Supporting Information for

*Computational Scaling Relationships Predict Experimental Activity and Rate Limiting Behavior in Homogenous Water Oxidation*

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Table S1. The experimentally reported rate constants for each of the 19 TMCs considered in this work. The rate constant for each TMC is reported in at least one of source 1, source 2, or source 3. The computed Ru(II)-O₂ ∆E_{IP} is reported in kcal/mol.

| Name | Ru(II)-O₂ ∆E_{IP} (kcal/mol) | Source 1: Rate Constant s⁻¹ | Source 1: Rate Constant M⁻¹s⁻¹ | Source 2: Rate Constant s⁻¹ | Source 3: Rate Constant s⁻¹ |
|------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-----------------------------|
| 1a   | 45.2                          | 1.90E-04                    |                               | 5.10E-04                    | 3.40E-02                    |
| 1b   | 49.23                         | 7.50E-04                    |                               |                             |                             |
| 1c   | 51.26                         | 1.40E-03                    |                               |                             |                             |
| 1d   | 39.78                         | 3.30E+01                    |                               |                             |                             |
| 1e   | 42.48                         | 1.70E+02                    |                               |                             |                             |
| 1f   | 31.96                         | 5.00E-04                    | 5.15E+02                      |                             |                             |
| 1g   | 46.95                         |                             | 2.60E-04                      |                             |                             |
| 1h   | 41.52                         |                             | 1.10E-03                      |                             |                             |
| 1i   | 48.08                         |                             | 2.00E-04                      |                             |                             |
| 2a   | 46.12                         |                             | 5.40E-04                      | 4.30E-02                    |                             |
| 2g   | 47.87                         |                             | 2.80E-04                      |                             |                             |
| 3a   | 44.09                         |                             | 5.20E-04                      | 2.40E-01                    |                             |
| 3h   | 40.49                         |                             | 1.20E-03                      |                             |                             |
| 4a   | 46.55                         |                             | 6.80E-04                      |                             |                             |
| 4i   | 49.41                         |                             | 3.30E-04                      |                             |                             |
| 5a   | 43.96                         |                             | 4.40E-01                      |                             |                             |
| 6a   | 44.54                         |                             | 6.10E-02                      |                             |                             |
| 7a   | 40.96                         | 5.20E+01                    |                             |                             |                             |
| 8a   | 43.62                         | 4.10E+00                    |                             |                             |                             |

Table S2. Possible spin states for each of seven intermediates in the WNA catalytic cycle, one of which was assigned as the ground state for each intermediate. States are labelled by spin multiplicity (2S+1).

| Intermediate | Low Spin | Intermediate Spin | High Spin |
|--------------|----------|-------------------|-----------|
| Ru(II)-OH₂   | 1        | 3                 | 5         |
| Ru(III)-OH   | 2        | 4                 | 6         |
| Ru(IV)=O     | 1        | 3                 | 5         |
| Ru(V)=O      | 2        | 4                 | --        |
| Ru(III)-OOH  | 2        | 4                 | 6         |
| Ru(II)-O₂    | 1        | 3                 | 5         |
| Ru(III)-O₂   | 2        | 4                 | 6         |
Figure S1. Plots of the spin splitting energies when comparing the LS (low spin, spin multiplicity = 1 or 2), IS (intermediate spin, spin multiplicity = 3 or 4), and HS (high spin, spin multiplicity = 5 or 6) states. Numbers are assigned to intermediates based on the order they appear in Scheme 1, starting with "I" for Ru(II)-OH$_2$ and ending with "VII" for Ru(III)-O$_2$. The HS state is always higher in energy than the IS state (bottom) and the LS state (middle). The IS state is lower in energy than the LS state for intermediates III, VI, and VII, and the LS state is the lowest in energy for all other intermediates (top).
Table S3. Initial structures were generated either using molSimplify or through modification of the optimized structure of transition metal complex 1a.

| Complex       | Structure Generated from |
|---------------|--------------------------|
| 1a            | molSimplify              |
| 1b            | molSimplify              |
| 1c            | molSimplify              |
| 1d            | molSimplify              |
| 1e            | molSimplify              |
| 1f            | molSimplify              |
| 1g            | 1a                       |
| 1h            | 1a                       |
| 1i            | 1a                       |
| 2a            | 1a                       |
| 2g            | 1a                       |
| 3a            | 1a                       |
| 3h            | 1a                       |
| 4a            | 1a                       |
| 4i            | 1a                       |
| 5a            | 1a                       |
| 6a            | 1a                       |
| 7a            | molSimplify              |
| 8a            | molSimplify              |
| graphene      | molSimplify              |
| unconstrained 1a | molSimplify    |
| unconstrained graphene | molSimplify |

Table S4. Geometric parameters employed to determine if the structure converged to an octahedral geometry. These checks are based on the arrangement of the metal center and of the atoms in the first coordination shell. Coordination number must be preserved as 6, with coordination judged by interatomic distances being within 1.37x the sum of the respective elements’ covalent radii. Additionally, we established maximums for the mean and maximum (max.) deviation in the angle ($\Delta\theta$ (C$_i$-M-C$_j$)) formed by two coordinating atoms and the metal) from the expected values of 90° or 180°. Lastly, the maximum overall difference between metal-coordinating atom bond lengths for all ligands and ligands in the equatorial (eq.) plane were required to be within the given thresholds.

|                        |                     |
|------------------------|---------------------|
| **Coordination number**| 6                   |
| **First coordination shell** |               |
| $\text{mean}(\Delta\theta \ (\text{C}_i\text{-M}\text{-C}_j))$ | $25^\circ$          |
| $\text{max}(\Delta\theta \ (\text{C}_i\text{-M}\text{-C}_j))$   | $50^\circ$          |
| $\text{max}(\Delta d)$  | 1.00 Å              |
| $\text{max}(\Delta d_{\text{eq}})$ | 0.35 Å         |
Table S5. A record of geometry optimizations which were attempted, but excluded from further analysis, including the reason for the exclusion of each Numbers are assigned to intermediates based on the order they appear in Scheme 1, starting with "I" for Ru(II)-OH$_2$ and ending with "VII" for Ru(III)-O$_2$. A list of all calculations that failed the criteria for a successful calculation described in the Computational Details is available in the Supporting Information .zip.

| Name                     | Intermediate | Spin Multiplicity | Reason                     |
|--------------------------|--------------|-------------------|----------------------------|
| 1g                       | V            | 6                 | Not Converged              |
| 3h                       | IV           | 4                 | Not Converged              |
| 1g                       | II           | 6                 | Non-octahedral Geometry    |
| 3h                       | V            | 6                 | Non-octahedral Geometry    |
| unconstrained graphene   | VI           | 5                 | Non-octahedral Geometry    |
| unconstrained graphene   | VII          | 6                 | Non-octahedral Geometry    |
| graphene                 | VI           | 5                 | Non-octahedral Geometry    |
| graphene                 | V            | 4                 | Non-octahedral Geometry    |
| graphene                 | V            | 6                 | Non-octahedral Geometry    |
| graphene                 | VII          | 6                 | Non-octahedral Geometry    |
| graphene                 | II           | 4                 | Non-octahedral Geometry    |
| graphene                 | II           | 6                 | Non-octahedral Geometry    |
| unconstrained 1a         | VI           | 5                 | Non-octahedral Geometry    |
| unconstrained 1a         | II           | 4                 | Non-octahedral Geometry    |
| unconstrained 1a         | VII          | 4                 | Non-octahedral Geometry    |
| unconstrained 1a         | VII          | 6                 | Non-octahedral Geometry    |
| 1f                       | VII          | 2                 | Spin Contaminated          |
| 1d                       | VII          | 2                 | Spin Contaminated          |
| 8a                       | VI           | 5                 | Non-octahedral Geometry    |
| 1a                       | VII          | 6                 | Non-octahedral Geometry    |
| 1c                       | VII          | 6                 | Non-octahedral Geometry    |
| 1c                       | VI           | 5                 | Non-octahedral Geometry    |
| 1f                       | VII          | 6                 | Non-octahedral Geometry    |
| 1f                       | I            | 3                 | Non-octahedral Geometry    |
| 1f                       | VI           | 5                 | Non-octahedral Geometry    |
| 1b                       | VI           | 5                 | Non-octahedral Geometry    |
| 1b                       | VII          | 6                 | Non-octahedral Geometry    |
| 7a                       | VII          | 6                 | Non-octahedral Geometry    |
| 7a                       | VI           | 5                 | Non-octahedral Geometry    |
| 1d                       | VII          | 6                 | Non-octahedral Geometry    |
| 1e                       | I            | 5                 | Non-octahedral Geometry    |
| 1e                       | VII          | 6                 | Non-octahedral Geometry    |
**Table S6.** A list of calculations for which the original conditions failed to produce a result which satisfied our criteria for a successful calculation (see Computational Details), and recovery of the calculation was attempted. The procedure used to attempt recovery of each jobs is listed, along which a record of if that recovery strategy was successful. Numbers are assigned to intermediates based on the order they appear in Scheme 1, starting with "I" for Ru(II)-OH$_2$ and ending with "VII" for Ru(III)-O$_2$.

| Name  | Intermediate | 2S+1 | Calculation Type              | Recovery Step 1 | Recovery Step 2 | Successfully Recovered |
|-------|---------------|------|-------------------------------|-----------------|-------------------|------------------------|
| 8a    | VII           | 2    | camB3LYP Single Point         | 0% HFX          | original parameters | TRUE                   |
| 8a    | VII           | 2    | ωPBEh Single Point             | 0% HFX          | original parameters | TRUE                   |
| 8a    | VII           | 2    | ωb97x Single Point             | 0% HFX          | original parameters | TRUE                   |
| 8a    | VII           | 2    | Empty-Site Single Point        | 0% HFX          | original parameters | TRUE                   |
| 8a    | VII           | 2    | Geometry Optimization         | 0% HFX          | original parameters | TRUE                   |
| 8a    | VII           | 2    | Empty-Site Single Point        | 0% HFX          | original parameters | TRUE                   |
| 1f    | VII           | 2    | Geometry Optimization         | 0% HFX          | original parameters | TRUE                   |
| 1f    | V             | 4    | Geometry Optimization         | Levelshifts adjusted to 1.0 and 0.1 Ha | original parameters | TRUE                   |
| 1f    | IV            | 2    | ωPBEh Single Point             | 0% HFX          | original parameters | TRUE                   |
| 1f    | IV            | 2    | ωb97x Single Point             | 0% HFX          | original parameters | TRUE                   |
| 1f    | IV            | 2    | camB3LYP Single Point          | 0% HFX          | original parameters | TRUE                   |
| 1b    | VII           | 2    | Empty-Site Single Point        | 0% HFX          | original parameters | TRUE                   |
| 1c    | VII           | 2    | Empty-Site Single Point        | 0% HFX          | original parameters | TRUE                   |
| 1c    | VII           | 2    | Empty-Site Single Point        | 0% HFX          | original parameters | TRUE                   |
| 1e    | VII           | 2    | Geometry Optimization         | 0% HFX          | original parameters | TRUE                   |
| 1e    | VII           | 2    | Geometry Optimization         | 0% HFX          | original parameters | TRUE                   |
| 1e    | VII           | 2    | Geometry Optimization         | 0% HFX          | original parameters | TRUE                   |
| 1e    | VII           | 2    | Geometry Optimization         | 0% HFX          | original parameters | TRUE                   |
| unconstrained graphene | VII | 2    | Geometry Optimization         | 0% HFX          | original parameters | TRUE                   |
| graphene | VI | 5    | Vertical Ionization Potential Final Spin 4 | 0% HFX | original parameters | TRUE                   |
| unconstrained graphene | VII | 2    | Empty-Site Single Point        | 0% HFX          | original parameters | TRUE                   |

**Text S1.** To generate calculations using alternative fractions of Hartree-Fock exchange, we varied the exchange percentage in increments of 5%. Each calculation used the optimized geometry and wavefunction of the preceding calculation as its initial guess. The spin contamination recovery strategy was not utilized for these calculations, as it would require further modifying the fraction of Hartree-Fock exchange. Calculations with the camB3LYP, ωb97x, and ωPBEh functionals were carried out as single points with the optimized structure and wavefunction from the B3LYP calculation as the initial guess.
Figure S2. Benchmarks comparing the performance of 10 functionals in comparison to the experimentally measured oxidation potentials for PCET 1 (Ru(II)-OH$_2$ → Ru(III)-OH $\Delta G$), PCET 2 (Ru(II)-OH → Ru(IV)=O $\Delta G$), and Ru(IV)=O $\Delta G_{ox}$. All values are reported relative to the oxidation potential of 1a. All energies are obtained from a single point calculation of the B3LYP (BLYP 20% Hartree-Fock exchange) optimized structures. The ob97x functional has the highest overall $R^2$ value, however this is strongly influenced by a single data point corresponding to complex 7a.
Text S2. ∆G was calculated as

\[ ∆G = ∆E_{SCF} + ∆E_{vib} - T∆S + ∆G_{solv} \] (1)

where E_{SCF} is the gas-phase electronic energy, E_{vib} - TS is the thermal correction based on vibrational modes, and ∆G_{solv} is the free energy of solvation. The energy of e⁻ was based on the standard hydrogen electrode (-4.24 V = -97.78 kcal/mol). The energy of H⁺ was based on the widely accepted value for the energy of H⁺ solvation (-265.9 kcal/mol), with a slight correction for the free energy of a gas phase H⁺:

\[ \frac{3}{2} kT + PV - TS = -6.3 \text{ kcal/mol} \] (2)

The energy of O₂ and H₂O were taken as E_{SCF} (including the solvation energy) from a calculation using the same settings as those for the TMCs and were found to be -150.26 kcal/mol and -76.42 kcal/mol, respectively. The free energy corrections (E_{vib} - TS) were 0.00 kcal/mol for O₂ and 0.02 kcal/mol for H₂O.

∆E_{LD} was calculated as

\[ ∆E_{LD} = E - (E_{empty} + E_{O_2}) \] (3)

Where E is the solvated electronic energy of the whole complex (E = E_{SCF} + ∆G_{solv}). The solvated empty-site energy, E_{empty}, is obtained from a single point calculation of the TMC with the O₂ ligand removed. E_{O₂} is the energy of an oxygen molecule with the O-O bond distance observed in the complex, as determined by a single point calculation including solvation.

∆E_{IP} was calculated as

\[ ∆E_{IP} = E - (E_{ionized} + E_{e^-}) \] (4)

E is the solvated electronic energy of the whole complex. E_{ionized} is the energy of the complex with a single electron removed, based on a single point calculation which includes implicit solvent. E_{e^-} is the energy of a single electron, which was defined previously.
**Table S7.** Values for the $\Delta E_{\text{vib}}$ - TAS correction at 300 K for each step in the WNA catalytic cycle, as obtained from the calculation of normal vibrational modes, in kcal/mol. Reaction steps are indicated based on the numerical index of the reactant and product in the WNA catalytic cycle, as shown in Scheme 1. For example, "I" for Ru(II)-OH$_2$, "VI" for Ru(II)-O$_2$, and "VII" for Ru(III)-O$_2$. The entropic contributions of translational and rotational modes are not considered. The calculations were carried out for each system independently and the difference is reported here. The average value of this correction can be substantial (>10 kcal/mol), but the standard deviations in these corrections are uniformly small (<1 kcal/mol).

| Name | I-II | II-III | III-IV | IV-V  | V-VI  | VI-VII | VII-I | VI-I |
|------|------|--------|--------|-------|-------|--------|-------|------|
| 4i   | -12.75 | -13.31 | -0.53  | -11.05 | -13.99 | 0.12   | -10.44 | 2.43 |
| 1i   | -12.99 | -13.00 | -0.72  | -11.21 | -14.1  | 0.65   | -10.82 | 2.82 |
| 3a   | -12.69 | -12.88 | -0.45  | -11.28 | -14.62 | 0.99   | -10.96 | 2.72 |
| 1g   | -12.76 | -13.04 | -0.26  | -11.38 | -14.30 | 0.40   | -10.61 | 2.55 |
| 6a   | -13.65 | -12.91 | 0.39   | -12.13 | -13.37 | -0.24  | -10.93 | 2.47 |
| 1h   | -11.77 | -14.11 | 0.21   | -12.39 | -13.93 | 0.42   | -9.39  | 2.80 |
| 2a   | -12.71 | -13.09 | -0.36  | -11.24 | -14.44 | 0.71   | -10.78 | 2.64 |
| 4a   | -12.61 | -13.29 | -0.52  | -10.40 | -14.98 | 0.35   | -10.35 | 2.61 |
| 3h   | -12.60 | -13.09 | 1.25   | -13.05 | -14.23 | 0.34   | -10.41 | 2.53 |
| 2g   | -12.71 | -13.13 | -0.37  | -11.24 | -13.28 | -0.53  | -10.64 | 1.54 |
| 5a   | -12.76 | -12.98 | 1.38   | -13.19 | -14.06 | 0.35   | -10.69 | 2.42 |
| 8a   | -12.86 | -13.47 | 0.06   | -11.06 | -14.39 | 0.18   | -10.41 | 2.63 |
| 1a   | -12.11 | -13.55 | -0.74  | -10.88 | -14.46 | 0.68   | -10.24 | 2.54 |
| 1c   | -13.24 | -12.99 | -0.33  | -11.39 | -13.97 | 0.21   | -10.74 | 2.72 |
| 1f   | -13.17 | -13.79 | 0.33   | -11.99 | -13.54 | 0.39   | -10.6  | 2.96 |
| 1b   | -13.01 | -13.17 | 0.00   | -11.59 | -14.11 | 0.25   | -10.58 | 2.68 |
| 7a   | -12.27 | -14.13 | 0.40   | -11.37 | -14.86 | 0.34   | -9.57  | 3.04 |
| 1d   | -12.65 | -13.25 | 0.62   | -12.24 | -14.89 | 0.30   | -9.72  | 3.22 |
| 1e   | -13.15 | -13.50 | 0.74   | -12.31 | -14.86 | 0.73   | -9.99  | 3.89 |
| average | -12.76 | -13.30 | 0.06   | -11.65 | -14.23 | 0.35   | -10.41 | 2.70 |
| standard deviation | 0.41 | 0.37 | 0.61 | 0.72 | 0.49 | 0.34 | 0.44 | 0.43 |
Table S8. ∆G (in eV) for each step in the WNA catalytic cycle for complex 1a. Numbers are assigned to intermediates based on the order they appear in Scheme 1, starting with "I" for Ru(II)-OH₂ and ending with "VII" for Ru(III)-O₂. Two pathways are possible. In pathway 1, oxidation of Ru(II)-O₂ occurs before dissociation of the oxygen ligand. In pathway 2, oxidation occurs before dissociation. We add -1.6 eV to the steps involving electron transfer (I-II, II-III, III-IV, V-VI, and VI-VII) to account for the oxidation potential of the oxidant.

| Reaction Step | Both Pathways | Pathway 1 | Pathway 2 |
|---------------|---------------|-----------|-----------|
| II-III        | -0.62         |           |           |
| III-IV        | 0.67          |           |           |
| IV-V          | -1.06         |           |           |
| V-VI          | -0.79         |           |           |
| VI-I          |               | 1.11      |           |
| I-II          |               | -0.71     |           |
| VI-VII        |               |           | 0.15      |
| VII-II        |               |           | 0.25      |
Table S9. Tabulated values (in eV) for the vertical ionization potentials ($\Delta E_{IP}$) and reorganization energies ($\lambda$) of both non-proton-coupled electron transfer steps. The variation in reorganization energy is small in comparison to the variation $\Delta E_{IP}$ and both values occur in well-defined ranges in our data set.

| Name | Ru(IV)=O $\Delta E_{IP}$ | Ru(IV)=O to Ru(V)=O $\lambda$ | Ru(II)-O$_2$ $\Delta E_{IP}$ | Ru(II)-O$_2$ to Ru(II)-O$_3$ $\lambda$ |
|------|-----------------|-----------------|-----------------|-----------------|
| 1a   | 6.80            | 0.26            | 6.20            | 0.24            |
| 1b   | 6.94            | 0.25            | 6.37            | 0.23            |
| 1c   | 7.11            | 0.37            | 6.46            | 0.22            |
| 1d   | 6.55            | 0.26            | 5.96            | 0.22            |
| 1e   | 6.64            | 0.25            | 6.08            | 0.18            |
| 1f   | 5.95            | 0.14            | 5.63            | 0.27            |
| 1g   | 6.87            | 0.26            | 6.28            | 0.23            |
| 1h   | 6.66            | 0.24            | 6.04            | 0.24            |
| 1i   | 6.90            | 0.25            | 6.32            | 0.23            |
| 2a   | 6.86            | 0.27            | 6.24            | 0.24            |
| 2g   | 6.93            | 0.27            | 6.32            | 0.23            |
| 3a   | 6.69            | 0.30            | 6.15            | 0.25            |
| 3h   | 6.59            | 0.29            | 6.00            | 0.23            |
| 4a   | 6.87            | 0.26            | 6.26            | 0.24            |
| 4i   | 6.97            | 0.26            | 6.38            | 0.23            |
| 5a   | 6.67            | 0.31            | 6.15            | 0.25            |
| 6a   | 6.77            | 0.27            | 6.17            | 0.24            |
| 7a   | 6.30            | 0.11            | 6.02            | 0.28            |
| 8a   | 6.84            | 0.30            | 6.13            | 0.41            |
| Standard Deviation | 0.26 | 0.06 | 0.19 | 0.04 |
| Range | 1.16 | 0.26 | 0.84 | 0.23 |
Text S3. The free energy barrier in outer sphere electron transfer according to Marcus theory is most frequently expressed as:

\[ \Delta G^\dagger = (4\lambda)^{-1}(\Delta G^\circ + \lambda)^2 \]  \hspace{1cm} (1)

where \( \lambda \) is the reorganization energy and \( \Delta G^\circ \) is the free energy of reaction. However, we can take advantage of the relationship to the vertical ionization potential:

\[ \Delta G^\circ = \Delta E_{IP} - \lambda \]  \hspace{1cm} (2)

to rewrite the expression in terms of the vertical ionization potential and reorganization energy:

\[ \Delta G^\dagger = (4\lambda)^{-1}(\Delta E_{IP})^2 \]  \hspace{1cm} (3)

For our specific dataset, we can approximate this expression by taking advantage of the relatively constant \( \lambda \) values and the well-defined range of \( \Delta E_{IP} \). Treating \( \lambda \) as a constant and noting that \( (\Delta E_{IP})^2 \) is approximately linear over the range from 5.5eV to 7.0eV, we arrive at:

\[ \Delta G^\dagger \propto \Delta E_{IP} \]  \hspace{1cm} (4)

Table S10. Tabulated values (in kcal/mol) for each of the seven DFT properties identified as potentially rate limiting for each of the 19 TMCs considered in this work.

| Name | Ru(IV)=O \( \Delta G_{ox} \) | Ru(IV)=O \( \Delta E_{IP} \) | Ru(II)-O \( \Delta G_{ox} \) | Ru(II)-O \( \Delta E_{IP} \) | WNA \( \Delta G \) | Ru(II)-O \( \Delta E_{LD} \) | Ru(II)-O \( \Delta E_{LD} \) |
|------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1a   | 52.36          | 59.12          | 40.34          | 45.20          | -24.43         | 11.97          | 6.33           |
| 1b   | 56.49          | 62.36          | 44.18          | 49.23          | -28.83         | 11.58          | 6.90           |
| 1c   | 57.40          | 66.16          | 46.35          | 51.26          | -30.08         | 10.64          | 6.91           |
| 1d   | 47.81          | 53.23          | 34.95          | 39.78          | -24.31         | 6.40           | 3.98           |
| 1e   | 50.32          | 55.40          | 39.07          | 42.48          | -27.30         | 5.96           | 4.09           |
| 1f   | 36.58          | 39.38          | 26.02          | 31.96          | -5.79          | 17.17          | 7.58           |
| 1g   | 54.55          | 60.71          | 42.03          | 46.95          | -26.79         | 11.76          | 6.58           |
| 1h   | 50.45          | 55.76          | 36.41          | 41.52          | -22.47         | 12.92          | 6.48           |
| 1i   | 54.88          | 61.45          | 43.40          | 48.08          | -27.60         | 11.17          | 6.57           |
| 2a   | 53.72          | 60.30          | 41.29          | 46.12          | -26.16         | 11.63          | 6.31           |
| 2g   | 55.45          | 62.00          | 41.99          | 47.87          | -28.04         | 11.46          | 6.56           |
| 3a   | 49.17          | 56.60          | 39.40          | 44.09          | -20.39         | 12.24          | 6.10           |
| 3h   | 48.78          | 54.26          | 35.63          | 40.49          | -19.75         | 13.23          | 6.33           |
| 4a   | 54.10          | 60.56          | 41.40          | 46.55          | -26.27         | 11.48          | 6.39           |
| 4i   | 56.47          | 63.04          | 44.28          | 49.41          | -29.86         | 10.78          | 6.61           |
| 5a   | 50.25          | 56.10          | 38.64          | 43.96          | -21.46         | 12.30          | 6.09           |
| 6a   | 52.42          | 58.36          | 38.73          | 44.54          | -24.23         | 12.11          | 6.26           |
| 7a   | 45.46          | 47.57          | 34.82          | 40.96          | -17.46         | 13.40          | 5.92           |
| 8a   | 53.04          | 59.89          | 34.34          | 43.62          | -18.63         | 13.70          | 3.23           |
Figure S3. Principal component analysis of the natural orbital population for the metal atom and the catalytic oxygen for intermediate 1 (top). The two principal components contain 78% and 17% of the explained variance, respectively. We assign each of the 19 TMCs to one of three clusters: blue (15 TMCs), red (2 TMCs), and green (2 TMCs). The bar chart shows the natural orbital population for each orbital in an alternative representation (top).
Figure S4. Scatter plots (left) and bar charts (right) for the natural orbital populations of the metal center and catalytic oxygen for each of the seven intermediates. The same clusters would be assigned for Ru(II)-OH₂, Ru(II)-O₂, and Ru(III)-O₂. The blue and green clusters are less differentiated in Ru(III)-OH, Ru(IV)=O, Ru(V)=O, and Ru(III)-OOH because the overall electron density around the metal center is reduced in these intermediates. For open shell intermediates, the sum of the electron occupations in the spin-majority and spin-minority orbitals is used.
Table S11. The electron density of the natural bonding orbitals for the metal center and the catalytic oxygen for each of the 19 TMCs considered in this work in the Ru(II)-OH$_2$ intermediate. We assign each TMC to one of three clusters (blue, red, and green) in Figure 3 based on these orbital populations. Electron densities which differentiate key TMCs from the blue cluster are highlighted in red or green.

| Name | Ru          |          | O          |          | Cluster |
|------|-------------|----------|------------|----------|---------|
|      | s | d$_{xy}$ | d$_{xz}$ | d$_{yz}$ | d$_{x^2-y^2}$ | d$_{z^2}$ | s | p$_x$ | p$_y$ | p$_z$ |       |
| 1a   | 0.41 | 1.86    | 1.86    | 1.83    | 0.81     | 0.71     | 1.72 | 1.86 | 1.54 | 1.75 | blue  |
| 1b   | 0.42 | 1.84    | 1.87    | 1.84    | 0.82     | 0.70     | 1.72 | 1.87 | 1.54 | 1.74 | blue  |
| 1c   | 0.40 | 1.83    | 1.88    | 1.82    | 0.82     | 0.71     | 1.72 | 1.87 | 1.54 | 1.75 | blue  |
| 1d   | 0.40 | 1.85    | 1.84    | 1.79    | 0.82     | 0.89     | 1.73 | 1.86 | 1.53 | 1.77 | red   |
| 1e   | 0.39 | 1.82    | 1.85    | 1.80    | 0.83     | 0.89     | 1.73 | 1.87 | 1.54 | 1.77 | red   |
| 1f   | 0.39 | 1.90    | 1.82    | 1.83    | 0.77     | 0.64     | 1.73 | 1.58 | 1.75 | 1.81 | green |
| 1g   | 0.41 | 1.85    | 1.86    | 1.83    | 0.81     | 0.70     | 1.72 | 1.87 | 1.54 | 1.75 | blue  |
| 1h   | 0.42 | 1.87    | 1.85    | 1.84    | 0.81     | 0.70     | 1.72 | 1.86 | 1.54 | 1.75 | blue  |
| 1i   | 0.40 | 1.84    | 1.87    | 1.82    | 0.81     | 0.71     | 1.72 | 1.87 | 1.54 | 1.75 | blue  |
| 2a   | 0.41 | 1.86    | 1.85    | 1.83    | 0.81     | 0.71     | 1.72 | 1.87 | 1.54 | 1.75 | blue  |
| 2g   | 0.41 | 1.86    | 1.86    | 1.83    | 0.81     | 0.70     | 1.72 | 1.87 | 1.54 | 1.74 | blue  |
| 3a   | 0.42 | 1.85    | 1.88    | 1.83    | 0.81     | 0.70     | 1.72 | 1.86 | 1.54 | 1.75 | blue  |
| 3h   | 0.42 | 1.87    | 1.87    | 1.84    | 0.80     | 0.69     | 1.72 | 1.86 | 1.54 | 1.76 | blue  |
| 4a   | 0.41 | 1.86    | 1.83    | 1.84    | 0.82     | 0.71     | 1.72 | 1.87 | 1.54 | 1.75 | blue  |
| 4i   | 0.40 | 1.84    | 1.84    | 1.83    | 0.82     | 0.71     | 1.72 | 1.87 | 1.54 | 1.74 | blue  |
| 5a   | 0.42 | 1.85    | 1.88    | 1.83    | 0.81     | 0.70     | 1.72 | 1.86 | 1.54 | 1.75 | blue  |
| 6a   | 0.42 | 1.86    | 1.86    | 1.83    | 0.81     | 0.70     | 1.72 | 1.86 | 1.54 | 1.75 | blue  |
| 7a   | 0.41 | 1.85    | 1.85    | 1.85    | 0.81     | 0.70     | 1.72 | 1.86 | 1.54 | 1.75 | blue  |
| 8a   | 0.44 | 1.88    | 1.90    | 1.91    | 0.75     | 0.66     | 1.72 | 1.58 | 1.85 | 1.74 | green |
| Average | 0.41 | 1.85 | 1.86 | 1.83 | 0.81 | 0.72 | 1.72 | 1.83 | 1.57 | 1.75 |     |
| Standard Deviation | 0.01 | 0.02 | 0.02 | 0.02 | 0.02 | 0.06 | 0.00 | 0.09 | 0.08 | 0.02 |     |
Figure S5. Scatter plots for the correlation between each of the seven DFT parameters for the 15 TMCs determined to have a common electronic state. The $R^2$ values associated with each of these plots is presented in Figure 4.

Table S12. Linear functions (in kcal/mol) relating each of the six remaining DFT values in comparison to our chosen scaling parameter (Ru(II)-O$_2$ $\Delta$E$_{IP}$). Functions fit the form: $y = ax + b$.

| Property (y) | a     | b     |
|--------------|-------|-------|
| Ru(IV)=O $\Delta$G$_{ox}$ | 0.77  | 18.21 |
| Ru(IV)=O $\Delta$E$_{IP}$ | 0.94  | 16.47 |
| Ru(II)-O$_2$ $\Delta$G$_{ox}$ | 1.00  | -5.03 |
| WNA $\Delta$G | -0.93 | 16.91 |
| Ru(II)-O$_2$ $\Delta$E$_{LD}$ | -0.23 | 22.53 |
| Ru(III)-O$_2$ $\Delta$E$_{LD}$ | 0.06  | 3.69  |
Table S13. Tabulated values for the experimentally measured first-order rate constant for each of the 15 TMCs in the majority electronic state in comparison to the rate predicted by our descriptor and exponential fit. Error factor describes the ratio comparing the predicted and experimentally measured rate constants, expressed as a number greater than 1. The error in the prediction is low for all cases, indicating excellent agreement between theory and experiment.

| Comp IP (eV) | Experimental Rate Constant (s⁻¹) | Predicted Rate Constant (s⁻¹) | Error Factor |
|--------------|---------------------------------|-------------------------------|--------------|
| **Experimental Data Set 1** | | | |
| 1a | 1.96 | 1.90E-04 | 1.92E-04 | 1.01 |
| 1b | 2.13 | 7.50E-04 | 7.29E-04 | 1.03 |
| 1c | 2.22 | 1.40E-03 | 1.43E-03 | 1.02 |
| **Experimental Data Set 2** | | | |
| 1a | 1.96 | 5.10E-04 | 5.16E-04 | 1.01 |
| 1g | 2.04 | 2.60E-04 | 3.76E-04 | 1.45 |
| 1h | 1.8 | 1.10E-03 | 1.01E-03 | 1.09 |
| 1i | 2.08 | 2.00E-04 | 3.06E-04 | 1.53 |
| 2a | 2 | 5.40E-04 | 4.37E-04 | 1.24 |
| 2g | 2.08 | 2.80E-04 | 3.18E-04 | 1.14 |
| 3a | 1.91 | 5.20E-04 | 6.32E-04 | 1.22 |
| 3h | 1.76 | 1.20E-03 | 1.22E-03 | 1.02 |
| 4a | 2.02 | 6.80E-04 | 4.04E-04 | 1.68 |
| 4i | 2.14 | 3.30E-04 | 2.40E-04 | 1.38 |
| **Experimental Data Set 3** | | | |
| 1a | 1.96 | 3.40E-02 | 6.39E-02 | 1.88 |
| 2a | 2 | 4.30E-02 | 2.48E-02 | 1.73 |
| 3a | 1.91 | 2.40E-01 | 2.02E-01 | 1.19 |
| 5a | 1.91 | 4.40E-01 | 2.31E-01 | 1.90 |
| 6a | 1.93 | 6.10E-02 | 1.27E-01 | 2.08 |

Table S14. Exponential fits which relate our computationally derived descriptor (Ru(II)-O₂ ΔE_{IP}) to experimentally measure rate constants. Functions fit the form: \( y = 10^{ax+b} \).

|          | a    | b    |
|----------|------|------|
| Source: 1| 3.32 | -10.22 |
| Source: 2| -1.82 | 0.29 |
| Source: 3| -10.32 | 19.04 |
Figure S6. Scatter plots showing the extent to which the scaling relationships generalize to distinct electronic states. Points are colored according to either their cluster assignment in Figure 2 (red, green, or blue) or to indicate that these TMCs are calculations aimed to investigate the effects of conformationally constrained ligands (orange). The scaling relationships previously identified for the 15 TMCs in the majority electronic states are also shown (gray). The correlation between Ru(II)-O2 ΔEIP and Ru(II)-O2 ΔELD is also shown in Figure 6.
Table S15. The difference (in kcal/mol) between the computed value for each of the seven DFT properties and the value derived from our scaling relationships, by TMC. Values for which the actual value is less than the scaling relationship are defined as negative. Ru(II)-O$_2$ $\Delta$E$_{IP}$ is excluded from this table, as it would always be zero.

| Name | Ru(IV)=O $\Delta$G$_{ox}$ | WNA $\Delta$G | Ru(II)-O$_2$ $\Delta$G$_{ox}$ | Ru(IV)=O $\Delta$E$_{IP}$ | Ru(II)-O$_2$ $\Delta$E$_{LD}$ | Ru(III)-O$_2$ $\Delta$E$_{LD}$ |
|------|-----------------|--------------|-----------------|-----------------|-----------------|-----------------|
| 1a   | -0.53           | 0.58         | 0.15            | 0.04            | -0.04           | -0.07           |
| 1b   | 0.28            | 0.10         | 0.03            | -0.37           | 0.50            | 0.25            |
| 1c   | -0.23           | 0.57         | 0.13            | 1.01            | 0.03            | 0.14            |
| 1g   | 0.14            | 0.04         | 0.11            | 0.00            | 0.16            | 0.07            |
| 1h   | 0.20            | -0.50        | -0.02           | 0.12            | 0.05            | 0.30            |
| 1i   | -0.29           | 0.22         | 0.29            | -0.24           | -0.17           | -0.01           |
| 2a   | -0.01           | -0.06        | 0.18            | 0.27            | -0.16           | -0.15           |
| 2g   | 0.30            | -0.25        | -0.56           | 0.31            | 0.07            | -0.01           |
| 3a   | -2.38           | 2.77         | 0.28            | -1.03           | -0.03           | -0.23           |
| 3h   | -0.49           | 0.78         | 0.16            | -0.26           | 0.12            | 0.21            |
| 4a   | 0.03            | 0.14         | -0.05           | 0.17            | -0.21           | -0.09           |
| 4i   | 0.16            | -0.53        | -0.02           | 0.01            | -0.25           | -0.05           |
| 5a   | -1.44           | 1.90         | -0.16           | -1.30           | 0.00            | -0.24           |
| 6a   | -0.07           | 0.27         | -0.51           | -0.05           | -0.06           | -0.10           |
| 7a   | -3.41           | 2.79         | -0.76           | -5.46           | 0.39            | -0.23           |

minority electronic state 1 (green)

| Name | Ru(IV)=O $\Delta$G$_{ox}$ | WNA $\Delta$G | Ru(II)-O$_2$ $\Delta$G$_{ox}$ | Ru(IV)=O $\Delta$E$_{IP}$ | Ru(II)-O$_2$ $\Delta$E$_{LD}$ | Ru(III)-O$_2$ $\Delta$E$_{LD}$ |
|------|-----------------|--------------|-----------------|-----------------|-----------------|-----------------|
| 1f   | -4.95           | 5.18         | -0.61           | -5.24           | 2.02            | 1.97            |
| 8a   | 0.97            | 3.74         | -2.97           | 1.68            | 1.28            | -3.08           |

minority electronic state 2 (red)

| Name | Ru(IV)=O $\Delta$G$_{ox}$ | WNA $\Delta$G | Ru(II)-O$_2$ $\Delta$G$_{ox}$ | Ru(IV)=O $\Delta$E$_{IP}$ | Ru(II)-O$_2$ $\Delta$E$_{LD}$ | Ru(III)-O$_2$ $\Delta$E$_{LD}$ |
|------|-----------------|--------------|-----------------|-----------------|-----------------|-----------------|
| 1d   | -0.82           | -3.03        | 0.17            | -0.53           | -6.69           | -2.10           |
| 1e   | -0.48           | -3.38        | 1.18            | -0.80           | -6.51           | -2.15           |
Table S16. Tabulated values (in kcal/mol) for each of the seven DFT properties which are possibly rate limiting for the four TMCs involved in investigating the effects of ligand constrains. The results are 1a are duplicated here for clarity. Ru(II)-O2 ΔGox and Ru(III)-O2 ΔELD are not available for the unconstrained version for 1a since the calculations involved in computing these properties failed to pass the criteria described in the methods section.

| Name                        | Ru(IV)=O ΔGox | Ru(IV)=O ΔEIP | Ru(II)-O2 ΔGox | Ru(II)-O2 ΔEIP | WNA ΔG | Ru(II)-O2 ΔELD | Ru(III)-O2 ΔELD |
|-----------------------------|---------------|---------------|----------------|----------------|--------|----------------|----------------|
| 1a                          | 52.36         | 59.12         | 40.34          | 45.20          | -24.43 | 11.97          | 6.33           |
| Unconstrained 1a            | 64.52         | 68.49         | 49.12          | -28.17         | 11.55  |                |                |
| Graphene Analog             | 50.73         | 55.16         | 43.18          | 58.71          | -19.98 | 20.00          | 7.79           |
| Unconstrained Graphene Analog | 62.67       | 69.92         | 48.47          | 52.38          | -28.39 | 17.16          | 8.26           |

Figure S7. Comparison of energetics of the WNA catalytic cycle for the graphene analog system when the ligands are either conformationally constrained (blue) or unconstrained (red). Inset structures (top) show the bonds which are removed to construct an unconstrained equivalent. Each step is identified as an intermediate labelled between I and VI, with the labels chosen to match the arrangement of intermediates in Scheme 1. The formation of intermediate Ru(V)=O is significantly more endothermic when the conformational constraints are removed.
Table S17. ΔG (in eV) for each step in the WNA catalytic cycle for TMCs involved in comparing catalysts with and without conformationally constrained ligands. Numbers are assigned to intermediates based on the order they appear in Scheme 1, starting with "I" for Ru(II)-OH₂ and ending with "VII" for Ru(III)-O₂. We add -1.6 eV to the steps involving electron transfer (I-II, II-III, III-IV, V-VI, and VI-VII) to account for the oxidation potential of the oxidant. This information is represented graphically in Figure 7.

|       | 1a            | Unconstrained 1a | Graphene Mimic | Unconstrained Graphene Mimic |
|-------|---------------|------------------|----------------|-------------------------------|
| II-III| -0.62         | -0.76            | -0.72          | -0.83                         |
| III-IV| 0.67          | 1.20             | 0.60           | 1.12                          |
| IV-V  | -1.06         | -1.22            | -0.87          | -1.23                         |
| V-VI  | -0.79         | -0.97            | -0.55          | -0.60                         |
| VI-I  | 1.11          | 1.16             | 1.21           | 1.20                          |
| I-II  | -0.71         | -0.81            | -1.07          | -1.06                         |
| VI-VII| 0.15          | --               | 0.27           | 0.50                          |
| VII-I | 0.25          | --               | -0.13          | -0.36                         |

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