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4. Supplementary References
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 1H and 13C. 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 Har or Car when not noted otherwise. Quaternary 13C are indicated as Cquat. The olefinic protons and 13C atoms of the two coordinated C=C moieties in dbcot (dibenzo[a,e]cyclooctatetraene) are indicated as Holef and Colef, respectively. The protons and carbon atoms of the diazabutadiene moiety are denoted as Hadad and Cadad, respectively. [Ru2 H(µ-H)(Me2(dad))(dbcot)2], [Ru(µ-H)(Me2(dad))(dbcot)2]PF6, and [Ru(OTf)(µ-H)(Me2(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 microwave 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 \([\text{Ru}(\text{OTf})(\mu-\text{H})(\text{Me}_2(\text{dad}))(\text{dbcot})_2]\) (2)

Route 1 (adapted from ref. [S1]): \([\text{RuH}(\mu-\text{H})(\text{Me}_2(\text{dad}))(\text{dbcot})_2]\) 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: \([\text{RuH}(\mu-\text{H})(\text{Me}_2(\text{dad}))(\text{dbcot})_2]\) 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 %.

1H NMR (400 MHz, Acetonitrile-\(d_3\)) δ 7.45 (s, 2H, CH\(^{\text{dad}}\)), 7.08 – 7.04 (m, 2H, H\(^{\text{ar}}\)), 7.04 – 6.99 (m, 2H, H\(^{\text{ar}}\)), 6.88 (dddd, \(J = 16.7, 6.2, 5.3, 3.3\) Hz, 6H, H\(^{\text{ar}}\)), 6.81 – 6.73 (m, 6H, H\(^{\text{ar}}\)), 4.84 (d, \(J = 9.1\) Hz, 2H, CH\(^{\text{olef}}\)), 4.47 (d, \(J = 9.1\) Hz, 2H, CH\(^{\text{olef}}\)), 4.06 (d, \(J = 8.6\) Hz, 2H, CH\(^{\text{olef}}\)), 4.00 (d, \(J = 8.6\) Hz, 2H, CH\(^{\text{olef}}\)), 2.02 (d, \(J = 0.9\) Hz, 6H, CH\(^{\text{dad}}\)), -7.39 (s, 1H). 13C NMR (101 MHz, CD\(_3\)CN) δ 147.9 (s, 2C, C\(^{\text{quat}}\)), 147.5 (s, 2C, C\(^{\text{quat}}\)), 145.6 (s, 2C, C\(^{\text{quat}}\)), 143.5 (s, 2C, C\(^{\text{quat}}\)), 128.6 (2 CH, C\(^{\text{ar}}\)), 128.3 (2 CH, C\(^{\text{ar}}\)), 127.3 (2 CH, C\(^{\text{ar}}\)), 127.3 (2 CH, C\(^{\text{ar}}\)), 127.0 (2 CH, C\(^{\text{ar}}\)), 126.8 (2 CH, C\(^{\text{ar}}\)), 126.7 (2 CH, C\(^{\text{ar}}\)), 126.2 (2 CH, C\(^{\text{ar}}\)), 121.0 (s, 2C, CH\(^{\text{dad}}\)), 84.8 (s, 2C, CH\(^{\text{olef}}\)), 81.2 (s, 2C, CH\(^{\text{olef}}\), 75.9
(s, 2C, CH$_{2}^{olef}$), 69.2 (s, 2C, CH$_{2}^{olef}$), 40.6 (2 CH$_{3}$, CH$_{3}^{lad}$). $^{19}$F NMR (376 MHz, CD$_{3}$CN) $\delta$ -79.2 (s, OTf). MALDI HRMS (m/z): [Ru$_{2}$(Me$_{2}$(dad))(dbcot)$_{2}$H]$^{+}$ calcd. For C$_{36}$H$_{33}$N$_{2}$Ru$_{2}$ 697.0725; found: 697.0732.

c. **Synthesis of [Ru(OH$_{2})$(µ-H)(Me$_{2}$(dad))(dbcot)$_{2}$]$^{+}$**

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(µ-H)(Me$_{2}$(dad))(dbcot)$_{2}$] (130 mg, 187 µmol) in THF (5 mL, 35 mM). The mixture was heated to 60 $^\circ$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 (3x1 mL) and hexanes (3x1 mL). After drying at HV overnight, a brightly red solid of the composition [Ru(OH$_{2})$(µ-H)(Me$_{2}$(dad))(dbcot)$_{2}$]HSO$_{4}$·0.34 THF·1.25 H$_{2}$SO$_{4}$ was obtained. Yield: 110 mg, 62 %.

$^{1}$H NMR (500 MHz, Acetonitrile-$d_{3}$) $\delta$ 7.48 (s, 2H, NCH), 7.46 – 7.32 (s (br), 4H, H$_{2}$O/H$_{3}$O$^{+}$), 7.06 (dd, $J_{HH} = 5.6$, 3.4 Hz, 2H, H$^{a'}$), 7.04 – 6.98 (m, 2H, H$^{a''}$), 6.94 – 6.84 (m, 6H, H$^{ab}$), 6.84 – 6.72 (m, 6H, H$^{abc}$), 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$_{3}$CN) $\delta$ 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$_{3}^{lad}$). 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$_{2}$(dad))(dbcot)$_{2}$H]$^{+}$ calcd. For C$_{36}$H$_{33}$N$_{2}$Ru$_{2}$ 697.0725; found: 697.0729. Elemental analysis calcd for C$_{36}$H$_{36}$N$_{2}$O$_{5}$Ru$_{2}$S·0.34 C$_{4}$H$_{8}$O·1.25 H$_{2}$SO$_{4}$ 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(µ-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)(µ-H)(Me₂(dad))(dbcot)]⁺BF₄⁻

A 50% solution of HBF₄ 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)(Me₂(dad))(dbcot)] (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 HBF₄ proceeds faster than with H₂SO₄.) The mixture was left at room temperature overnight which caused more solid to precipitate. The mother liquors were 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)(µ-H)(Me₂(dad))(dbcot)]BF₄ 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.

1H NMR (400 MHz, Acetonitrile-d₃) δ 7.45 (s, 2H, NCH), 7.09 – 7.03 (m, 2H, Hₜₕ), 7.05 – 6.98 (m, 2H, Hₜₕ), 6.93 – 6.84 (m, 6H, Hₜₕ), 6.81 – 6.73 (m, 6H, Hₜₕ), 4.84 (d, Jₜₕ = 9.1 Hz, 2H, Hₜₖ), 4.47 (d, Jₜₕ = 9.1 Hz, 2H, Hₜₖ), 4.06 (d, Jₜₕ = 8.6 Hz, 2H, Hₜₖ), 4.00 (dd, Jₜₕ = 8.6, 1.0 Hz, 2H, Hₜₖ), 2.84 (s, br, 2H, H₂O) 2.02 (d, Jₜₕ = 0.9 Hz, 6H, CH₃), -7.40 (s, 1H, Hₕ).

13C NMR (126 MHz, CD₃CN) 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, CH₃dad). Elemental analysis calcd (%) for C₃₆H₃₅BF₄N₂ORu₂ was: C 54.01, H 4.41, N 3.50 found: C 53.90, H 4.44, N 3.53.

e. Synthesis of IrO₂

The IrO₂ anode for the complete electrolysis cell was synthetized as described in [S2]. In brief, 247 mg of IrCl₃*3H₂O (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, the structures were solved with SHELXT, followed by least-squares refinement against full matrix (versus F2) with SHELXL. All non-hydrogen atoms were refined anisotropically. The crystal structures of [Ru(OH₂)(μ-H) (Me₂(dad))(dbcot)]₂BF₄ and [Ru(NCCH₃)(μ-H) (Me₂(dad))(dbcot)]₂PF₆ are reported in figure 1 in the main text, crystal data and further crystallographic details are reported in table S1 and S2.

g. DFT calculations

All calculations were carried out with ORCA 4.2.0. Geometry optimizations were performed at the PBE0-D3BJ/def2-SVP/def2-TZVP(Ru) level of theory. Solvent effects were taken into account implicitly by using the cpcm model with water as solvent and a gaussian charge scheme. 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. 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 (hv = 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 Au4f7/2 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)(µ-H)(Me\(_2\)dad)(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\(_2\)O\(_2\)/H\(_2\)SO\(_4\) 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\textsuperscript{TM}) 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\textsuperscript{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 experiements in aqueous environment were acquired in a standard pyrex\textsuperscript{®} 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 µgRu 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 H₂PO₄/HPO₄²⁻ buffer solution (pH 7.4) or 0.25 M HClO₄ 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 H₂PO₄/HPO₄²⁻ buffer solution (pH 7.4) or 0.25 M HClO₄ 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 H₂SO₄ solution, under N₂ 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 [Ru₂(OTf)(µ-H)(Me₂dad)(dbcot)₂]/Cink 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 H₂SO₄ solution or H₂O 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 cm² Scribner cell fixture using a 4 Nm screwing torque. The anode was realized mixing in an agate mortar 40 mg of IrO₂ with 20 mg of Cₖ 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 cm², Beakert). The electrode has the 66.6% wt IrO₂ loading (c.a. 7 mgₖₐ₉ₐ₈ₙ 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 [Ru₂(OTf)(μ-H)(Me₂dad)(dbcot)₂] /Cₖ catalyst (3.06% wt. Ru or 0.445% wt. Ru); the so obtained dense paste was spread onto a 5 cm² 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 mgRu cm⁻² 2@Cₖ or 0.04 mgRu cm⁻² for the seven time diluted catalyst 2₃₉₈@Cₖ.

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.

\[
FE \text{ (\%)} = \frac{\text{mol}_{H_2}^{\text{real}}}{\text{mol}_{H_2}^{\text{theoretic}}} * 100 \quad \text{Eq.1}
\]

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.

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

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.

\[
\text{Energy consuption (kWh kg}_{H_2}^{-1}) = \frac{\int V(t)I(t) \, d(t)}{kg_{H_2}^{\text{real}}} \quad \text{Eq.3}
\]

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-d8 (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\(_2\)O (0.15 µL, 7.5 µmol, 1.1 eq.) was added to the tube. After measuring \(^1\)H-NMR, H\(_2\)SO\(_4\) (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@\(\text{C}^k\) 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$_3$CN (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: ($\delta$ 7.46 (s, 2H, CH$^{\text{dad}}$), 7.35-7.18 (m, 2H, CH$^{\text{ar}}$), 7.13-7.02 (m, 2H, CH$^{\text{ar}}$), 6.92-6.85 (m, 8H, CH$^{\text{ar}}$), 6.84-6.74 (m, 2H, CH$^{\text{ar}}$), 6.75-6.61 (m, 2H, CH$^{\text{ar}}$), 4.86 (d, $J_{\text{HH}} = 9.1$ Hz, 2H, CH$^{\text{olef}}$), 4.78 (d, $J_{\text{HH}} = 9.3$ Hz, 2H, CH$^{\text{olef}}$), 4.08 (d, $J_{\text{HH}} = 8.7$ Hz, 2H, CH$^{\text{olef}}$), 4.02 (d, $J_{\text{HH}} = 8.5$ Hz, 2H, CH$^{\text{olef}}$), 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(µ-H)(NCCD₃)(Me₂(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 (3e, formed from 2 recrystallized in CH$_3$CN).
Figure S2: $^1$H- (top) and $^{13}$C- (bottom) NMR spectra of [Ru(OH)$_2$(μ-H)(Me$_2$(dad))(dbcot)$_2$]$_3$BF$_4$ (3a) in CD$_3$CN (in-situ forms 3c and free H$_2$O).
Figure S3: $^1$H- (top) and $^{13}$C- (bottom) NMR spectra of [Ru(OH$_2$)(µ-H)(Me$_2$(dad))(dbcot)$_2$]$_3$(HSO$_4$)(SO$_4$) -0.34 THF·H$_2$SO$_4$ (3a).
Figure S4: $^1$H- (top) and $^{13}$C- (bottom) NMR spectra of [Ru(OH)$_2$(μ-H)(Me$_2$(dad))(dbcot)$_2$](HSO$_4$)(SO$_4$)·0.34 THF·H$_2$SO$_4$ (3a).
The TGA data suggest that in the solid, H$_2$O 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$_3$)(µ-H)Me$_2$(dad))(dbcot)$_2$]OTf·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(OH₂)(µ-H)(Me₂(dad))(dbcot)₂]₃(HSO₄)(SO₄) (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$_2$)(µ-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 measurements

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

(a) Scheme of the electrolysis test cell experimental set up.

(b) Picture of the electrolysis test station.

Figure S9: (a) Scheme of the electrolysis test cell experimental set up. (b) Picture of the electrolysis test station.
Figure S10: High magnification HAADF-STEM (Z contrast) image of \( \text{2@C} \) 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$_3$CN 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$_2$SO$_4$ 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)(trop₂dad)] benchmark 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$_2$PO$_4$/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$_2$dad)] 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$_3$CN of 10$^{-3}$ M complex 2 in 20 ml of 0.1M Bu$_4$NPF$_6$ buffer solution (blue line) or in 20 ml of a 0.1M Bu$_4$NPF$_6$ 5M Milli-Q water solution (red line) or in 20 ml of a 0.1M Bu$_4$NPF$_6$ 0.25M H$_2$SO$_4$ - 5M H$_2$O solution (black line).
3. Supplementary tables

Table S1: Crystal data and structure refinement for [Ru$_2$(OH)$_2$($\mu$-H)(Me$_2$(dad))(dbcot)$_2$]BF$_4$

| Property                  | Value                              |
|---------------------------|------------------------------------|
| Empirical formula         | C$_{36}$H$_{35}$BF$_4$N$_2$ORu$_2$  |
| 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)                         |
| $\alpha$/°                | 78.9600(10)                        |
| $\beta$/°                 | 76.8190(10)                        |
| $\gamma$/°                | 85.7730(10)                        |
| Volume/Å³                 | 1603.87(5)                         |
| Z                         | 2                                  |
| $\rho_{calc}$/g/cm$^3$    | 1.657                              |
| $\mu$/mm$^{-1}$           | 8.098                              |
| F(000)                    | 803.0                              |
| Crystal size/mm$^3$       | 0.042 $\times$ 0.036 $\times$ 0.02 |
| Radiation                 | CuK$\alpha$ ($\lambda$ = 1.54184) |
| $2\Theta$ 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$>$$\sigma$(I)] | R$_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$_3$)(µ-H)(Me$_2$(dad))(dbcot)$_2$]PF$_6$

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C$_{44}$H$_{45}$F$_6$N$_6$PRu$_2$           |
| 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)                                 |
| $\alpha$/°                                    | 90                                         |
| $\beta$/°                                     | 98.846(2)                                  |
| $\gamma$/°                                    | 90                                         |
| Volume/Å$^3$                                   | 4177.47(12)                                |
| Z                                             | 4                                          |
| $\rho_{\text{calc}}$/g/cm$^3$                 | 1.598                                      |
| $\mu$/mm$^{-1}$                               | 0.828                                      |
| F(000)                                        | 2032.0                                     |
| Crystal size/mm$^3$                           | 0.49 $\times$ 0.16 $\times$ 0.11           |
| Radiation                                     | MoKα ($\lambda = 0.71073$)                |
| 2$\Theta$ 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$_{\text{int}} = 0.0602$, R$_{\text{sigma}} = 0.0383$] |
| Data/restraints/parameters                    | 10726/0/542                                |
| Goodness-of-fit on F$^2$                      | 1.233                                      |
| Final R indexes [I$>2\sigma$(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

\[
\text{[Ru}_2\text{H}_2(\text{Me}_2(\text{dad})(\text{dbcot})_2] + \text{H}_3\text{O}^+ \quad (1-\text{H}_3\text{O}^+)\]

| Atom | X             | Y             | Z             |
|------|---------------|---------------|---------------|
| Ru   | 8.13813165218872 | 10.64682124564211 | 17.22672015943617 |
| Ru   | 10.48919618588997 | 11.90568054402451 | 17.24016377057114 |
| N    | 9.95516452606099 | 9.963905270728    | 18.0187161850304  |
| N    | 9.50106584141107 | 10.82065621069377 | 15.64379253813145 |
| C    | 7.31864584086485 | 11.26690530336746 | 19.1097070722285  |
| H    | 8.08358269092886 | 11.28668093184408 | 19.89292904503773 |
| C    | 6.78229260062793 | 10.00173055688789 | 18.7633604260544  |
| H    | 7.16461209845646 | 9.1332127234202   | 19.31147354024827 |
| C    | 10.32869449167464 | 13.8726740939388  | 16.49577718268875 |
| H    | 9.54567603014170 | 13.97628095174508 | 15.73506263567726 |
| C    | 6.11887500438998 | 13.27334489833331 | 20.07496811052821 |
| H    | 6.3283368237949  | 12.91054325928870 | 21.08514520274414 |
| C    | 6.5493592992757  | 12.53301232958027 | 18.97154848528290 |
| C    | 6.3020618633629  | 13.00428825572757 | 17.67557071983042 |
| C    | 13.82475946209939 | 14.47703212683597 | 16.07436643543642 |
| H    | 13.64634966396172 | 14.83749746012517 | 15.05740919526479 |
| C    | 10.78993472089475 | 12.92895902607090 | 19.0568768175509  |
| 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    | 12.0303375038959  | 12.36556834433601 | 18.61438893207802 |
| H    | 12.39125582481782 | 11.48585349993030 | 19.16099399651979 |
| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| C    | 6.8231132266174 | 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    | 10.25742529986308 | 14.85983737487156 | 17.6105931985454 |
| C    | 10.16552322020402 | 9.46189097686559 | 19.36609773525907 |
| H    | 9.62738138659398 | 10.08196630198199 | 20.09209805765485 |
| H    | 11.23365108392435 | 9.45471817968724 | 19.62994846062462 |
| H    | 9.77863095208869 | 8.4332085927640 | 19.43797315271789 |
| C    | 6.27862158562520 | 10.94090621165616 | 16.18191539103130 |
| H    | 6.35027740822886 | 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 | 13.21196373735394 | 18.00580399973393 |
| C    | 10.39857825775648 | 15.25021568465570 | 19.99846847647712 |
| H    | 10.56326170186747 | 14.86864663841171 | 21.01020717283730 |
| C    | 5.14261634297825 | 10.3429956739174 | 16.93833812190081 |
| C    | 10.48983436491876 | 14.38073322271449 | 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 | 18.1201831949073 | 18.34984196301983 |
| C    | 10.07612989176976 | 16.59419383699542 | 19.79812520309585 |
\[
\text{[Ru}_2\text{H}_3(\text{Me}_2\text{dad})(\text{dbcot})_2]^+ + \text{H}_2\text{O} \quad (6-\text{H}_2\text{O})
\]

- 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
|     |      |      |      |      |
|-----|------|------|------|------|
| 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  | 14.8969124585715   | 16.77980863210577  |
| H   | 15.7387388366810   | 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  | 20.5024444816890  |
| C   | 3.9755092252778    | 10.05949396007522  | 16.50713762895331  |
| H   | 3.80954426275753   | 10.34081589930771  | 15.4639370437828  |
| C   | 14.27285605365125  | 13.69041805174037  | 18.76534171259762  |
| H   | 14.45060182026774  | 13.36742586849560  | 19.79490756893398  |
| C   | 15.21819559996064  | 14.4732023239032   | 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   | 19.1775435679106  |
| H   | 8.92765109422214    | 12.18121267793133  | 17.75372085914649  |
| H   | 7.86148929715220    | 9.03607348011290   | 16.54645240965710  |
| O   | 7.87986077192512    | 8.0900936933812    | 14.79181034681085  |
| H   | 7.80029629944006    | 8.88605113492411   | 17.40176002131593  |
| H   | 6.95337804971629    | 8.0406925028301    | 14.52070974101978  |
| H   | 8.07923932148336    | 7.18760635667948   | 15.07481818191654  |
$$[\text{Ru}_2\text{H(Me}_2\text{dad})(\text{dbcot})_2]^* + \text{H}_2\text{O} + \text{H}_2 \quad (\text{TS1}) $$

|        |            |            |            |            |
|--------|------------|------------|------------|------------|
| Ru     | -0.73592461283115 | -1.60962536662603 | -0.34172249026855 |
| Ru     | 1.65606432939943  | -0.34287147683925  | -0.35162634542282 |
| N      | 1.12883720936822  | -2.23544000023307  | 0.53797618422866  |
| N      | 0.7033433274748   | -1.45062495389621  | -1.9380287314342  |
| 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   | -2.6182425523564  |
| 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  | -2.52515459283979 |
| 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  | -2.57465318048666  | -0.37821262765237 |
| H      | 2.99998452201762  | -3.11752238426798  | -0.08125892043934 |
| C      | 1.25669178352300  | 2.60563170518568   | -0.1008920051415  |
| C      | 1.30929702897751  | -2.69407312364257  | 1.91338685038245  |
| H      | 0.80962525769384  | -1.99970784224767  | 2.61157295497177  |
| H      | 2.38384084171635  | -2.76540766881611  | 2.1756922936101   |
\[ \text{[Ru}_2\text{H(OH)}_2\text{(Me}_2\text{dad)}\text{(dbcot)}_2]^{+} + \text{H}_2 \quad (3a-\text{H}_2) \]

\[
\begin{align*}
\text{Ru} & \quad 8.15691933379512 & \quad 10.63342892971193 & \quad 17.19955174596576 \\
\text{Ru} & \quad 10.50484401486477 & \quad 11.86990533465470 & \quad 17.27395046575617 \\
\text{N} & \quad 9.95451970786443 & \quad 9.96465807011599 & \quad 18.06220613347282 \\
\text{N} & \quad 9.57879778351387 & \quad 10.82648080684096 & \quad 15.65320300614214 \\
\text{C} & \quad 7.30318411138939 & \quad 11.32986260423496 & \quad 19.05964119757783 \\
\text{H} & \quad 8.05881401491356 & \quad 11.35473982707915 & \quad 19.85071680443080 \\
\text{C} & \quad 6.76199141297012 & \quad 10.06892351118563 & \quad 18.73047537136772 \\
\text{C} & \quad 7.14065210177334 & \quad 9.20604201144443 & \quad 19.29178549430474 \\
\text{C} & \quad 10.35814688465208 & \quad 13.83464633679056 & \quad 16.52318173584584 \\
\text{H} & \quad 9.59601638481791 & \quad 13.93054996221221 & \quad 15.7405980429782 \\
\text{C} & \quad 6.13061002399299 & \quad 13.3792163710800 & \quad 19.95424711008095 \\
\text{C} & \quad 6.31157238191186 & \quad 13.03367430375069 & \quad 20.97568911661009 \\
\text{C} & \quad 6.56450593866260 & \quad 12.60610909374267 & \quad 18.8749361714148 \\
\text{C} & \quad 6.35634789079076 & \quad 13.05415142270449 & \quad 17.56547753589881 \\
\text{C} & \quad 13.85775009531831 & \quad 14.46912693928245 & \quad 16.19773905958742 \\
\text{H} & \quad 13.70274745470889 & \quad 14.83085866396771 & \quad 15.17750790783735 \\
\text{C} & \quad 10.76064485280162 & \quad 12.88560244166753 & \quad 19.10093518551988 \\
\text{H} & \quad 10.25825123264738 & \quad 12.38555845956732 & \quad 19.93740555260326 \\
\text{C} & \quad 12.88614743299822 & \quad 13.67089507874318 & \quad 16.80658367732824 \\
\text{C} & \quad 10.73537961637896 & \quad 10.14248174930213 & \quad 15.85972983196789 \\
\text{H} & \quad 11.46646185501012 & \quad 9.99830697183184 & \quad 15.05957709165941 \\
\end{align*}
\]
|    |    |    |    |    |
|----|----|----|----|----|
| 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  | 6.84417837730828  | 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  | 10.2128125831200  | 9.37672905194898  | 19.69129937449000 |
| C  | 9.65665741042167  | 8.45115608794310  | 19.47440234231100 |
| 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 |
| C  | 8.74367423252359  | 12.21559910865202 | 14.31362404186916 |
| C  | 5.40405266575095  | 9.90631815676887  | 18.14514978649308 |
| C  | 9.87590822804688  | 16.14688093492428 | 17.4435860924416 |
| 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  | 10.3291313850851 | 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 |
[Ru₂H(OH)(Me₂(dad))(dbcot)]^+

Ru  8.19198930273976  10.54760799314640  17.0330471897671
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
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | 9.53084640372152 | 13.92979526423471 | 15.70106867896552 |
| C    | 6.25554116575873  | 13.11146165953666 | 20.02004177949162 |
| H    | 6.47292308306607  | 12.70672477377163 | 21.01215733663829 |
| C    | 6.64882365604312  | 12.4040445445832  | 18.88171420505138 |
| C    | 6.39527559182627  | 12.92962680697844 | 17.60965722140230 |
| C    | 13.7896443814106  | 14.53557995961931 | 16.04468825997530 |
| H    | 13.59010179540421 | 14.95069414460436 | 15.05292747976627 |
| C    | 10.83655106971636 | 12.7297766702043  | 18.95828000950267 |
| H    | 10.3750324767252  | 12.1704602018353  | 19.7839462920889 |
| C    | 12.85927247275633 | 13.67910293454578 | 16.63864103738666 |
| C    | 10.72588164039061 | 10.15652823228327 | 15.58111106203783 |
| H    | 11.42743547407055 | 10.06340301664714 | 14.74775340680452 |
| C    | 11.57465996902136 | 13.29146597863005 | 15.99140296572689 |
| H    | 11.64299041968817 | 13.0532059596193  | 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  | 16.8564062777759 |
| 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  | 19.8785837608166 |
| H    | 11.30521754823541 | 9.19262610642717  | 19.35076546338964 |
| H    | 9.79262374410419  | 8.2630287334961  | 19.1270390093664 |
| C    | 6.33595393311640  | 10.93006539773748 | 16.02734149556733 |
| H    | 6.42177798489448  | 10.68083903653434 | 14.96264966606852 |
| C    | 9.23081182987267  | 11.3522866773087  | 14.13339828601009 |
| H    | 8.64989910387826  | 10.59912293582775 | 13.57891614033690 |
| H    | 10.14318911513156 | 11.58415335120876 | 13.5647403113292 |
| H    | 8.62515004005942  | 12.2617134460146  | 14.21871894894567 |
| C    | 5.47814186742432  | 9.73911194259607  | 18.02851752050612 |
| C    | 9.81722599859230  | 16.04938468514155 | 17.51649119796789 |
| H    | 9.59584435608390  | 16.46684848619879 | 16.5302694764258 |
|     | x    | y    | z    |
|-----|------|------|------|
| C   | 5.75110247901828 | 14.16198924499533 | 17.47963577072985 |
| H   | 5.57441414005629  | 14.57853231845554  | 16.48436384848162  |
| C   | 13.11801972794067  | 13.13521014236257  | 17.90192585775499  |
| C   | 10.33714384668743  | 19.61715298006115  | 20.03560160693937  |
| H   | 10.52243004438251  | 14.52655511935981  | 21.02167808070339  |
| C   | 5.21863223584477   | 20.26642170848173  | 16.7531886165622   |
| C   | 10.47443208860610  | 14.16818173644561  | 18.89445059353470  |
| C   | 5.61033307164188   | 19.3417404294600   | 19.88735365162035  |
| H   | 5.31544017132393   | 14.90009566220167  | 20.77917845947109  |
| C   | 14.97736580656295  | 19.84444371789955  | 16.71123158785061  |
| H   | 15.71047186167743  | 15.50438641183205  | 16.24039029558830  |
| C   | 5.35926999441569   | 18.8667922057639   | 18.61855296482327  |
| H   | 4.86727373866996   | 15.83694980808911  | 18.5150748677968   |
| 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   | 18.7261540284554   |
| H   | 4.67656370899553   | 8.65223235425747   | 19.71189297501410  |
| C   | 2.93697293222658   | 9.46874145615029   | 16.89497950856549  |
| 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   | 8.53252874905635   | 16.31791212385602  |
| H   | 7.95309345133972   | 8.47551238178145   | 15.35295317410492  |
| H   | 6.99086250778879   | 8.17374200024329   | 16.51332808962570  |
\[
[Ru_2H_2(Me_2(dad))(dbcot)]_2 + H_2O \quad (1-H_2O)
\]

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Ru      | 8.13 | 10.75 | 17.14 |
| Ru      | 10.50 | 12.00 | 17.17 |
| N       | 9.49 | 10.03 | 17.88 |
| N       | 9.47 | 11.23 | 15.55 |
| C       | 7.28 | 12.23 | 19.03 |
| H       | 8.03 | 11.23 | 19.83 |
| C       | 6.80 | 9.96  | 18.60 |
| H       | 7.02 | 9.08  | 19.12 |
| C       | 10.39 | 14.01 | 16.52 |
| H       | 9.59 | 14.17 | 15.78 |
| C       | 5.96 | 13.10 | 20.10 |
| H       | 6.16 | 12.69 | 21.09 |
| C       | 6.45 | 12.46 | 18.97 |
| H       | 6.91 | 12.46 | 18.97 |
| C       | 13.89 | 14.51 | 16.20 |
| H       | 13.70 | 14.92 | 15.03 |
| C       | 10.82 | 12.94 | 19.02 |
| H       | 10.39 | 12.44 | 19.86 |
| C       | 6.77 | 12.70 | 16.53 |
| H       | 7.21 | 12.97 | 15.77 |
| C       | 10.94 | 9.83  | 16.95 |
| H       | 11.87 | 10.05 | 17.92 |
| C       | 10.39 | 14.95 | 17.67 |
| H       | 9.63 | 10.57 | 19.95 |
| H       | 11.24 | 9.48  | 19.46 |

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|   |   |   |   |   |   |
|---|---|---|---|---|---|
| H | 9.81238034745436 | 8.44470898896148 | 19.21485307275593 |
| C | 6.29209822536443 | 11.01627963681167 | 16.08986661082355 |
| H | 6.37240049077567 | 10.79904891523416 | 15.01844477677581 |
| C | 9.16356015255217 | 11.5432124854430 | 14.24000193365164 |
| H | 8.65272812282378 | 10.77699407852221 | 13.63664002146523 |
| H | 10.07448640473718 | 11.85779322405386 | 13.70820335042550 |
| C | 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 | 14.16540323388285 | 17.57505322302990 |
| H | 5.25311312959540 | 14.58577346795296 | 16.58297578386667 |
| C | 13.1693199349382 | 13.19689872370854 | 17.92639976414784 |
| C | 10.62950190883029 | 15.2440401284023 | 20.06547014696296 |
| H | 10.8083280722487 | 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 | 15.1096351099028 | 14.76587968700675 | 16.6681711807351 |
| H | 15.87298335616533 | 15.36976010036739 | 16.17072491003707 |
| C | 4.95448461571313 | 14.80932610281934 | 18.71480979967222 |
| H | 4.38017604509213 | 15.73396837463961 | 18.61495264813911 |
| C | 10.12563706208221 | 17.14735229890011 | 18.66163073224784 |
| H | 9.91283124132221 | 18.21386219429877 | 18.55191662906067 |
| 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 |
[Ru$_2$H(Me$_2$(dad))(dbcot)$_2$]$^+$ + OH$^-$ + H$_2$  (TS2)

TS2

H  4.62143011681967  8.71955158858806  19.74719431729937
C  2.88068275455502  9.54665885077585  16.93389742159381
H  1.88875511901305  9.43957420811843  16.4871341183788
C  3.14025956576002  9.01400989694693  18.1975964369747
H  2.35258134304963  8.4881528561762  18.7435144344220
H  8.97277838470021 12.43384706224727 17.66523322895097
H  7.71382872543917  9.34238115462934  16.55288590821097
O  8.50370506287507  7.05939656066248  17.58548474080994
H  8.0177856308563  6.8988348972212  18.40366783351231
H  8.29702643640045  7.98835024934880  17.38104565437352

[Ru$_2$H(Me$_2$(dad))(dbcot)$_2$]$^+$ + OH$^-$ + H$_2$  (TS2)

TS2

Ru  -0.78177238627358  -1.70313239882021  -0.5266337300332
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  2.17367645575272
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  -1.97121821559999
C  -2.47211158562742  1.07948885900388  2.43576807072259
H  -2.24193495619757  0.69421008566649  3.44183308622752
C  -2.16821439810339  0.29917310165610  1.3060358409376
C  -2.42964842791709  0.80153322333376  0.01304582782136
C  4.84056758300473  2.3738033921488  -1.55949405344273
H  4.65196552656866  2.75659137512471  -2.5768800619145
C  1.83443074391390  0.59260386992313  1.36790812169690
H  1.37259785365721  0.05694202297372  2.2176486005638
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

48
\[
[Ru_2H(OH)(Me_2(dad))(dbcot)_2] + H_2 \quad (5-H_2)
\]

\[
\begin{align*}
C & \quad 0.58526283320468 & \quad 4.69240582727003 & \quad 0.90950331880306 \\
H & \quad 0.23294912608014 & \quad 5.72675970533231 & \quad 0.77490518539032 \\
C & \quad 0.82951016917088 & \quad 4.19352638640111 & \quad 2.2030369631662 \\
H & \quad 0.668996674257347 & \quad 4.83579049156790 & \quad 3.0799402308383 \\
C & \quad -5.10595827601425 & \quad -1.93570006659600 & \quad -1.25513659781284 \\
H & \quad -5.30635463589613 & \quad -1.55812034836202 & \quad -2.27056121836281 \\
C & \quad 5.32932513998686 & \quad 1.37979139688123 & \quad 1.02720065308615 \\
H & \quad 5.52336686374794 & \quad 0.97649022552781 & \quad 2.03392204401471 \\
C & \quad 6.26118460851474 & \quad 2.23683683344826 & \quad 0.41477405936467 \\
H & \quad 5.67231166670446 & \quad -2.94356892614331 & \quad 1.31287052516734 \\
C & \quad -4.573290824128298 & \quad -3.35552411470804 & \quad 2.31105076363636 \\
H & \quad -6.13755040388021 & \quad -2.52415533117888 & \quad -0.50363192125847 \\
H & \quad -7.15062813094261 & \quad -2.6014405906309 & \quad -0.92788278056505 \\
C & \quad -5.87051737554096 & \quad 3.02859675757170 & \quad 0.78121146665003 \\
H & \quad -6.67370905684021 & \quad -3.50236998918446 & \quad 1.36663121924867 \\
H & \quad -0.10325956675999 & \quad -0.17536384801026 & \quad -0.0945334627528 \\
H & \quad -1.15351787018442 & \quad -3.2718786707060 & \quad -2.52676524481140 \\
O & \quad -0.93763861052850 & \quad -4.27971389433848 & \quad -0.52961568053949 \\
H & \quad -1.03708321173904 & \quad -3.8952361770744 & \quad -1.53979848475502 \\
H & \quad -0.01355563103122 & \quad -4.60351757908980 & \quad -0.50663417579533
\end{align*}
\]
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | 2.35564577624493 | 4.18834873499492 | 3.02090487280738 |
| C    | 0.60123489861879 | 2.93155979855907 | 3.04540541562776 |
| C    | -0.79883320337365 | 2.89076275464037 | 3.03417956519470 |
| C    | -1.38037886706126 | 0.26719742866922 | -4.14056256804864 |
| H    | -2.47341238923971 | 0.22493394901216 | -4.1424420899172 |
| C    | 1.35189951963709 | 1.43539372214975 | -0.72864685256345 |
| H    | 2.21853840342125 | 1.57914967078959 | -0.07224910672162 |
| C    | -0.68979235475735 | 0.26254499804549 | -2.9262235660391 |
| 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 | -1.5862299970307 |
| H    | 2.26060557758839 | -0.35687635481619 | -1.51314736023772 |
| C    | -1.43595081287552 | 1.54738927888283 | 2.99248574500466 |
| H    | -2.28606736661201 | 1.47520895074033 | 2.30640086452734 |
| C    | 0.76342132538542 | -2.02374960256760 | 0.64188628996048 |
| H    | 1.37761017044267 | -2.73312915432034 | 0.08037527559466 |
| C    | -0.76947151454689 | 2.64970928881419 | -1.09647079746808 |
| C    | 2.76672873152214 | -0.96877212115931 | 1.42395450755311 |
| H    | 3.11555234628510 | 0.06462424400916 | 1.53485010831397 |
| H    | 3.22531795631048 | -1.40085702630613 | 0.52143763551201 |
| H    | 3.1106743968502 | -1.53988613373450 | 2.30061858093294 |
| C    | -1.42861067874703 | 0.65613478464598 | 4.09913265887978 |
| H    | -2.27587163548473 | -0.03565625436714 | 4.17720349275417 |
| C    | -2.71263082600150 | -1.13663043234869 | 1.39638286733045 |
| H    | -3.02708180401088 | -1.74786529751663 | 2.25690981336688 |
| H    | -3.13603356730314 | -1.57599366530115 | 0.48024476677698 |
| H    | -3.12574033218866 | -0.12962298546573 | 1.52674154399003 |
| C    | 0.64022553840257 | 1.04293519921141 | 5.39413794602337 |
| C    | -1.49566660577517 | 3.81224785397629 | -1.36514984482367 |
| H    | -2.58888319191917 | 3.78200701156808 | -1.34916281044410 |
| C    | -1.53035435226667 | 4.08002577444325 | 3.00762393105025 |
| H    | -2.62306040029208 | 4.04286521395612 | 2.98003910368227 |
### [Ru$_2$H(OH)(Me$_2$dad))(dbcot)$_2$]

|     |  
|-----|-----------------------------------------------|
| Ru  | 8.20947488789152 10.52637427092874 17.00667579178967  
| 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  
| H   | 7.29216462272765 8.95730661120393 19.03148840223971  
| C   | 10.33406004330155 13.81378313684751 16.45195770289589  
| H   | 9.54838820670318 13.94121922692262 15.69764366377931  
| C   | 6.24986370304496 13.06128314910995 19.99364579357775  
| H   | 6.64817951567182 12.65502030752226 20.98502748784428  
| C   | 6.66490872108003 12.36755327910990 18.85432766508064  
| C   | 6.40725956987343 12.89464558588237 17.58268086805478  
| C   | 13.80798492548427 14.54920035319574 16.06514275723282  
| H   | 13.61509175082398 14.96478839484386 15.07211213385963  
| C   | 10.83252129675649 12.73450442058599 18.95338878813117  
| H   | 10.3652335709753 12.18205362956882 19.77737565791325  
| C   | 12.87290762036454 13.69237852885802 16.65144442529918  
| C   | 10.76424065105075 10.17260807238358 15.56603649498824  
| C   | 11.47698192114074 10.09588876074573 14.74014051652730  
| C   | 11.59302295787406 13.30287792749295 15.99417726896572  
| H   | 11.66850894429374 13.07852644175987 14.92301796826114  
| C   | 12.08668320857347 12.23979508927721 18.47299391630355  
| H   | 12.47465335724432 11.33463487172297 18.96693840693500  
| C   | 6.92395953699463 12.13091068622049 16.41620017970160  
| H   | 7.37304502955689 12.75293256116422 15.63476373773613  
| C   | 11.01979964080376 9.63500556396107 16.83901902987537  
| H   | 11.94615147094172 9.10635822952611 17.08038028026900  
| C   | 10.22764505374354 14.72797341952363 17.62422891751292  
| C   | 10.26948614736549 9.27232138599505 19.08640707658572  
| H   | 9.74849388140670 9.85848025725909 19.85258208539755  
| H   | 11.33944516813467 9.22711031707827 19.34168926952630  

*The structure of the complex is shown on page 53.*
| C    | 6.37362211536339 | 10.88764793880688 | 16.0053524207798 |
|------|-----------------|-------------------|-----------------|
| H    | 9.2663648743613 | 11.36826148670141 | 14.11921659323526 |
| C    | 8.2736068474436 | 10.60828677681632 | 13.54138335733639 |
| H    | 10.18932993034812 | 11.63782584127692 | 13.56612074268175 |
| C    | 8.4026222099763 | 12.25690879462833 | 14.2046783892496 |
| C    | 5.50707586679097 | 9.71282402377724 | 18.00188701707863 |
| C    | 9.84490752486497 | 16.06669900139500 | 17.51088318678671 |
| C    | 5.73750022442389 | 14.11361847113117 | 17.45590119157768 |
| H    | 5.55521666811556 | 14.53056419748368 | 16.46143734486950 |
| C    | 13.12362585730640 | 13.14757212429343 | 17.91719211656825 |
| C    | 10.34779628567632 | 14.97704988928248 | 20.0320032849888 |
| H    | 10.52742718669426 | 14.54180072009631 | 21.0192354775590 |
| C    | 5.24382667231558 | 10.24141114401354 | 16.72734612566906 |
| C    | 10.48048585523989 | 14.18048529888171 | 18.89233076256546 |
| C    | 5.8365568420216 | 14.28181754738281 | 19.86403488731742 |
| H    | 5.27469496279075 | 14.83102607208794 | 20.75703629484453 |
| C    | 14.99256786390711 | 14.85728607289038 | 16.73833773360628 |
| H    | 15.72912421362803 | 15.5164821005993 | 16.27168141065288 |
| C    | 5.32824847343603 | 14.80772438366829 | 18.59647393728286 |
| C    | 4.81872064591662 | 15.76927464367352 | 18.4951248634688 |
| C    | 9.71032071339056 | 16.85850519551058 | 18.653693082590718 |
| H    | 9.39583050917249 | 17.90104268622858 | 18.56011513034101 |
| C    | 9.96223851108584 | 16.31416748776079 | 19.91372956364177 |
| H    | 9.84587341959373 | 16.92909300422811 | 20.80985153409337 |
| C    | 3.96423129729197 | 10.11801935687815 | 16.17795762588758 |
| H    | 3.76585194109219 | 10.51734910170555 | 15.1793927240639 |
| C    | 14.30573534485876 | 13.46275262991418 | 18.59131905411151 |
| H    | 14.50092560438921 | 13.02729182854011 | 19.5755075372539 |
| C    | 15.24129347118378 | 14.31484078910377 | 18.00029465497197 |
| H    | 16.17229701509177 | 14.54838671170677 | 18.52325008497430 |
| C    | 4.48857512416625 | 9.06902701933999 | 18.71058090470675 |
Table S5: Complex impregnation on C^k, 1mg_{Ru} cm^{-2} catalyst loading (3.06% wt.\textsubscript{Ru}).

| Reactants | Expected Quantity |
|-----------|-------------------|
| [Ru\textsubscript{2}(µ-H)(Me\textsubscript{2}dad)(dbcot)]\textsubscript{2}OTf | 36.0 mg (0.04 mmol\textsubscript{complex}) |
| C\textsubscript{k} | 214.0 mg |
| CH\textsubscript{3}CN for complex dissolution | 15 mL |
| CH\textsubscript{3}CN for C\textsubscript{k} suspension | 20 mL |

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

| Reactants | Expected Quantity |
|-----------|-------------------|
| [Ru\textsubscript{2}(µ-H)(Me\textsubscript{2}dad)(dbcot)]\textsubscript{2}OTf | 3.6 mg (0.005 mmol\textsubscript{complex}) |
| C\textsubscript{k} | 214.0 mg |
| CH\textsubscript{3}CN for complex dissolution | 5 mL |
| CH\textsubscript{3}CN for C\textsubscript{k} suspension | 20 mL |

Table S7: Ink preparation.

| Reactants | Quantity |
|-----------|----------|
| [Ru\textsubscript{2}(µ-H)(Me\textsubscript{2}dad)(dbcot)]\textsubscript{2}OTf / C\textsubscript{k} (3.06% wt.\textsubscript{Ru}) | 7.0 mg (0.008 mmol\textsubscript{complex}) |
| Milli-Q water | 600 mg |
| Component      | Quantity |
|---------------|----------|
| EtOH          | 600 mg   |
| Nafion 5%wt.  | 12 mg    |
Table S8: Surface composition determined by XPS analysis.

|                  | CIs   | NiS   | Ru3d  | 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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