Supporting Information

Nucleophilic attack by OH_2 or OH^- - A detailed investigation on pH dependent performance of a Ru catalyst.

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Computational details

All Density Functional Theory (DFT) calculations were carried out with Jaguar 8.3 program package by Schrödinger LLC.1 For geometry optimisations, solvation energies, and frequency calculations, Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP-D3) was used with the LACVP** core potential and basis set, while single point energy corrections were performed with the B3LYP-D3 functional using the LACV3P^{**++} basis set which, as suggested by Martin, was augmented with two f-polarisation functions on Ru. Frequency calculations were performed on the optimised geometries to verify that the geometries correspond to minima or first-order saddle points (transition states) on the potential energy surface (PES). The Gibbs free energies are calculated at standard state of 1 atm (g) and 1M(aq) and the G of each species is defined as the following equation G = E(B3LYP-D3/LACV3P^{**++} 2f on Ru) + G_{solv} + ZPE + H_{298} - TS_{298} + 1.9 kcal/mol (The 1.9 kcal/mol is a concentration correction to the free energy of solvation which by default is calculated at 1M(g) to 1M(aq) in Jaguar). Based on the gas-phase optimised structures, the effect of solvent was evaluated by single-point calculations using the Poisson-Boltzmann reactive field implemented in Jaguar 8.3 (PBF) with the standard settings for water.

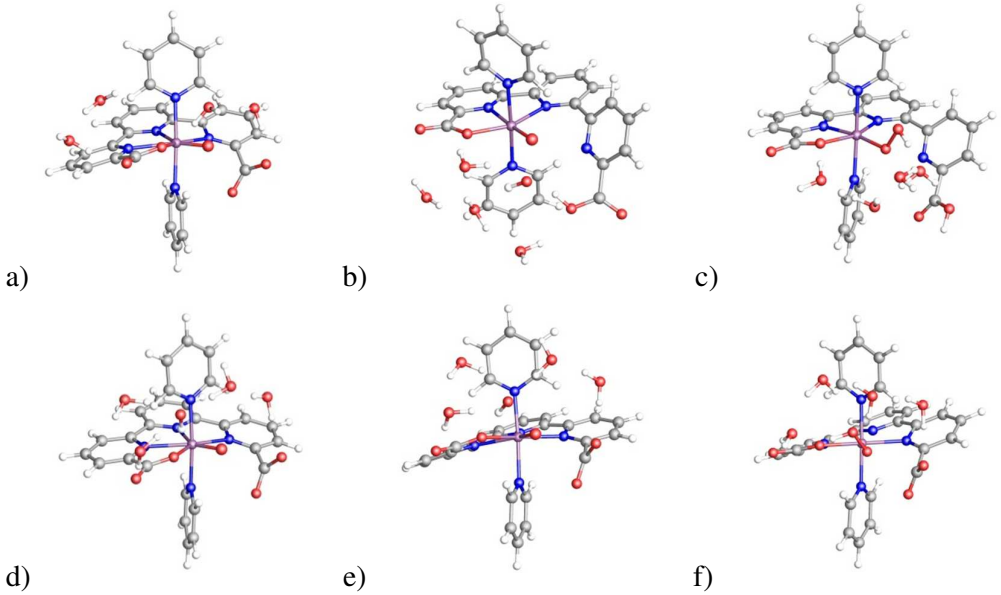

Figure S1. DFT optimized geometries of a) **1**; b) **ts2**; c) **3**; d) **pre-4**; e) **ts5**; f) **6**. (Purple = Ru; Red = O; Blue = N; Grey = C; White = H).

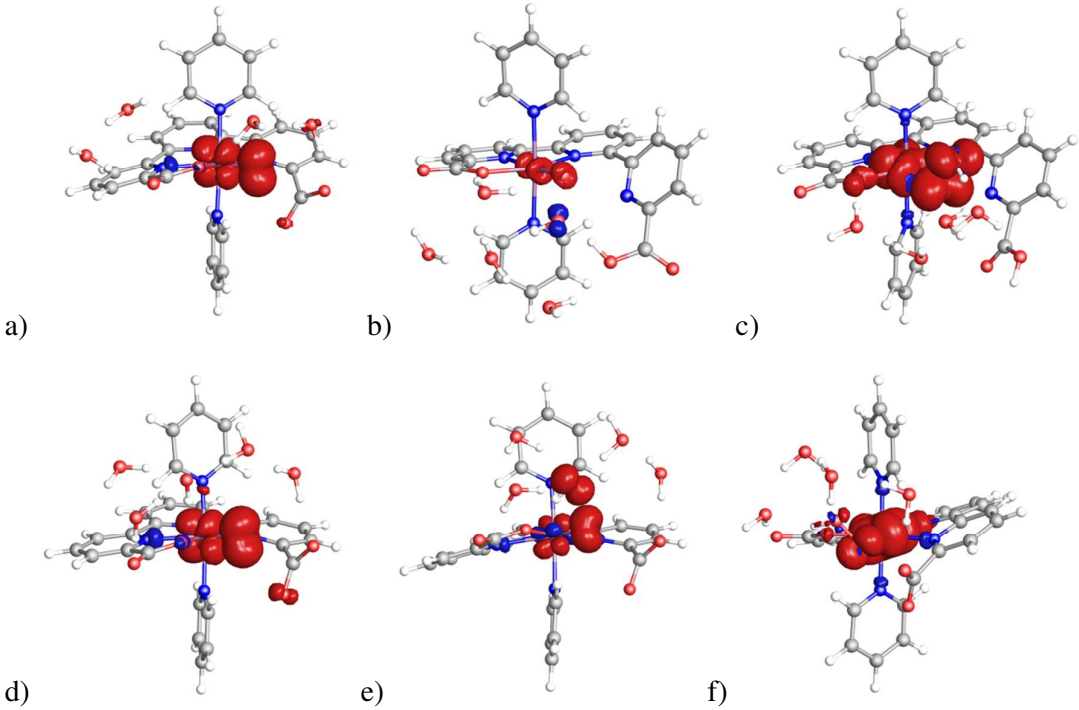

Figure S2. Plot of electron spin density of the optimized geometries of a) **1**; b) **ts2**; c) **3**; d) **pre-4**; e) **ts5**; f) **6**. (Purple = Ru; Red = O; Blue = N; Grey = C; White = H).

Energies of the calculated geometries.

Figure S1a

E (B3LYP-D3/LACV3P**++ 2f(Ru))(a.u.) = -2090.350726

ZPE (kcal mol^{-1}) = 328.198

G_{solv} (a.u.) = -0.116605

DH_{298} (kcal mol^{-1}) = 26.94

DS_{298} (cal K^{-1} mol^{-1}) = 245.976

Figure S1b

E (B3LYP-D3/LACV3P**++ 2f(Ru))(a.u.) = -2166.80516

ZPE (kcal mol^{-1}) = 343.726

G_{solv} (a.u.) = -0.1044358

DH_{298} (kcal mol^{-1}) = 27.963

DS_{298} (cal K^{-1} mol^{-1}) = 257.774

Figure S1c

E (B3LYP-D3/LACV3P**++ 2f(Ru))(a.u.) = -2166.84258

ZPE (kcal mol^{-1}) = 345.284

G_{solv} (a.u.) = -0.09592

DH_{298} (kcal mol^{-1}) = 27.519

DS_{298} (cal K^{-1} mol^{-1}) = 257.277

Figure S1d

E (B3LYP-D3/LACV3P**++ 2f(Ru))(a.u.) = -2166.329381

ZPE (kcal mol^{-1}) = 334.83

G_{solv} (a.u.) = -0.1394358

DH_{298} (kcal mol^{-1}) = 27.58

DS_{298} (cal K^{-1} mol^{-1}) = 253.087

Figure S1e

E (B3LYP-D3/LACV3P**++ 2f(Ru))(a.u.) = -2166.332822

ZPE (kcal mol^{-1}) = 333.473

G_{solv} (a.u.) = -0.12865

DH_{298} (kcal mol^{-1}) = 26.871

DS_{298} (cal K^{-1} mol^{-1}) = 247.09

Figure S1f

E (B3LYP-D3/LACV3P**++ 2f(Ru))(a.u.) = -2166.39599

ZPE (kcal mol^{-1}) = 337.645

G_{solv} (a.u.) = -0.0798283

DH_{298} (kcal mol^{-1}) = 27.69

DS_{298} (cal K^{-1} mol^{-1}) = 253.908