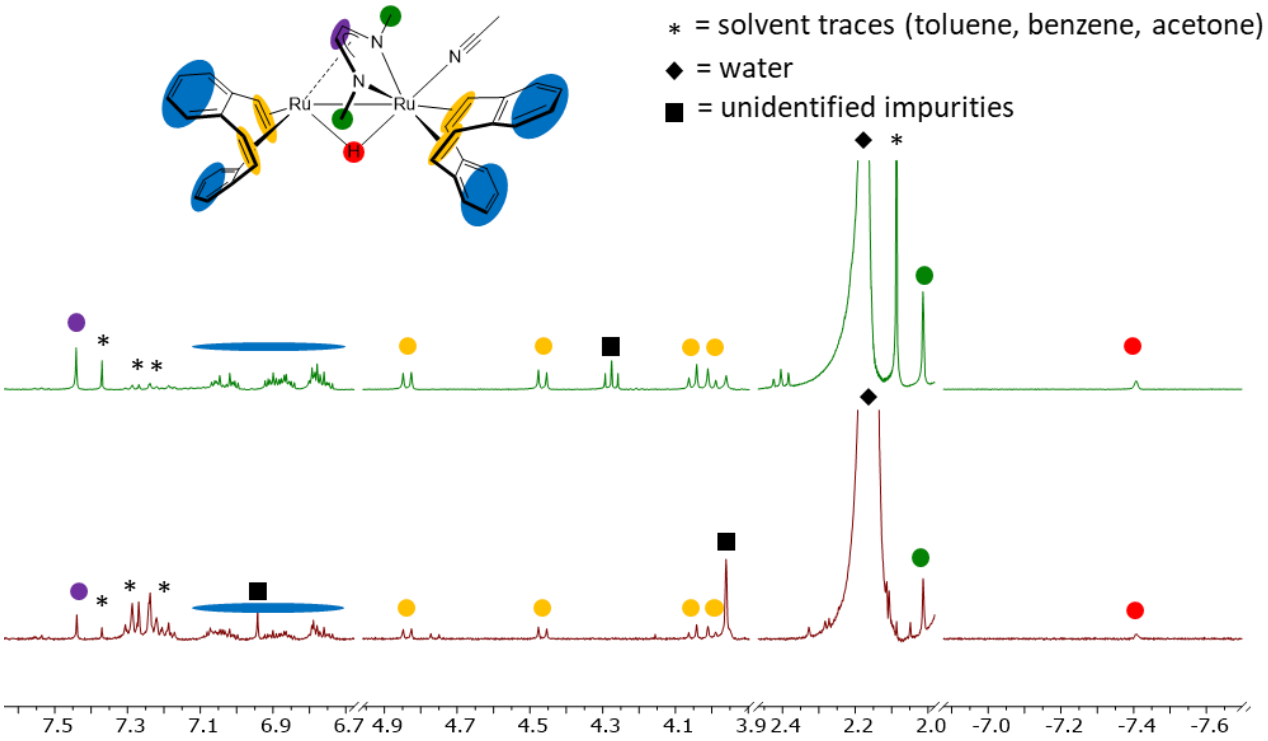


Figure S11: ^{1}H-NMR spectra in CD_3CN of complex (**2**) extracted from the fresh **2@C^{k}** cathode (top) and the exhaust **2@C^{k}** cathode (bottom) after 24 hours of electrolysis at pH 1 (0.1M H_2SO_4 feeding solution). Regions that do not show any signals of interest are not indicated for clarity.

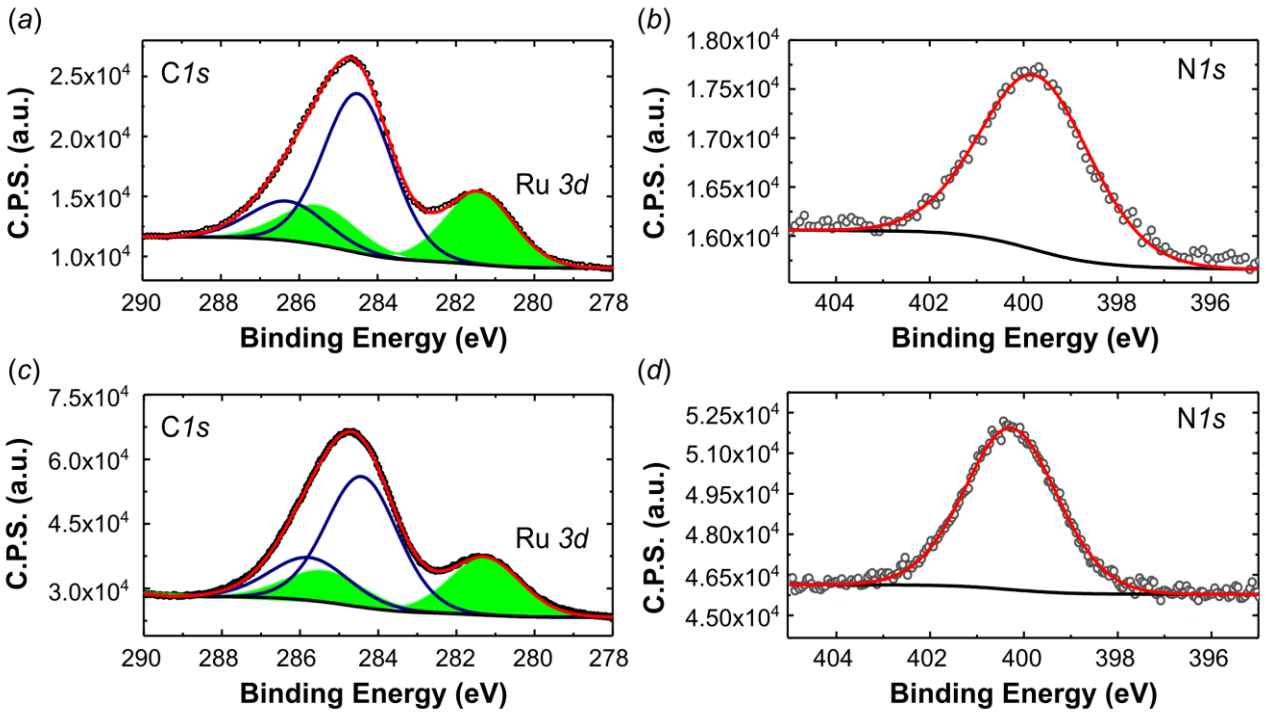


Figure S12: High resolution XPS spectra (a) C1s,Ru 3d and (b) N 1s of pristine **2** and (c) C1s Ru 3d and (d) N1s of the $[K(dme)_2][Ru(H)(trop_2dad)]$ benchmarck compound.

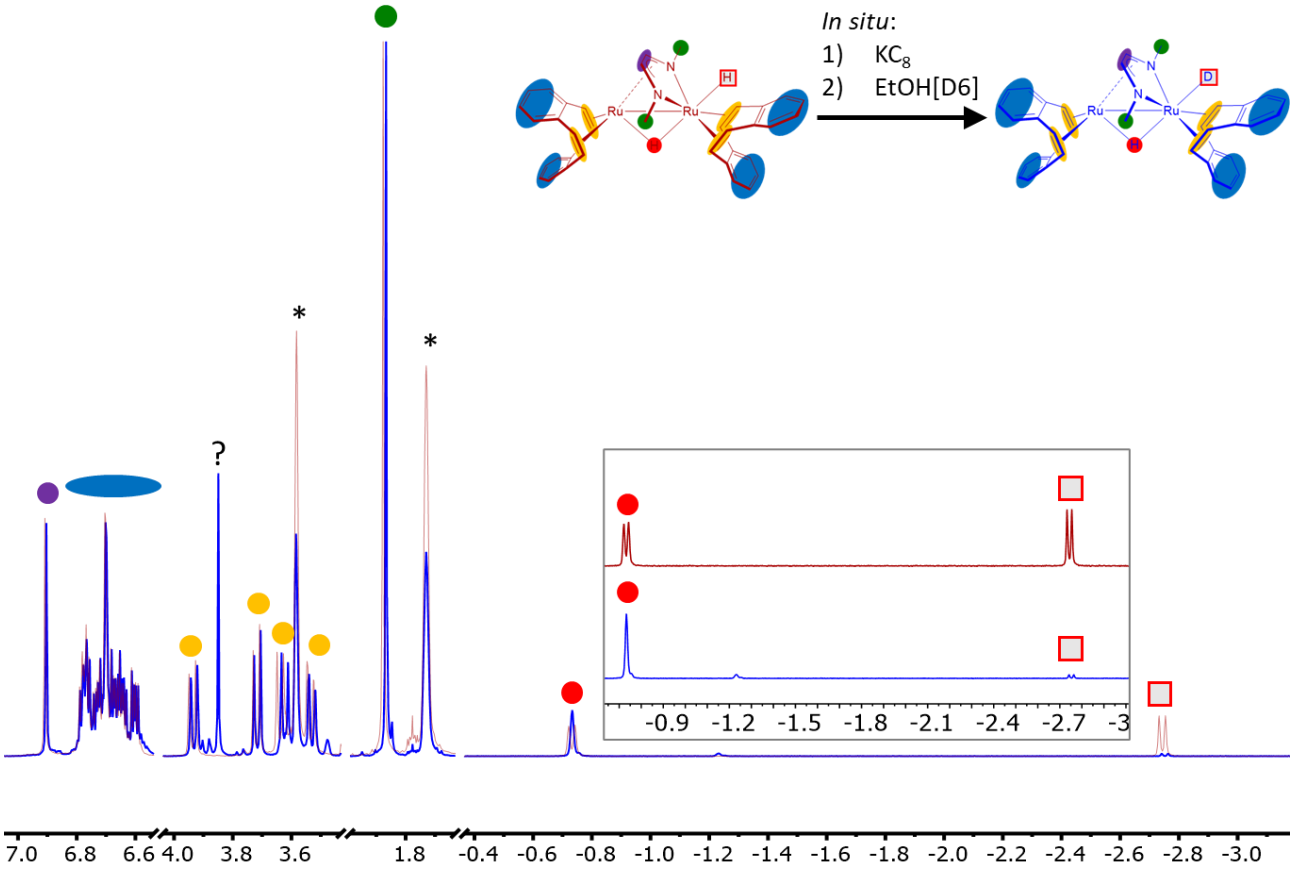


Figure S13: Overlaid ^{1}H-NMR spectra of [Ru_2(μ-H)H(Me_2(dad))(dbcot)$_2$] **1** (red) and [Ru_2(μ-H)D(Me_2(dad))(dbcot)$_2$] **1[D]** (blue). Regions that do not show any signals of interest are not indicated for clarity.

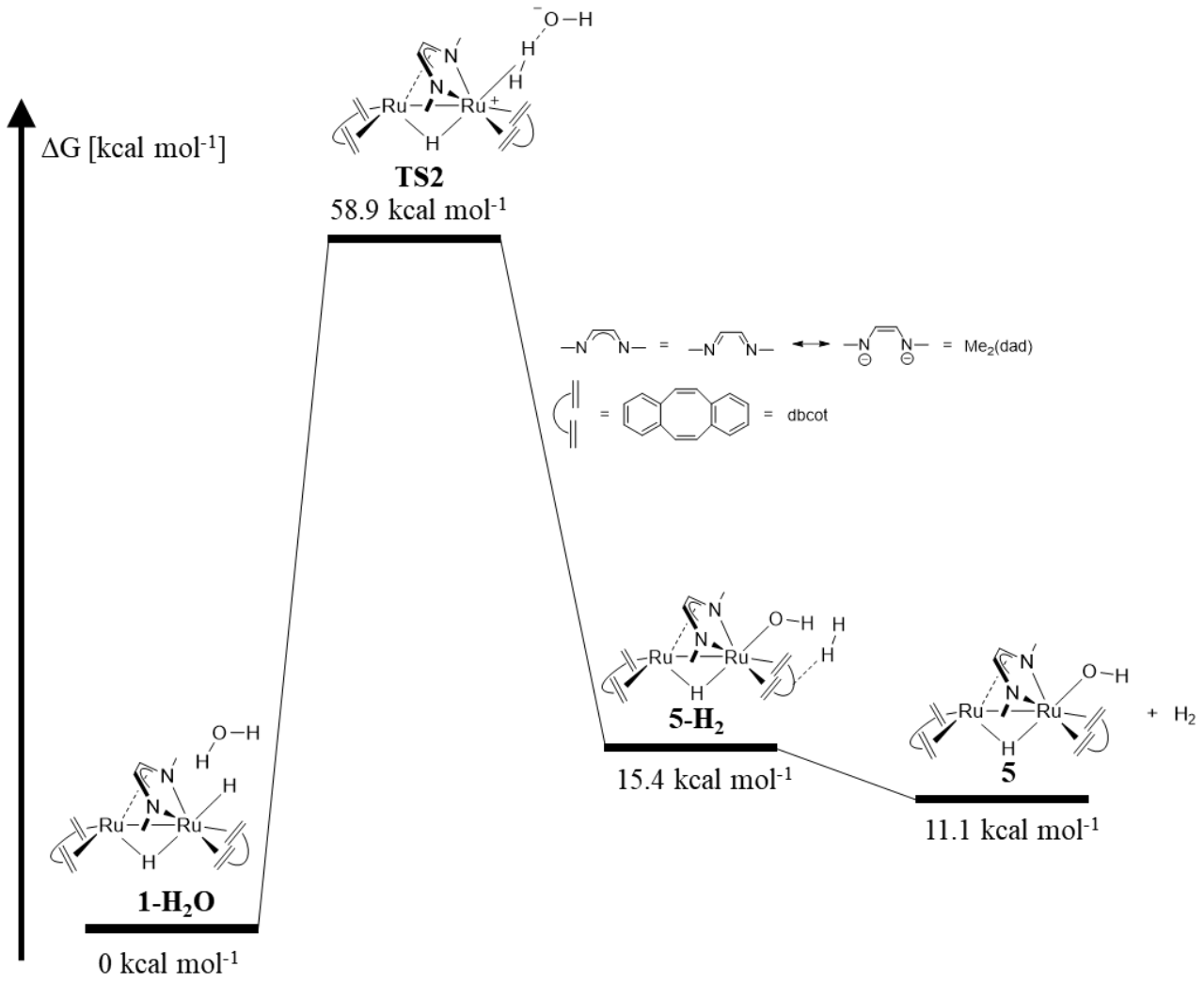


Figure S14: Mechanism of hydrogen evolution in neutral solution calculated by DFT (Orca 4.2.0, PBE0-D3BJ/def2-SVP/def2-TZVP(Ru), cpcm water (surfacetype vdw_gaussian)).

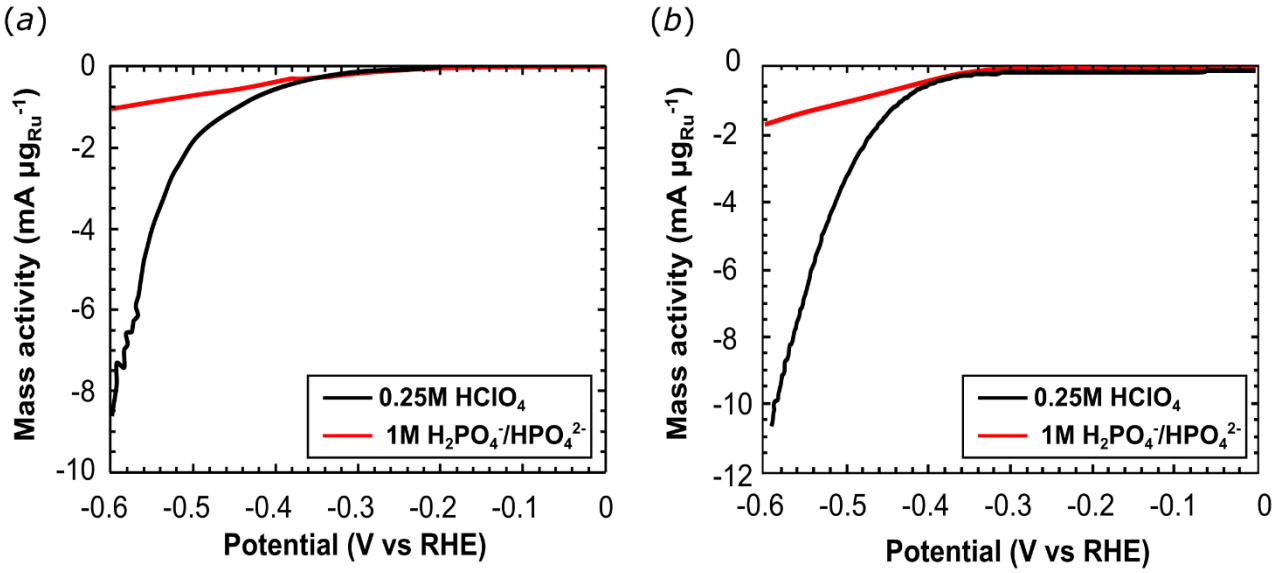


Figure S15: Electrochemical characterization of a glassy carbon electrode coated with (a) **2@C^k** and (b) **3a@C^k**. LSVs in 0.25 M $HClO_4$ (black line) and 1 M $H_2PO_4^-/HPO_4^{2-}$ buffer (red line).

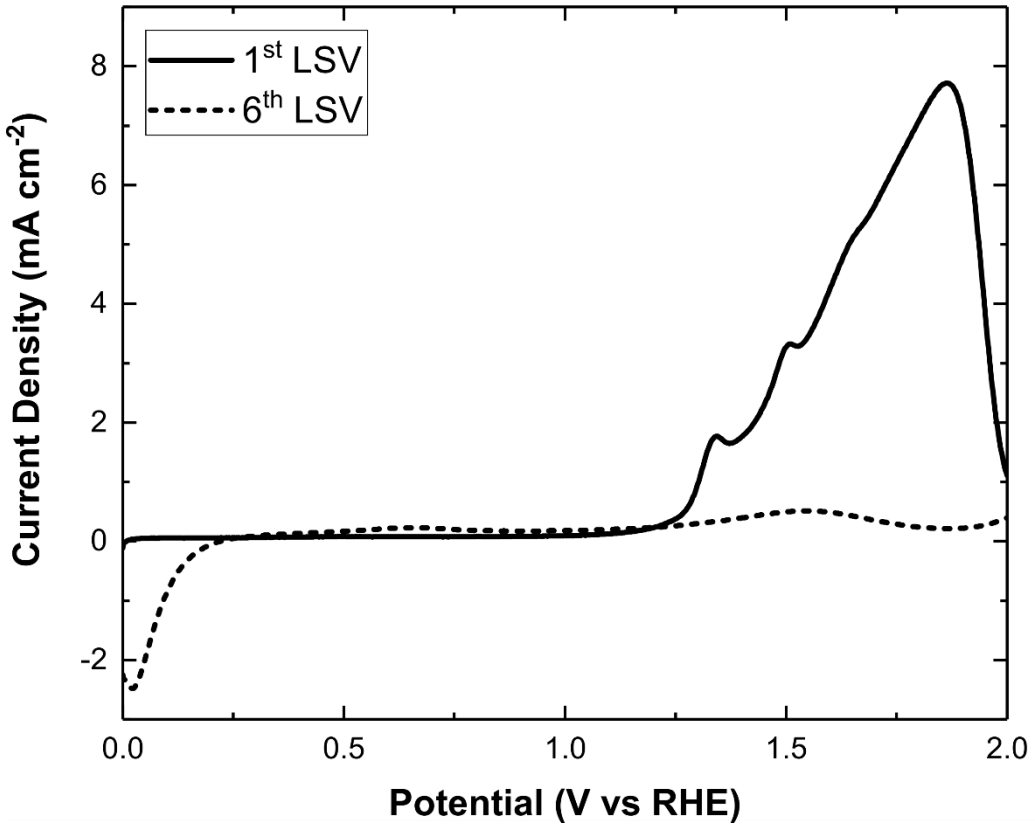


Figure S16: Electrochemical characterization of **2@C^k** for the OER in 0.25 M $HClO_4$.

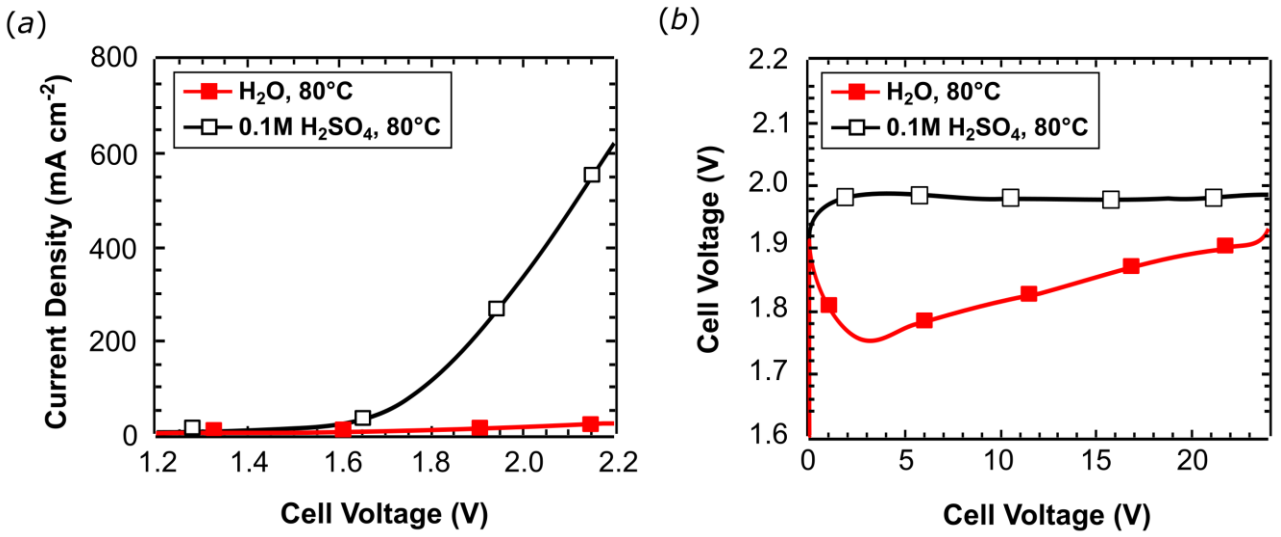


Figure S17: Activity of $[K(dme)_2][Ru(H)(trop_2dad)]$ monomer in PEM electrolysis. (a) Potentiodynamic curves recorded at 80°C with acidic feed (black) and standard water (red line) with a 10 mV s^{-1} scan rate. (b) Chronopotentiometric experiments recorded at 80°C applying a 400 mA cm^{-2} current load performed with acidic feed (black line) and water (red line).

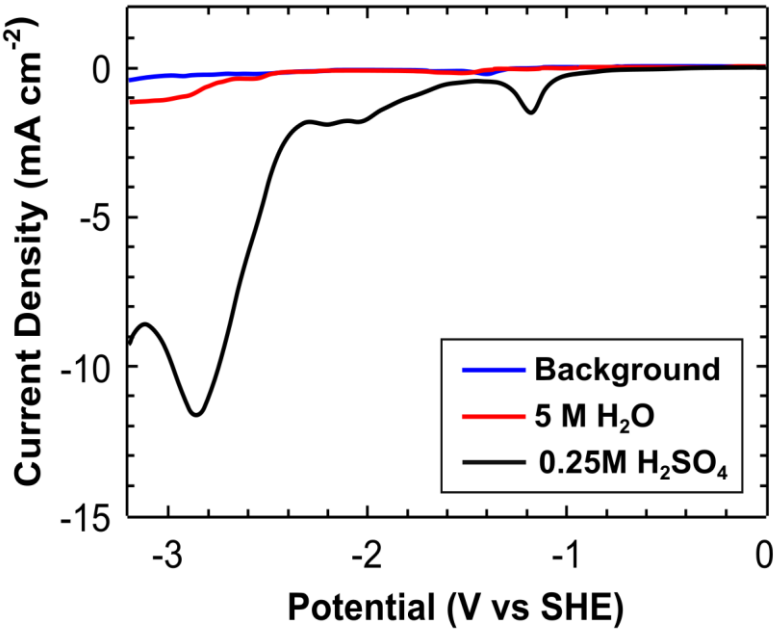


Figure S18: Linear Sweep Voltammetry (LSV) in CH_3CN of 10^{-3} M complex **2** in 20 ml of 0.1M Bu_4NPF_6 buffer solution (blue line) or in 20 ml of a 0.1M Bu_4NPF_6 5M Milli-Q water solution (red line) or in 20 ml of a 0.1M Bu_4NPF_6 0.25M H_2SO_4 - 5M H_2O solution (black line).

3. **Supplementary tables**

Table S1: Crystal data and structure refinement for $[Ru_2(OH_2)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]BF_4$

Empirical formula	$C_{36}H_{35}BF_4N_2ORu_2$
Formula weight	800.10
Temperature/K	100.01(11)
Crystal system	triclinic
Space group	*P*-1
a/Å	9.54690(10)
b/Å	10.1082(2)
c/Å	17.4002(3)
α/°	78.9600(10)
β/°	76.8190(10)
γ/°	85.7730(10)
Volume/Å^3	1603.87(5)
Z	2
ρ_{calc}g/cm^3	1.657
μ/mm^{-1}	8.098
F(000)	803.0
Crystal size/mm^3	0.042 × 0.036 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.302 to 159.796
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-22 \leq l \leq 22$
Reflections collected	40297
Independent reflections	6799 [R_{int} = 0.0421, R_{sigma} = 0.0262]
Data/restraints/parameters	6799/1/432
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.0954
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.0971
Largest diff. peak/hole / e Å^{-3}	2.47/-1.67

Table S2: Crystal data and structure refinement for $[Ru_2(NCCH_3)(\mu\text{-}H)(Me_2(dad))(dbcot)_2]PF_6$

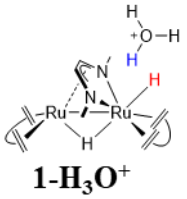
Empirical formula	$C_{44}H_{45}F_6N_6PRu_2$
Formula weight	1004.97
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.6141(2)
b/Å	12.2041(2)
c/Å	27.4630(5)
α/°	90
β/°	98.846(2)
γ/°	90
Volume/Å^3	4177.47(12)
Z	4
ρ_{calc}g/cm^3	1.598
μ/mm^{-1}	0.828
F(000)	2032.0
Crystal size/mm^3	0.49 × 0.16 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.38 to 58.552
Index ranges	$-17 \leq h \leq 17$, $-16 \leq k \leq 16$, $-37 \leq l \leq 37$
Reflections collected	105366
Independent reflections	10726 [R_{int} = 0.0602, R_{sigma} = 0.0383]
Data/restraints/parameters	10726/0/542
Goodness-of-fit on F^2	1.233
Final R indexes [I>=2σ (I)]	R_1 = 0.0462, wR_2 = 0.0982
Final R indexes [all data]	R_1 = 0.0621, wR_2 = 0.1033
Largest diff. peak/hole / e Å^{-3}	1.03/-1.00

Table S3: EIS data

Rs (Ω)	**8.3**
R1 (Ω)	0.35
R2 (Ω)	596.4

Table S4: DFT Cartesian coordinates of optimized molecular structures

$[Ru_2H_2(Me_2(dad))(dbcot)_2] + H_3O^+$ ($1\text{-}H3O^+$)



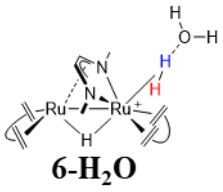
$1\text{-}H_3O^+$

Ru	8.13813165218872	10.64682124564211	17.22672015943617
Ru	10.48919618588997	11.90568054402451	17.24016377057114
N	9.95516452606099	9.96390505270728	18.01871361850304
N	9.50106584141107	10.82065621069377	15.64379253813145
C	7.31865784086485	11.26690530336746	19.10970707722285
H	8.08358269092886	11.28668093184408	19.89292904503773
C	6.78229260062793	10.00173055688789	18.76333604260544
H	7.16461209845646	9.13321272344202	19.31147354024827
C	10.32869449167646	13.87267409393088	16.49577718268875
H	9.54567603014170	13.97628095174508	15.73506263567726
C	6.11887500438998	13.27334489983331	20.07496811052821
H	6.32833368237949	12.91054325928870	21.08514520274414
C	6.54935929927757	12.53301232958027	18.97154848528290
C	6.30206018633629	13.00428825572757	17.67557071983042
C	13.82475946209939	14.47703212683597	16.07436643543642
H	13.64634966396172	14.83749746012517	15.05740919526479
C	10.78993472089475	12.92895902607090	19.05658678175509
H	10.29938995667542	12.43825846439385	19.90569040844403
C	12.86234548301280	13.68772814504168	16.70912059723813
C	10.70586125376688	10.19877193726618	15.81581368764316
H	11.42030467012431	10.09941481062563	14.99489704910482
C	11.57196083254662	13.30120137666859	16.07049796044257
H	11.64281840218916	13.01163958935003	15.01498113853734
C	12.03033775038959	12.36556834433601	18.61438893207802
H	12.39125582481782	11.48585349993030	19.16099399651979

C	6.82331132266174	12.19878175094902	16.53784951641325
H	7.28948748546959	12.78535260291236	15.73914954947003
C	10.95863374720234	9.73454500734205	17.11447614244102
H	11.88617465134086	9.23474874599001	17.40402111459551
C	10.25742529886308	14.85983737487156	17.61059391985454
C	10.16552332020402	9.46189097686559	19.36609773525907
H	9.62738138659398	10.08196630198199	20.09209805765485
H	11.23365108392435	9.45471817968724	19.62994846062462
H	9.77863095208869	8.43320852927640	19.43797315271789
C	6.27862158562520	10.94090621165616	16.18191539103130
H	6.35027747082286	10.64861252015972	15.12831108729926
C	9.19364091826810	11.28347066595331	14.30166518395634
H	8.67546577706058	10.48426027772074	13.74978662157281
H	10.10674204919265	11.55660123297318	13.75189262436005
H	8.53255392297452	12.15696091910682	14.34174298904708
C	5.39624572066288	9.86816752439702	18.23427959196403
C	9.93757576147169	16.20548224810981	17.41479288460677
H	9.74188223211953	16.57316845689403	16.40349561701219
C	5.62711715443943	14.21304140903833	17.49145630474462
H	5.45263674656887	14.58626134288227	16.47848231378012
C	13.09473120327361	13.21199637735394	18.00580399973393
C	10.39857825775648	15.25021568465570	19.99846847647712
H	10.56326170186747	14.86864663841171	21.01020717283730
C	5.14216034297825	10.34249956739174	16.93833812190081
C	10.48983436491876	14.38073322274149	18.90922213182160
C	5.44477439983423	14.48178393967099	19.88774266700153
H	5.12126185513823	15.06462656134737	20.75379048450928
C	15.01801320998874	14.78711375674664	16.73097471110930
H	15.77559022659261	15.39301263657670	16.22725159686810
C	5.19932150996733	14.95150154204218	18.59673377541168
H	4.68286233216220	15.90318490938674	18.44868370610135
C	9.84555168558748	17.07128856673858	18.50703146174354
H	9.58156345835152	18.12018381949073	18.34984196301983
C	10.07612989176976	16.59419383699542	19.79812520309585

H	9.99324582722261	17.26813950183552	20.65465192340023
C	3.85900674235626	10.22942251563514	16.39741512365239
H	3.66706328364037	10.58891669168888	15.38268243063555
C	14.28609047489247	13.52879815599586	18.66264239132274
H	14.46714504237844	13.14656742258662	19.67127460343477
C	15.24859990074174	14.31360348517365	18.02374617489561
H	16.18640865594787	14.54806364084616	18.53396062376176
C	4.36483145640032	9.28609661884052	18.97546415069801
H	4.56954205827280	8.90880831432854	19.98128049788703
C	2.83178387240356	9.64557885410971	17.14120416798195
H	1.83234481391321	9.55048344042924	16.70902970339428
C	3.08461729954912	9.17401532568979	18.43023925266452
H	2.28408132837371	8.70853285709627	19.01081548365100
H	8.92448780507964	12.31158412574418	17.67742937698768
H	7.53808123016250	9.22200153179322	16.75101256098193
O	8.93070600314634	7.48449741850525	16.38389002031147
H	8.40892169631159	8.41342745850927	16.62615742356768
H	8.29620862441180	6.90370491477627	15.92087552745912
H	9.16526843694019	7.03595350773246	17.21984377629422

$[Ru_2H_3(Me_2(dad))(dbcot)_2]^+ + H_2O$ (6-H_2O)



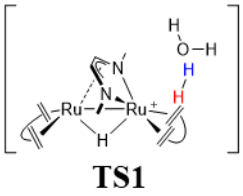
6-H_2O

Ru	8.25735657259835	10.53667280217311	17.37335222934727
Ru	10.55869133249081	11.85653458484832	17.37061979550706
N	10.06620982655199	9.95758600444678	18.23980835676889
N	9.63822236957772	10.69569063933003	15.82065274358832
C	7.38042555811288	11.29068278933373	19.23584867374333
H	8.15418826775703	11.34483617079554	20.00729231676285
C	6.82487985199616	10.02658234311671	18.98032832468531
H	7.19800868004438	9.19016266761795	19.58146453828324
C	10.34141305105486	13.77578917348353	16.52151257397736
H	9.57089470731075	13.80699811329104	15.74196960059050
C	6.26831922623711	13.40303849391080	20.03774195191358
H	6.46674442488885	13.10529066495137	21.07076730345247
C	6.66097881751267	12.56892183714372	18.98913822787904

C	6.43343108967267	12.95698965636516	17.66431679772676
C	13.82186751165417	14.48549362879344	16.12330883721656
H	13.64858501082311	14.78427325971076	15.08576104169505
C	10.79445511041394	12.97958989937908	19.14126494131615
H	10.31145718905599	12.51183168270212	20.00718744968823
C	12.87658882254921	13.69884883064900	16.78620505713055
C	10.83501860054901	10.07682250167106	16.03723496812978
H	11.55705107138367	9.93508331915914	15.22941537078116
C	11.61244847437264	13.23398597540517	16.14927836723167
H	11.71136499575720	12.88599278679490	15.11375787625516
C	12.06124516245462	12.44642086020803	18.74448740872960
H	12.44418767521307	11.60394067864521	19.33331910328152
C	6.92435513521963	12.06833361425193	16.57835592194345
H	7.41866336208687	12.58745871870161	15.75224052704642
C	11.07048757845395	9.67495032910561	17.35999178073597
H	11.99440156391257	9.19042194187643	17.68562521300823
C	10.19702985192375	14.80724049555574	17.58708410638279
C	10.24232643031871	9.50235593304766	19.60865135863061
H	9.71267872936121	10.16429637580586	20.30291386076562
H	11.30678336195531	9.47818092740323	19.88455847069001
H	9.82659402998068	8.48825568238531	19.70953115116625
C	6.37126812115583	10.80721569433060	16.29519747315279
H	6.46821595902234	10.44512761204901	15.26648831361111
C	9.32416923879681	11.05280888686917	14.44721058033463
H	8.79247183937014	10.20818419974179	13.98534219549951
H	10.24031493204881	11.26083960933659	13.87569411241509
H	8.68085192270132	11.93931734250248	14.41744740082226
C	5.46167401543189	9.85562376933025	18.40703818246054
C	9.80414053607711	16.12049018235778	17.31844933900272
H	9.61011287669078	16.42617606602538	16.28649116470011
C	5.81422727995189	14.17841225583872	17.39242942190258
H	5.65886433804631	14.48717268461756	16.35528207614372
C	13.10360147383622	13.29966969094269	18.10872356301174
C	10.25987999116125	15.31857128890007	19.95494250158536

H 10.42187086672494 14.99599655973280 20.98731083252762
C 5.23931917368234 10.23697784718629 17.07620296624281
C 10.42589350578159 14.40464000798121 18.91188263283373
C 5.64781534099663 14.62281922442740 19.76342999430351
H 5.35313307345301 15.27960288763662 20.58539208473628
C 14.99314671553400 14.86969124585715 16.77980863210577
H 15.73873883366810 15.47264236457203 16.25515478528986
C 5.42129303121158 15.01014357167087 18.44206192421016
H 4.94871451012145 15.97132902486977 18.22596857605194
C 9.63627865583577 17.03010042898637 18.36462444300412
H 9.31461270139542 18.05243624998795 18.15056969000076
C 9.86437990850738 16.62968817564206 19.68197874400158
H 9.72143229240299 17.33745492336500 20.50244444816890
C 3.97550592252778 10.05949396007522 16.50713762895331
H 3.80954426275753 10.34081589930771 15.46393704378286
C 14.27285605365125 13.69041805174037 18.76534171259762
H 14.45060182026774 13.36742586849560 19.79490756893398
C 15.21819559996064 14.47320232339032 18.09933018065831
H 16.13956884639999 14.76544618040288 18.60954369366325
C 4.41951861839793 9.30654931770121 19.15824275940149
H 4.60229371568344 8.99966520900183 20.19146632493317
C 2.93616659645322 9.51458104885759 17.26184178069387
H 1.95175106804736 9.37235840684731 16.80911353732701
C 3.15739897341266 9.13983970779862 18.58782952821709
H 2.34719911164419 8.70409658028811 19.17754435679106
H 8.92765109422214 12.18121267793133 17.75372085914649
H 7.86148929715220 9.03607348011290 16.54645240965710
O 7.87986077192512 8.09000936933812 14.79181034681085
H 7.80029629944006 8.88605113492411 17.40176002131593
H 6.95337804971629 8.04063925028301 14.52070974101978
H 8.07923932148336 7.18760635667948 15.07481818191654

$[Ru_2H(Me_2(dad))(dbcot)_2]^+ + H_2O + H_2$ (TS1)



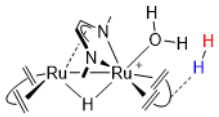
TS1

Ru	-0.73592461283115	-1.60962536662603	-0.34172249026855
Ru	1.65606432939943	-0.34287147683925	-0.35162634542282
N	1.12883720936822	-2.23544000023307	0.53797618422866
N	0.70333433274748	-1.45062495389621	-1.93802827314342
C	-1.54304517731891	-0.83154579192123	1.51682378875456
H	-0.77844940032497	-0.80168480668338	2.31247916780014
C	-2.12342282240125	-2.10659251938466	1.24342009391625
H	-1.75109545854699	-2.94564209855001	1.85884088551737
C	1.43194386038064	1.59291247119417	-1.18768268155478
H	0.66312012766517	1.62976784938624	-1.98086720902811
C	-2.56954901996207	1.33255330728775	2.35019251629452
H	-2.35829571403672	1.02766520261693	3.38708133040860
C	-2.23342545929335	0.47060830176838	1.29008442106000
C	-2.46661770739757	0.87245269108492	-0.04418364681773
C	4.92431954658460	2.35828088394159	-1.57760696119184
H	4.74367444947284	2.67101826711049	-2.61824255253564
C	1.89750323430713	0.76131043445354	1.44332887370184
H	1.42997019576834	0.27253110192887	2.31759225538447
C	3.98553711791426	1.54229513557859	-0.92065459494095
C	1.85584037686783	-2.15253781201277	-1.71497760564685
H	2.57822648434052	-2.34475814334513	-2.52515454928397
C	2.72399250316153	1.06212649729118	-1.56042393583485
H	2.82730494760237	0.71532103747695	-2.60567109123396
C	3.18227889654127	0.24571613437252	1.02520229479029
H	3.57583579069873	-0.61235072432004	1.60162376910082
C	-2.00464396902390	-0.03364461682519	-1.13331982689566
H	-1.52081410450322	0.48259717440168	-1.97996583994821
C	2.08763712874732	-2.57465318408466	-0.37821262765237
H	2.99998452201762	-3.11752238426798	-0.08125892043934
C	1.25669178352300	2.60563170518568	-0.10089290051415
C	1.30929702897751	-2.69407312364257	1.91338685038245
H	0.80962525769384	-1.99970784224767	2.61157295497177
H	2.38384084171635	-2.76540766881611	2.17569222936101

H	0.84593535426664	-3.69518303274204	2.02792093898645
C	-2.58152799113382	-1.30723287011337	-1.41561682587844
H	-2.47483672232207	-1.66654996439159	-2.45358808306413
C	0.41262104557437	-1.04707214138655	-3.31179563021801
H	-0.19103053943159	-1.84692913867114	-3.78391535744695
H	1.34594053051532	-0.89612403091328	-3.88997190431403
H	-0.17258810460250	-0.11041174687853	-3.31744614136165
C	-3.49590700193186	-2.28337591868370	0.68697144523719
C	0.80371380054250	3.91374792328992	-0.35064627119535
H	0.59834481760040	4.22908568244606	-1.38586314399274
C	-3.03610566504342	2.13203458994645	-0.30702174291228
H	-3.18977707930921	2.45252108234483	-1.34932591080962
C	4.22013251468268	1.12449706263251	0.40595875120582
C	1.27090984810311	3.07835320935399	2.29409845507469
H	1.43155340908092	2.73962076715484	3.32982523047085
C	-3.72615433016435	-1.88072192055478	-0.64934797700725
C	1.49182252529166	2.18509480916292	1.23013105908776
C	-3.14757310318949	2.58458503686875	2.08296740809239
H	-3.39965528764021	3.26000844900411	2.91469326446406
C	6.09586783695598	2.75609672796519	-0.90978677680703
H	6.83576698157231	3.38479669822844	-1.42874891611978
C	-3.38112361722848	2.98388500310022	0.75520648658101
H	-3.81670031107117	3.97263690242764	0.54501540488691
C	0.58759987322493	4.80291103244522	0.71667636281612
H	0.21963237667329	5.82089041717622	0.51611067432043
C	0.82139647470152	4.38563275922949	2.03805958212107
H	0.63715680163874	5.07578545424737	2.87569780560792
C	-4.99272003523252	-2.08029022137573	-1.23076641406198
H	-5.16111601834234	-1.78461627271463	-2.27820786127856
C	5.39294803833382	1.52459334592444	1.07175610191210
H	5.57920926702477	1.18520110216465	2.10299676392358
C	6.32969421549741	2.34006833381485	0.41263866772275
H	7.25300098047944	2.64263782858397	0.93031919173581
C	-4.53438329898487	-2.88216578781835	1.42524304781025

H	-4.34427944148763	-3.21379346261184	2.45814207448382
C	-6.02906490425264	-2.66490315312908	-0.48411063445001
H	-7.01632690383671	-2.82104219890731	-0.94535188462861
C	-5.79989901306081	-3.06589049180074	0.84385175230273
H	-6.60715528612085	-3.53670121721404	1.42564796456569
H	-0.06837259091077	-0.09283752120909	0.02160945640325
H	-0.81408646376193	-4.15848570172847	-0.52144021947962
O	-1.11136438741429	-3.71287179502758	-2.60579164454815
H	-0.72452765691654	-4.22684467137868	0.24753052390552
H	-1.96239281416585	-4.19105808031032	-2.54297003408294
H	-0.46415464405978	-4.43368855933477	-2.74216060338063

$[Ru_2H(OH_2)(Me_2(dad))(dbcot)_2]^+ + H_2$ (3a-H_2)



3a-H_2

Ru	8.15691933379512	10.63342892971193	17.19955174596576
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N	9.95451970786443	9.96465807011599	18.06220613347282
N	9.57879778351387	10.82648080684096	15.65320300614214
C	7.30318411138939	11.32986260423496	19.05964119757783
H	8.05881401491356	11.35473982707915	19.85071680443080
C	6.76199141297012	10.06892351118563	18.73047537136772
H	7.14065210177334	9.20604201144443	19.29178549430474
C	10.35814688465208	13.83464633679056	16.52318173584584
H	9.59601638481791	13.93054996221221	15.74059804029782
C	6.13061002399299	13.37902163710800	19.95424711008095
H	6.31157238191186	13.03367430375069	20.97568911661009
C	6.56450593866260	12.60610909374267	18.87493461714148
C	6.35634789079076	13.05415142270449	17.56547753589881
C	13.85775009531831	14.46912693928245	16.19773905958742
H	13.70274745470889	14.83085866396771	15.17750790783735
C	10.76064485280162	12.88560244166753	19.10093518551988
H	10.25825123264738	12.38555845956732	19.93740555260326
C	12.88614743299822	13.67089507874318	16.80658367732824
C	10.73537961637896	10.14248174930213	15.85972983196789
H	11.46646185501012	9.99830697183184	15.05957709165941

C	11.61674750877322	13.27399598097682	16.13571305334214
H	11.71681192492862	12.97559180522561	15.08481995570241
C	12.01511684225820	12.33785890634847	18.68357465466369
H	12.36707811541414	11.45263586132850	19.22747237690650
C	6.88417837730828	12.21778917253448	16.45633270464208
H	7.39054531227056	12.77652536243415	15.66331952440839
C	10.94232427252305	9.67504994970158	17.17023062224576
H	11.84503604857916	9.13689439380005	17.47169328351089
C	10.23148008117620	14.81060382123199	17.64258163299908
C	10.11072782053966	9.45230779933197	19.41274272680489
H	9.60105381133874	10.10687770864527	20.12872484792219
H	11.17218215831200	9.37672905194898	19.69129993744900
H	9.65665741042167	8.45115608794310	19.47440423423110
C	6.33918935707986	10.96512143473023	16.10425584874512
H	6.46624961893476	10.64881214223230	15.06171013129348
C	9.31030966440633	11.27723187974019	14.29931180306463
H	8.70848951358897	10.51700166186804	13.77801462899255
H	10.24360504039626	11.43476768546360	13.73889588891178
H	8.74367423252359	12.21559910865202	14.31362404186916
C	5.40405266575095	9.90631815676887	18.14514978649308
C	9.87590822804688	16.14688093492428	17.44358609294416
H	9.70222258011393	16.51442359713791	16.42833753266873
C	5.71781878905927	14.27550331767118	17.33940900297602
H	5.57653019083977	14.63171124576659	16.31547904112428
C	13.08835850080552	13.19383337690616	18.10695302377669
C	10.27522674464895	15.18833382829102	20.03641750533428
H	10.41403252327924	14.80422288308187	21.05096408414946
C	5.19446615967692	10.34821081695578	16.82902804174379
C	10.43291313850851	14.32990996074706	18.94594685388881
C	5.48978447038484	14.59739519946961	19.72566681612331
H	5.16202155553593	15.20652988829753	20.57155715238641
C	15.03075537798729	14.78613869433454	16.88618728448440
H	15.79642077566298	15.39932472454811	16.40408359044024
C	5.28459715461393	15.04555750267855	18.41960302891109

H	4.79587384311178	16.00640802530731	18.24094747621152
C	9.71887009815149	17.00148545292007	18.53685974395843
H	9.42716272951863	18.04246543171128	18.37660862146425
C	9.91827149037687	16.52270861676906	19.83255215269447
H	9.78303468818431	17.18736756035500	20.68955738205359
C	3.94730487512289	10.16148130558990	16.22501477100992
H	3.79402064121533	10.48807724786440	15.19306444204129
C	14.26004728168923	13.51620277567816	18.79548933987121
H	14.41826056105001	13.13179945749486	19.80701199109419
C	15.23191600581987	14.31017065803159	18.18314725965279
H	16.15478731526880	14.55002833729801	18.71738853140826
C	4.36287440850311	9.28934541508343	18.84503005879668
H	4.53524673747822	8.93249674745272	19.86389334183357
C	2.91062737601567	9.55063119422450	16.92997999151148
H	1.93978551220934	9.40232744718036	16.45069728314651
C	3.11778873925664	9.11588517431140	18.24066103664508
H	2.30949868563536	8.62702637468765	18.79008478589638
H	8.81653772240226	12.18044091378133	17.64278568018960
H	5.35859821509268	6.65784873880677	16.52080958631737
O	7.82925620428329	8.60934421523971	16.50839702827357
H	5.05668695368561	7.14358516121184	17.02619232458474
H	6.89376440953802	8.36021095525082	16.43614706219484
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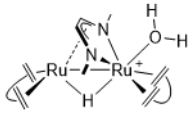
[$Ru_2H(OH_2)(Me_2(dad))(dbcot)_2$]$^+$



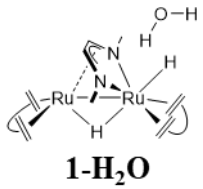
3a

Ru	8.19198930273976	10.54760799314640	17.03330471897671
Ru	10.52809739933618	11.80604701014733	17.08894411257244
N	10.02930719818105	9.85702383782355	17.79718318386743
N	9.55142746116078	10.83287946417659	15.45173468102280
C	7.39658489121309	11.12209198558409	18.96416831976540
H	8.18303857306579	11.10541574860149	19.72463908586499
C	6.85406330102868	9.87907872776298	18.57823145489758
H	7.26359168032247	8.98834212299816	19.07011661886581
C	10.32045286814715	13.80526682439632	16.45165601479158

H	9.53084640372152	13.92979526423471	15.70106867896552
C	6.25554116575873	13.11146165953666	20.02004177949162
H	6.47292308306607	12.70672477377163	21.01215733663829
C	6.64882365604312	12.40404454445832	18.88171420505138
C	6.39527559182627	12.92962680697844	17.60965722140230
C	13.78964443814106	14.53557995961931	16.04468825997530
H	13.59010179540421	14.95069414460436	15.05292747976627
C	10.83655106971636	12.72497766702043	18.95828000950267
H	10.37505324767252	12.17046024018353	19.78393462920889
C	12.85927247275633	13.67910293454578	16.63864103738666
C	10.72588164039061	10.15652823228327	15.58111106203783
H	11.42743547407055	10.06343031664714	14.74775340680452
C	11.57465996902136	13.29146597863005	15.99140296572689
H	11.64299041968817	13.05320595965193	14.92276881711679
C	12.08365501427325	12.22505475143588	18.46591169518036
H	12.47120267310642	11.31863009344628	18.94705012029613
C	6.88667211445015	12.16410666429591	16.43474545114209
H	7.35496744409731	12.77718165229024	15.65855680714328
C	10.98328665821819	9.62185530479435	16.85640462777759
H	11.90158065712754	9.07806894098228	17.09435271939055
C	10.21320805567996	14.71437685691839	17.62776172914246
C	10.23459951908145	9.27121920901978	19.10969883195562
H	9.74141085331564	9.87691034935330	19.87858376081666
H	11.30521754823541	9.19262610642717	19.35076546338964
H	9.79262374410419	8.26303287334961	19.12703900093664
C	6.33595393311640	10.93006539773748	16.02734149556733
H	6.42177798489448	10.68083903653434	14.96264966606852
C	9.23081182987267	11.35228667773087	14.13339828601009
H	8.64989910387826	10.59912293582775	13.57891614033690
H	10.14318911513156	11.58415335120876	13.56474031113292
H	8.62515004005942	12.26171344640146	14.21871894894567
C	5.47814186742432	9.73911194259607	18.02851752050612
C	9.81722599859230	16.04938468514155	17.51649119796789
H	9.59584435608390	16.46684848619879	16.53026944764258

C	5.75110247901828	14.16198924499533	17.47963577072985
H	5.57441414005629	14.57853231845584	16.48436384848162
C	13.11801972794067	13.13521014236257	17.90192585577549
C	10.33714384668743	14.96171529800615	20.03560160069393
H	10.52243004438251	14.52655511935981	21.02167808070339
C	5.21863223584477	10.26642170848173	16.75318864165622
C	10.47443208860610	14.16818173644561	18.89445059353470
C	5.61033307164188	14.34174024294600	19.88735365162035
H	5.31544017132393	14.90009566220167	20.77917845947109
C	14.97736580656295	14.84444371789955	16.71123158785061
H	15.71047186167743	15.50438641183205	16.24039029558830
C	5.35926999441569	14.86679222057639	18.61855296482327
H	4.86727373866996	15.83694980808911	18.51507486677968
C	9.67984229346910	16.83853557470202	18.66040450071220
H	9.35601995788968	17.87828410681637	18.56873178012570
C	9.94020272371732	16.29530795707835	19.91926152750122
H	9.82104270752346	16.90831032571165	20.81622833147410
C	3.94698394940073	10.12324784827804	16.19014877118292
H	3.75263015549580	10.51988119336760	15.19013348740233
C	14.30417847590245	13.44928569474415	18.56914798757351
H	14.50564889421949	13.01392053695412	19.55194390847830
C	15.23442006468161	14.30221916534238	17.97182530289225
H	16.16835721755962	14.53694442138871	18.48881506449610
C	4.46456168293761	9.07490365279436	18.72615440284554
H	4.67656370899553	8.65223235425747	19.71189297501410
C	2.93697293222658	9.46874145615029	16.89497590856549
H	1.94614608772775	9.35656404199741	16.44772660373129
C	3.19548034354741	8.94430013079461	18.16295320354550
H	2.40791650243597	8.42066297381933	18.71043806726093
H	8.85331110974183	12.07498376672718	17.53532690285336
O	7.87089106735635	8.53252874790563	16.31791212385602
H	7.95309345133972	8.47551238178145	15.35295317410492
H	6.99086250778879	8.17374200024329	16.51332808962570

[$Ru_2H_2(Me_2(dad))(dbcot)_2$] + H_2O (1-H_2O)



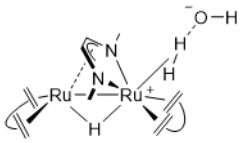
1-H_2O

Ru	8.13189407360036	10.75614352840958	17.13655010458239
Ru	10.50664114760287	12.00681429346345	17.17605992376185
N	9.94982386676137	10.03625397435717	17.88045711360381
N	9.47238265690445	11.00238441268241	15.55120728567872
C	7.28739700472031	11.23052285546955	19.03285854800581
H	8.03516158290815	11.23258450293805	19.83412542955859
C	6.80594292405551	9.96092654975491	18.60382320617939
H	7.20568939975207	9.08272502770524	19.12356614394527
C	10.39062858515675	14.00714221280325	16.51854696712862
H	9.59457934981886	14.17392351055237	15.78279954839804
C	5.95923500705730	13.10492109390901	20.10505339181549
H	6.17556902405731	12.69415108472444	21.09549662355349
C	6.45154733861473	12.46036542980637	18.96748605227948
C	6.19144494599507	12.99305264303862	17.69698732701934
C	13.89211859099463	14.51787137164887	16.02976615561456
H	13.70027919336271	14.92551928074353	15.03319882508206
C	10.88241831864001	12.94540544123830	19.02346676799215
H	10.39848680298201	12.44004588913981	19.86808901578248
C	12.92105480452799	13.73206340437119	16.65569464130676
C	10.67328129673797	10.36033375221149	15.68021877663365
H	11.37935216555687	10.29710415173854	14.84844238614891
C	11.60317597261793	13.41192164568844	16.03622659126633
H	11.63858834215394	13.16932065772999	14.96721290890736
C	12.09273087344611	12.35930850928578	18.52650481748571
H	12.43881872538243	11.44905348662150	19.03077416025875
C	6.77513043563270	12.28167244588503	16.52677163102839
H	7.20843294929235	12.94036780295476	15.76506098824575
C	10.93523091777389	9.83336872713332	16.95206669892562
H	11.86501166507028	9.31910056168340	17.20730711533514
C	10.39363185411367	14.95327563327604	17.67082911145791
C	10.17941837560442	9.48163354667391	19.20283581736025
H	9.62959797974140	10.05782954841989	19.95627692336067
H	11.24846250017397	9.48564596324886	19.46449898183856

H	9.81238034745436	8.44470898896148	19.21485307275593
C	6.29209822536443	11.01627963681167	16.08986661082355
H	6.37240049077567	10.79904891523416	15.01844477677581
C	9.16365015255217	11.54321242854430	14.24000193365164
H	8.65272812282378	10.77699407852221	13.63664002146523
H	10.07448640473718	11.85779322405386	13.70820335042550
H	8.49556189658055	12.40748979940370	14.33400073205436
C	5.42722121778042	9.80169488036080	18.06322284398447
C	10.13906946559034	16.32036025329654	17.53580699136697
H	9.93333916352509	16.73680671556351	16.54553632392003
C	5.44148032485294	14.16543023388285	17.57505322302990
H	5.25311312959540	14.58577346795296	16.58297578387667
C	13.16939199349382	13.19689872370854	17.92639976414784
C	10.62950190883029	15.24440041284023	20.06547014696296
H	10.80832807224287	14.81678906036679	21.05625987129038
C	5.16684144780151	10.33638108700208	16.79195617514939
C	10.64117346216513	14.41340101257557	18.94269373566797
C	5.21364189930839	14.27938950941363	19.97960719225924
H	4.84300016756284	14.78787281977628	20.87341163796746
C	15.10963651099028	14.76587968700675	16.66817148107351
H	15.87298335616533	15.36976010036739	16.17072491003707
C	4.95448461571313	14.80932610281934	18.71480979967222
H	4.38017604509213	15.73396837463691	18.61495264813911
C	10.12563706208221	17.14735229890011	18.66163037224784
H	9.91283124132221	18.21386219429877	18.55191662965067
C	10.37066022563884	16.60974279699766	19.92602817873799
H	10.35067030951670	17.25373577066447	20.80905407036956
C	3.89235485140387	10.20781569705498	16.23394768411610
H	3.69479976242327	10.61658842951388	15.23888592196320
C	14.38514688341956	13.45187235513293	18.56523204365212
H	14.57846371816057	13.02384900937807	19.55308499602170
C	15.35612655329806	14.23320917500618	17.93461300102907
H	16.31242906005722	14.41902128305308	18.43041906540050
C	4.41139014217077	9.14374583093389	18.76111260704354

H	4.62143011681967	8.71955158858806	19.74719431729937
C	2.88068275455502	9.54665885077585	16.93389742159381
H	1.88875511901305	9.43957420811843	16.48717341183788
C	3.14025956576002	9.01400989694693	18.19756946369747
H	2.35258134304963	8.48811528561762	18.74335144344220
H	8.97277838470021	12.43384706224727	17.66523322895097
H	7.71382872543917	9.34238115462934	16.55288590821097
O	8.50370506287507	7.05939656066248	17.58548474080994
H	8.01778556308563	6.89884384972212	18.40366783351231
H	8.29702646340045	7.98835024934880	17.38104565437352

$[Ru_2H(Me_2(dad))(dbcot)_2]^+ + OH^- + H_2$ (TS2)



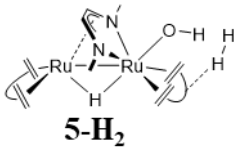
TS2

Ru	-0.78177238627358	-1.70313239882021	-0.52666337300332
Ru	1.59558637429004	-0.40423399491270	-0.48628761885007
N	1.12325912995653	-2.37454874703361	0.26779403846749
N	0.63926638352300	-1.44657032085979	-2.13736786973643
C	-1.49351379973142	-1.03034064992256	1.39873367562763
H	-0.70914975770844	-1.07990132291680	2.17367674557527
C	-2.13431212822976	-2.26569427716287	1.06688702442907
H	-1.77312280947310	-3.16004167548993	1.59999584350207
C	1.35107407719866	1.58072297458997	-1.18819667327545
H	0.57628372446754	1.67328674705634	-1.97121282155999
C	-2.47211158562742	1.07948858900388	2.43576807072259
H	-2.24193495619757	0.69421008566649	3.44183308622752
C	-2.16821439810339	0.29917310165610	1.30606358409376
C	-2.42964842791709	0.80153322333376	0.01304582782136
C	4.84056758300473	2.37830833921488	-1.55949405344273
H	4.65196552656866	2.75659137512471	-2.57688800619145
C	1.83443074391390	0.59260386992313	1.36790812169690
H	1.37259785365721	0.05694202297372	2.21764486005638
C	3.90786879687498	1.51897838244599	-0.95077771323995
C	1.83298203089574	-2.09734124852561	-1.97323723489191
H	2.55232761331584	-2.20105110339695	-2.80160894823811
C	2.64164380574104	1.07532667829616	-1.61069217992405

H	2.73757383009598	0.81363190650246	-2.68091804519559
C	3.11958631935993	0.09918824704552	0.91398999424602
H	3.52030114046826	-0.78246090442189	1.44843466025178
C	-2.01347454928466	-0.04503414799877	-1.14508342688304
H	-1.56594362494662	0.52409329182616	-1.97827051443167
C	2.09615998641091	-2.60021626772177	-0.67294413346681
H	3.03422402759804	-3.12062070504476	-0.41927365815073
C	1.20117476192665	2.53513547027722	-0.04627911593116
C	1.35249471277157	-2.90565821896182	1.60978791994492
H	0.82588498025166	-2.28658708730252	2.35742737394401
H	2.43292687648828	-2.92998478500185	1.85763833737356
H	0.94792731707654	-3.93587639692801	1.67067206565971
C	-2.66485214322127	-1.27068991360134	-1.49813330410649
H	-2.64486004936913	-1.53779910461913	-2.56731713558908
C	0.34584113366472	-0.90799174785613	-3.46502295762721
H	-0.23944082357753	-1.65805795164864	-4.03133732918572
H	1.27626619380706	-0.67085562666522	-4.01871951064454
H	-0.26230202465560	0.00993915235447	-3.37413365159375
C	-3.53684708947266	-2.34573470959854	0.56916132448585
C	0.77178919429108	3.86422939360984	-0.21174591665492
H	0.55973887997039	4.24486052238507	-1.22358492972841
C	-2.99161650519767	2.08129625946602	-0.14118623786480
H	-3.16837729166584	2.48047172051396	-1.15262741387087
C	4.15302759724414	1.01828193183060	0.34564574753899
C	1.26008596425881	2.86569324543229	2.37145818464736
H	1.43034250439364	2.46387973789769	3.38299716157456
C	-3.80531964446669	-1.83830237920522	-0.72440633095529
C	1.44717688910443	2.03274918237450	1.25359143210589
C	-3.03588032869147	2.35813885845452	2.27807339856354
H	-3.25672375167426	2.97300970468354	3.16415375199463
C	6.01719124029034	2.73532170733643	-0.87679461841440
H	6.75256005301455	3.39683691501677	-1.36040402185314
C	-3.29534251020420	2.85862975004734	0.99062391926596
H	-3.71988041872753	3.86667402795529	0.86563554583462

C	0.58526283320468	4.69240582727003	0.90950331880306
H	0.23294912608014	5.72675970533231	0.77490518539032
C	0.82951016917088	4.19352663864011	2.20030369631662
H	0.66899674527347	4.83579049156790	3.07999402308383
C	-5.10595827601425	-1.93570006659600	-1.25513659781284
H	-5.30635463589613	-1.55812034836202	-2.27056121836281
C	5.32932513998686	1.37979139688123	1.02720065308615
H	5.52336686374794	0.97649022552781	2.03392204401471
C	6.26118460851474	2.23683683344826	0.41477405936467
H	7.18791094987927	2.50737555167828	0.94415954426357
C	-4.57231166670446	-2.94356892614331	1.31287052516734
H	-4.35390824128298	-3.35552411470804	2.31105076363636
C	-6.13755040388021	-2.52415533117888	-0.50363192125847
H	-7.15062813094261	-2.60144405906309	-0.92788278056505
C	-5.87051737554096	-3.02859675757170	0.78121146665003
H	-6.67370905684021	-3.50236998918446	1.36663121924867
H	-0.10325956675099	-0.17536384801026	-0.09453334627528
H	-1.15351787018442	-3.27187886707060	-2.52676524481140
O	-0.93763861052850	-4.27971389433848	-0.52961568053949
H	-1.03708321173904	-3.89952361770744	-1.53979848475502
H	-0.01355563103122	-4.60351757908980	-0.50663417579533

[$Ru_2H(OH)(Me_2(dad))(dbcot)_2$] + H_2 (5-H_2)



5-H_2

Ru	-0.01200247281584	-0.01038193327782	2.66766943239531
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N	1.31934449982693	-1.01209977795005	1.36228076966743
N	-1.26475761598511	-1.08924482615289	1.34807809971830
C	1.31563230395563	1.62701397763447	3.01312874927057
H	2.17776917231876	1.60269244754410	2.33900233341595
C	1.34335146957034	0.73605824282483	4.11930913761174
H	2.22648362865230	0.09221211286263	4.20978498830650
C	-1.41759379123287	1.35577124989591	-0.74255483795053
H	-2.29686657918048	1.44802941020911	-0.09366820235616
C	1.26232749791139	4.16152770615410	3.03059800202183

H	2.35564577624493	4.18834873499492	3.02090487280738
C	0.60123489861879	2.93155979855907	3.04540541562776
C	-0.79883323037365	2.89076275464037	3.03417956519470
C	-1.38037886706126	0.26719742866922	-4.14056256804864
H	-2.47341238923971	0.22493394901216	-4.14244202899172
C	1.35189951963709	1.43539372214975	-0.72864685256345
H	2.21853840342125	1.57914967078959	-0.07224910672162
C	-0.68979235475735	0.26254499804549	-2.92622356606391
C	-0.64123073452658	-2.06539179016286	0.63366779312618
H	-1.20561885418284	-2.81081072442034	0.06649768945445
C	-1.36740926854091	0.20882593213244	-1.60026089583599
H	-2.21445809528264	-0.48522944744427	-1.53599165354435
C	1.37594471819627	0.28765930824333	-1.58622999970307
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H	-2.62306040029208	4.04286521395612	2.98003910368227

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H	0.17701247532750	-1.28606085415203	7.32584134564760
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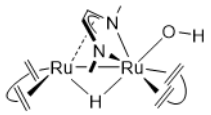
[$Ru_2H(OH)(Me_2(dad))(dbcot)_2$]



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Ru	10.54841101177366	11.81542822372808	17.08219803123842
N	10.05510935094558	9.85157130062550	17.77495667688575
N	9.58502191931337	10.83861092937375	15.43282485905182
C	7.43549482803677	11.09700289582656	18.91684183337684
H	8.20552475952298	11.07829548645250	19.69483626927733
C	6.89322618146058	9.84414439242459	18.52486310164681
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C	6.24986370304496	13.06128314910995	19.99336457935775
H	6.46817951567182	12.65502030752226	20.98502748784428
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C	6.40725956987343	12.89464558588237	17.58268086805478
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H	4.70192907826360	8.64795558176326	19.69715898805383
C	2.94997781431810	9.47718349153582	16.89146116254841
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H	2.42178037747097	8.44159777669151	18.71450372417985
H	8.93214203621000	12.12099565292011	17.52488772045544
O	7.97537035696773	8.64573348909406	16.27298989091980
H	7.05489363355380	8.37452336435715	16.36248156514224

Table S5: Complex impregnation on C^k, $1 mg_{Ru}$ cm^{-2} catalyst loading (3.06% $wt._{Ru}$).

Reactants	Expected Quantity
$[Ru_2(\mu\text{-}H)(Me_2dad)(dbcot)_2OTf]$	36.0 mg (0.04 mmol $_{complex}$)
C^k	214.0 mg
CH_3CN for complex dissolution	15 mL
CH_3CN for C^k suspension	20 mL

Table S6: Complex impregnation on C^k, $0.04 mg_{Ru}$ cm^{-2} catalyst loading (0.44% $wt._{Ru}$).

Reactants	Expected Quantity
$[Ru_2(\mu\text{-}H)(Me_2dad)(dbcot)_2OTf]$	3.6 mg (0.005 mmol $_{complex}$)
C^k	214.0 mg
CH_3CN for complex dissolution	5 mL
CH_3CN for C^k suspension	20 mL

Table S7: Ink preparation.

Reactants	Quantity
$[Ru_2(\mu\text{-}H)(Me_2dad)(dbcot)_2OTf]$ /C^k (3.06% $wt._{Ru}$)	7.0 mg (0.008 mmol $_{complex}$)
Milli-Q water	600 mg

EtOH	600 mg
Nafion 5%wt.	12 mg

Table S8: Surface composition determined by XPS analysis.

	C*1s*	**N*1s***	**Ru*3d***	**N/Ru**
Theoretical	89%	7%	5%	1.5
Pristine **2**	87.2%	7.3%	5.5%	1.3
Pristine 2 after 7 days electrolysis	87.8%	7.8%	4.5%	1.7

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