

Electronic Supplementary Information for:

Statistical Analysis of C–H Activation by Oxo Complexes Supports Diverse Thermodynamic Control Over Reactivity

Joseph E. Schneider, McKenna K. Goetz, and John S. Anderson

Department of Chemistry, The University of Chicago, Chicago, IL 60637, United States

Correspondence to: jsanderson@uchicago.edu

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Summary of Experimental Data

In Table S1 we list each metal oxo species considered, their references, their reported k_2 values for reactivity with 9,10-dihydroanthracene (DHA), any reported statistical or stoichiometric corrections to these k_2 values (the k_2 values were multiplied by these numbers prior to determining barrier heights), the temperature these k_2 values were collected at, and the resultant experimental reaction barriers (calculated as described in the main text methods). Where multiple temperatures or multiple experimental conditions are reported, only one set of those conditions was chosen to represent the metal oxo complex's reaction rate with DHA. We also list the experimental slope of $RT \log k_2$ vs. experimental substrate BDFE for cases with enough data to determine it (at least three different substrates with k_2 reported, counting DHA and xanthene as only one substrate due to their similar experimental BDFEs, and excepting the Co^{III} oxo complex whose kinetics trend not with BDFE but with $\text{p}K_{\text{a}}$). Chemdraws for each metal oxo complex are provided in Figure S1 (training set) and Figure S2 (test set).

Table S1. Metal oxo species analyzed with their experimental kinetics and barriers

Oxo	References	k_2^a (s^{-1})	Literature Correction	T ($^{\circ}\text{C}$)	PCET Barrier ^a (kcal/mol)	BDFE Slope ^b
$[\text{Fe}^{\text{IV}}(\text{O})(\text{Me}_3\text{NTB})(\text{MeCN})]^{2+}$	1	780	4	-40	2.30	-0.18
$[\text{Fe}^{\text{IV}}(\text{O})(\text{TMG}_2\text{dien})(\text{MeCN})]^{2+}$	2	5		-30	4.38	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{TMG}_3\text{tren})]^{2+}$	3	0.09		-30	7.46	
$[\text{Fe}^{\text{V}}(\text{O})(\text{TAML})]^-$	4,5	263	1	-37	3.54	-0.22
$[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{MeCN})]^{2+}$	6,7	0.2		0	7.99	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{N}_3)]^+$	6	2.4		0	6.64	-0.28
$[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{OCOCF}_3)]^+$	6	1.3		0	6.93	-0.35
$[\text{Fe}^{\text{IV}}(\text{O})(\text{TMCS})]^+$	6,8	7.5		0	6.02	
$[\text{Mn}^{\text{IV}}(\text{O})(\text{H}_3\text{buea})^-]$	9,10	0.038	8	30	8.50	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{TMP})]$	11	2.2		-15	6.18	
$[\text{Co}^{\text{III}}(\text{O})(\text{PhB}^{\text{tBu}}\text{Im}_3)]$	12,13	0.058	2	23	8.87	
$[\text{Ru}^{\text{IV}}(\text{O})(\text{H}^+\text{TPA})(\text{bpy})]^{3+}$	14	105		25	4.88	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{tpfpp})]$	15	13	1	15	5.82	-0.15
$[\text{Mn}^{\text{VII}}(\text{O})_4]^-$	16,17	0.12	4	25	9.47	-0.67
$[\text{Mn}^{\text{V}}(\text{O})_2(\text{tf}_4\text{tmap})]^{3+}$	18	240	1	15	4.53	-0.25
$[\text{Mn}^{\text{IV}}(\text{O})(\text{OH})(\text{tf}_4\text{tmap})]^{3+}$	18	4.9	1	15	6.36	-0.35
$[\text{Cr}^{\text{IV}}(\text{O})(\text{TMC})(\text{Cl})]^+$	19,20	0.21	1	-10	7.69	
$[\text{Ru}^{\text{VI}}(\text{O})_2(\text{TMC})]^{2+}$	21,22	0.036	1	35	10.4	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{N4Py})]^{2+}$	23,24	18		25	5.99	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{BnTPEN})]^{2+}$	23	100		25	4.94	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{Me}_2\text{TACN-Py}_2)]^{2+}$	23	7.4		25	6.54	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{BP1})]^{2+}$	23	1.1		25	7.57	
$[\text{Fe}^{\text{IV}}(\text{O})(\text{BP2})]^{2+}$	23	40		25	5.44	
$[\text{Ru}^{\text{IV}}(\text{O})(\text{bpy})_2(\text{py})]^{2+}$	22,25	125	1	23	4.77	-0.54
$[\text{Mn}^{\text{IV}}(\text{O})_2(\text{Me}_2\text{EBC})]$	26	0.015		15	10.3	-0.09
$[\text{Mn}^{\text{IV}}(\text{O})(\text{N4Py})]^{2+}$	27	3.6	1	25	6.94	
$[\text{Co}^{\text{IV}}(\text{O})(13\text{-TMC})]^{2+}$	28	0.083	1	-40	7.30	-0.20
$[\text{Fe}^{\text{IV}}(\text{O})(13\text{-TMC})]^{2+}$	29	4.7	1	-40	5.44	-0.51
$[\text{Ru}^{\text{VI}}(\text{O})_2(\text{L})]^{2+}$	30,31	7.45	4	25	6.08	-0.60
$[\text{Ru}^{\text{VI}}(\text{O})_2(\text{F}_{28}\text{-tpp})]$	32	22.5	1	25	6.08	-0.43

^aFor reactivity with 9,10-dihydroanthracene. ^bExperimental slope of $RT \log k_2$ vs. substrate BDFE.

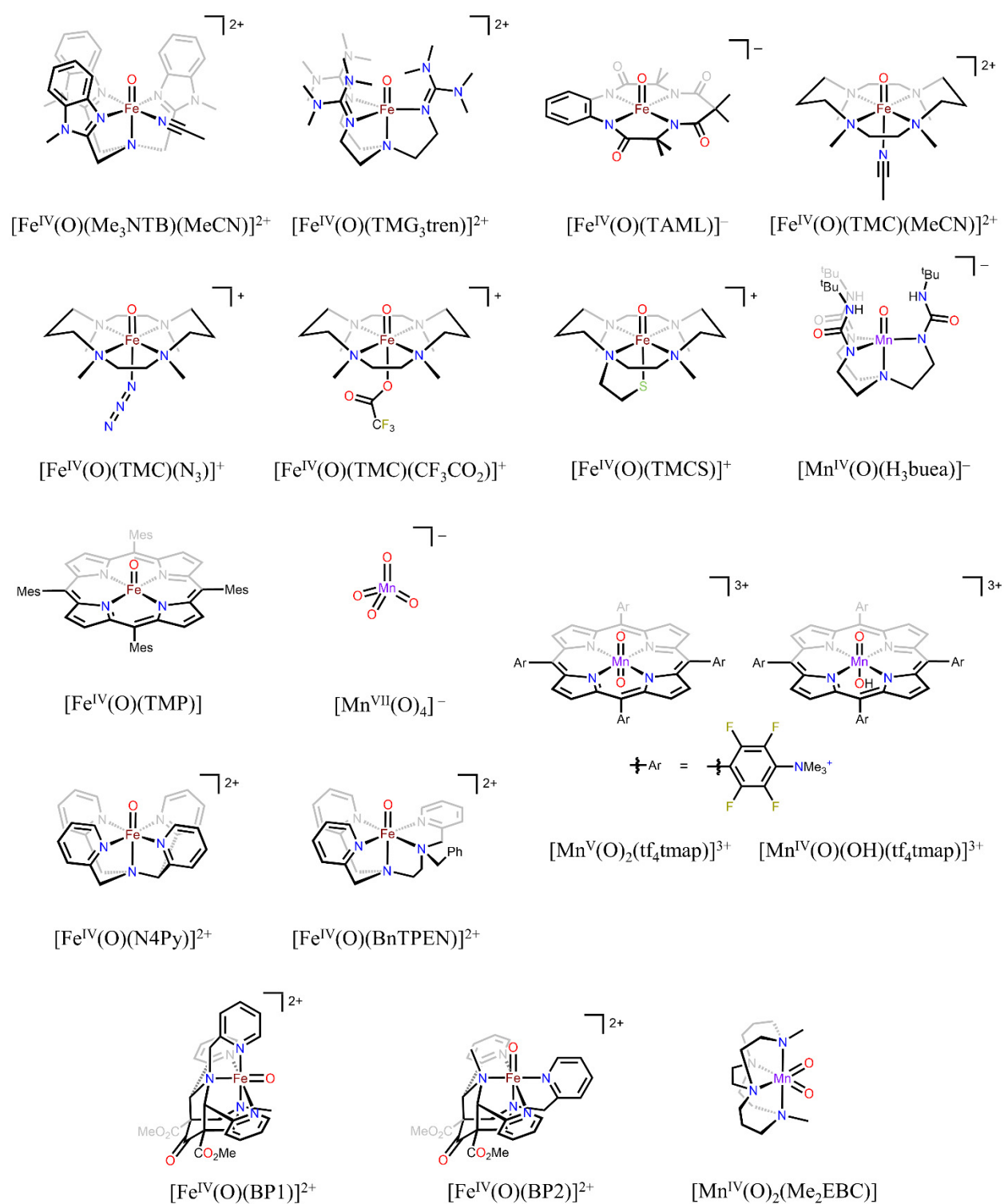


Figure S1. Metal oxo complexes in the training set. See Table S1 for references.

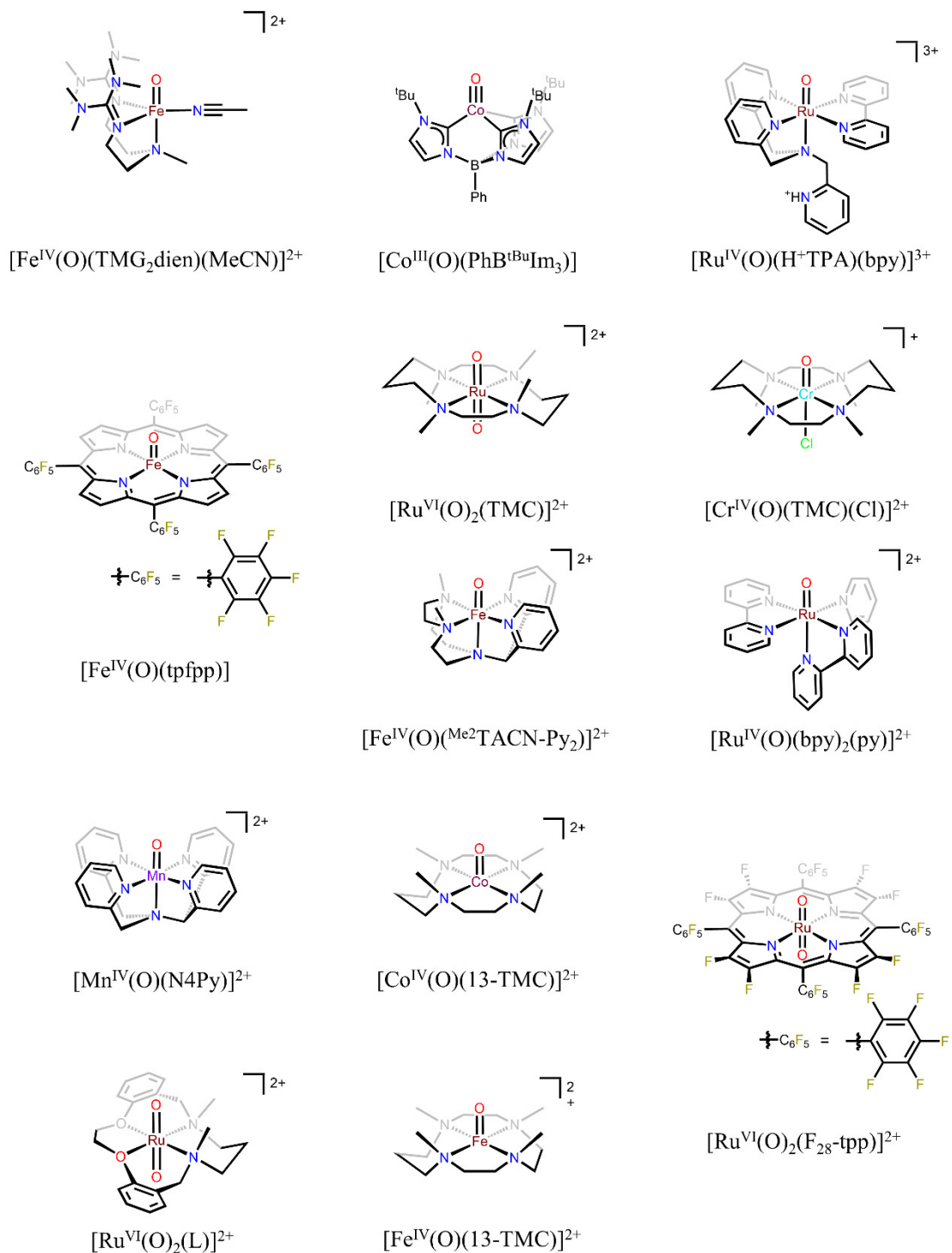


Figure S2. Metal oxo complexes in the test set. See Table S1 for references.

Summary of csv File Contents

In the accompanying data folder we include csv files containing all the data used in our regressions. For the data for various metal oxo complexes, each row corresponds to kinetic data of a particular metal oxo complex under a particular set of conditions; if a given metal oxo complex has k_2 values reported under different conditions (solvent, temperature, etc.) then multiple rows correspond to the same metal oxo complex. For the data on the kinetics of the Co^{III} oxo¹² each row pertains to a single substrate. In both spreadsheets each column has a short title for the data that is contained in that column. In Table S2, we give a longer description of what each column in the data files contains. The data directly used in our regressions are given in Table S3 (data relating to spin), Table S4 (data relating to reactivity with DHA), Table S6 (data related to reactivity with 1,4-cyclohexadiene (CHD)), Table S7 (data related to reactivity with fluorene), (data related to reactivity with xanthene), and Table S13 (steric parameters).

Table S2. Description of what each column in the accompanying csv file contains

Column Title	Description of Contents
Data Contained in “Oxos Data.csv”	
Name	The chemical formula of the oxo that the k_2 value(s) are reported for
Index	The numerical index assigned to the oxo that the k_2 value(s) are reported for
Training	1 if the row’s DHA k_2 value is included in the training set, 0 if not
Main Rate	1 if the row’s set of conditions is chosen to represent the metal oxo, 0 if not
Citation	The report the k_2 values are taken from
Note	Additional information relevant to the k_2 value
Metal	The metal of the metal oxo complex
Valency	The valency of the metal oxo complex
d count	The d-electron count of the metal oxo complex
Coordination	The coordination number (including the oxo) of the metal oxo complex
Axial Symmetry	The idealized axial symmetry about the M–O axis (C3 or C4); if the symmetry related ligands are not all equivalent then the symmetry is preceded by a “p”
N Oxos	The number of oxo ligands in the metal oxo complex
B(M,O)	The experimental M–O bond length, if reported (in Å)
v(M,O)	The experimental M–O stretching frequency, if reported (in cm^{-1})
BDE	The experimental bond dissociation (free) energy of MO–H, if reported (in kcal/mol)
pKa	The experimental pK_a of the protonated oxo, if reported
E0	The experimental reduction potential of the oxo, if reported (in V)
Charge	The charge of the metal oxo complex (in atomic charges)
Mass	The mass of the metal oxo complex (in AMU)
T	The temperature the k_2 value(s) are measured at (in °C)
kT	The thermal energy at temperature T (in kcal/mol), equivalently referred to as RT
Solvent	The solvent the k_2 value(s) are measured in
Abraham Alpha	Abraham’s hydrogen bond acidity of any protic component of the solvent; ^a 0 if the solvent is entirely aprotic.
Abraham Beta	The estimated hydrogen bond basicity of the metal oxo complex on Abraham’s scale
Abraham Alpha*Beta	The product of the hydrogen bond acidity and hydrogen bond basicity
Sub k_2^b	The k_2 value for the reaction between the indicated substrate reacting with the indicated metal oxo complex in the given conditions (in $\text{M}^{-1}\text{s}^{-1}$)
Sub Corr ^b	Any statistical and/or stoichiometric correction applied to the substrate’s k_2 value, if reported

Sub H_Act ^b	The experimental activation enthalpy of the reaction, if reported (in kcal/mol)
Sub S_Act ^b	The experimental activation entropy of the reaction, if reported (in cal/(mol K))
Sub KIE ^b	The experimental KIE on the substrate's k_2 value, if reported
Exp BDFE Slope	The experimental slope of the reaction between the metal oxo complex and various substrates at the given conditions, if there are enough k_2 values to determine it.
Mult O	The ground state spin multiplicity of the metal oxo complex
Mult OH	The ground state spin multiplicity of the corresponding metal hydroxide complex of the same overall charge
Δ Mult	The change in spin multiplicity between the metal oxo complex and the corresponding metal hydroxide complex
Mult O-	The spin multiplicity of the reduced metal oxo complex
Mult OH+	The spin multiplicity of the protonated metal oxo complex
%BV Tot	The total percent buried volume around the oxo ligand
%BV Dir ^c	The percent buried volume for the quadrant in the given direction from the oxo ligand
%BV Dev	The standard deviation of the percent buried volume of the four quadrants
Min Angle	The minimum cone angle on top of the M–O bond
Max Angle	The maximum cone angle on top of the M–O bond
Height	The height of the steric cavity the metal oxo resides in
Depth	The depth of the steric cavity the metal oxo resides in
Oxo Reorganization	The calculated electronic energy needed to distort the metal oxo to the metal hydroxide geometry
Hydroxide Reorganization	The calculated electronic energy needed to distort the metal hydroxide to the metal oxo geometry
Oxo Frequency	The calculated dominant stretching frequency of the M–O bond
Hydroxide Frequency	The calculated dominant stretching frequency of the M–OH bond
Length M-O	The calculated length of the M–O bond
Length M-OH	The calculated length of the M–OH bond
Δ Length M-O	The calculated change in length between the M–O and M–OH bond
Oxo Stretch	The energy needed to stretch the M–O bond to the length of the M–OH bond
Hydroxide Stretch	The energy needed to compress the M–OH bond to the length of the M–O bond
Total Δ Length M-L	The calculated total change of metal–ligand bond lengths upon reduction from the oxo to the hydroxide complex, excluding the reduced oxo ligand
IBO Spin O	The IBO spin density on the oxo ligand in the metal oxo complex
IBO Spin M	The IBO spin density on the metal in the metal oxo complex
Δ IBO Spin O	The change in IBO spin density on the oxo ligand oxygen upon PCET reduction
Δ IBO Spin M	The change in IBO spin density on the metal upon PCET reduction
Spin Excitation	The calculated energy needed for the metal oxo complex to access a spin surface within one spin multiplicity of the corresponding metal hydroxide complex
IBO Charge M Oxo	The IBO charge density on the metal in the metal oxo complex
IBO Charge O Oxo	The IBO charge density on the oxo ligand in the metal oxo complex
IBO Charge M Hydroxide	The IBO charge density on the metal in the metal hydroxide complex
IBO Charge O Hydroxide	The IBO charge on the hydroxide oxygen of the metal hydroxide complex
IBO Charge H Hydroxide	The IBO charge on the hydroxide hydrogen of the metal hydroxide complex
Δ IBO Charge O(H)	The net amount of charge gained by the oxo ligand upon PCET as measured by IBO charges, including the proton and any IBO charge on the hydroxide hydrogen
Sub Δ E_PCET ^b	The calculated change in the electronic energy upon PCET to the metal oxo complex from the indicated substrate
Sub Δ E_PT ^b	The calculated change in the electronic energy upon PT to the metal oxo complex from the indicated substrate

Sub ΔE_{ET}^b	The calculated change in the electronic energy upon ET to the metal oxo complex from the indicated substrate
Sub $\eta(E)^b$	The calculated asynchronicity of PCET to the metal oxo complex from the indicated substrate calculated with electronic energies
Sub $ \eta (E)^b$	The calculated absolute value of the asynchronicity of PCET to the metal oxo complex from the indicated substrate calculated with electronic energies
Sub ΔE_{CT} Average ^b	The calculated average of Sub ΔE_{PCET} and Sub ΔE_{PT}
Sub ΔG_{PCET}^b	The calculated change in the free energy upon PCET to the metal oxo complex from the indicated substrate
Sub ΔG_{PT}^b	The calculated change in the free energy upon PT to the metal oxo complex from the indicated substrate
Sub ΔG_{ET}^b	The calculated change in the free energy upon ET to the metal oxo complex from the indicated substrate
Sub $\eta(G)^b$	The calculated asynchronicity of PCET to the metal oxo complex from the indicated substrate calculated with free energies
Sub $ \eta (G)^b$	The calculated absolute value of the asynchronicity of PCET to the metal oxo complex from the indicated substrate calculated with free energies
Sub ΔG_{CT} Average ^b	The calculated average of Sub ΔG_{PCET} and Sub ΔG_{PT}
Sub PCET Barrier ^b	The calculated experimental reaction barrier of PCET to the metal oxo complex from the indicated substrate with an adjustment for the entropy of association

Data Contained in "CoIII Oxo Data.csv"

Substrate	The substrate whose data is contained in the given row
k_2	The k_2 value measured for reactivity between the Co ^{III} oxo and this substrate, or the reported k_{obs} value divided by the relevant substrate concentration (in M ⁻¹ s ⁻¹)
Mass	The mass of the substrate (in AMU)
BDE(kcal)	The experimental BDE of the substrate C–H bond (in kcal/mol), if reported ^d
pK _{a,exp} (DMSO)	The experimental pK _a of the substrate C–H bond, if reported ^e
ΔG_{PCET}	The calculated change in free energy upon PCET from the substrate to the Co ^{III} oxo
ΔG_{PT}	The calculated change in free energy upon PT from the substrate to the Co ^{III} oxo
ΔG_{ET}	The calculated change in free energy upon ET from the substrate to the Co ^{III} oxo
%BV	The sterics surrounding the substrate's reactive hydrogen

^aRef. ³³. ^bSub can be: DHA (9,10-dihydroanthracene), EtPh (ethylbenzene), CHD (1,4-cyclohexadiene), TPM (triphenylmethane), iPrPh (cumene), Tol (toluene), CyclOct (cyclooctane), DMB (2,3-dimethylbutane), CyclHex (cyclohexane), Xth (xanthene), Fl (fluorene), DPM (diphenylmethane), cCHD (1,3-cyclohexane), AcrH2 (10-methyl-9,10-dihydroacridine), BNAH (1-benzyl-1,4-dihydronicotinamide), Ind (indene), or CHxene (cyclohexene). Calculations were only performed with DHA, CHD, Xth, and Fl. ^cDir can be: SW, NW, NE, SE. ^dRef. 34. ^eRef. 35–37.

Table S3. Spin based parameters of each metal oxo complex

Oxo	Mult. ^a Oxo	Mult. ^a Hydroxide	Mult. ^a Protonated Oxo	Mult. ^a Reduced Oxo	Spin Excitation ^b (kcal/mol)	IBO Spin Density
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	3	6	3	6	16.0	0.852
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	5	6	5	6	0	0.697
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	5	6	5	6	0	0.662
[Fe ^V (O)(TAML)] ⁻	2	3	2	3	0	0.261
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺	3	6	3	6	10.6	0.760
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	3	6	3	6	7.2	0.691
[Fe ^{IV} (O)(TMC)(OCOCF ₃)] ⁺	3	6	3	6	8.3	0.699
[Fe ^{IV} (O)(TMCS)] ⁺	3	6	3	6	4.7	0.708
[Mn ^{IV} (O)(H ₃ buea)] ⁻	4	5	4	5	0	0.229
[Fe ^{IV} (O)(TMP)]	3	6	3	4	43.7	0.673
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	1	4	1	4	11.9	0.000
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺	3	2	3	2	0	0.929
[Fe ^{IV} (O)(tpfpp)]	3	4	3	4	0	0.695
[Mn ^{VII} (O) ₄] ⁻	1	2	1	2	0	0.000
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	1	4	1	2	24.5	0.000
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	4	5	4	5	0	0.546
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	3	4	3	4	0	-0.133
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	1	2	1	2	0	0.000
[Fe ^{IV} (O)(N ₄ Py)] ²⁺	3	6	3	6	75.5	0.814
[Fe ^{IV} (O)(BnTPEN)] ²⁺	3	6	3	6	18.0	0.813
[Fe ^{IV} (O)(^{Me} ₂ TACN-Py ₂)] ²⁺	3	6	3	6	73.6	0.795
[Fe ^{IV} (O)(BP1)] ²⁺	3	6	3	6	19.6	0.821
[Fe ^{IV} (O)(BP2)] ²⁺	3	6	3	6	19.8	0.830
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	3	2	3	2	0	0.924
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	4	5	4	5	0	0.162
[Mn ^{IV} (O)(N ₄ Py)] ²⁺	4	5	4	5	0	0.589
[Co ^{IV} (O)(13-TMC)] ²⁺	4	5	4	5	0	1.238
[Fe ^{IV} (O)(13-TMC)] ²⁺	3	6	3	6	17.7	0.691
[Ru ^{VI} (O) ₂ (L)] ²⁺	1	2	1	2	0	0.000
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	1	2	1	2	0	0.000

^aMultiplicity. ^bEnergy needed to access the lowest spin state of the oxo complex that is one multiplicity away from the multiplicity of the hydroxide; calculated at the ground spin state's optimized geometry.

Table S4. Kinetics, barrier heights, and thermodynamic parameters of reactivity with 9,10-dihydroanthracene

Oxo	k_2 (s ⁻¹) ^a	PCET Barrier (kcal/mol)	ΔG_{PCET} (kcal/mol)	ΔG_{PT} (kcal/mol)	ΔG_{ET} (kcal/mol)	$ \eta $ (kcal/mol)	ΔE_{PCET} (kcal/mol)	ΔE_{PT} (kcal/mol)	ΔE_{ET} (kcal/mol)
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	780	2.3	-15.9	57.7	29.3	20.0	-8.9	61.4	37.8
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	57	4.4	-9.3	57.5	39.2	12.9	-5	61.5	46
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	0.09	7.5	-7.2	54.5	47.5	4.9	-3.1	57.6	54.4
[Fe ^V (O)(TAML)] ⁻	263	3.5	-10.1	39.2	40.2	0.72	-6.9	43.2	44.8
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺	0.2	8.0	-6.5	68.2	36.8	22.2	1.5	71.9	46.8
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	2.4	6.6	-9.4	47.1	46.6	0.4	-2.1	50.5	56.0
[Fe ^{IV} (O)(TMC)(OCOCF ₃)] ⁺	1.3	6.9	-8.7	56.7	42.7	9.9	-1.3	60.1	52.7
[Fe ^{IV} (O)(TMCS)] ⁺	7.5	6.0	-8.5	40.1	50.1	7.0	-2.1	42.7	59.3
[Mn ^{IV} (O)(H ₃ buea)] ⁻	0.038	8.5	0.71	27.6	62.3	24.6	5.3	29.5	69.3
[Fe ^{IV} (O)(TMP)]	2.2	6.2	-10.9	39.3	67.7	20.1	-6.2	44.3	73.5
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	0.0584	8.9	-8.8	15.9	74.3	41.3	-3.2	19.6	82.7
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺	105	4.9	-4.5	75.9	41.9	24.1	-2.6	78.8	45.7
[Fe ^{IV} (O)(tpfpp)]	13	5.8	-8.0	50.1	57.3	5.1	-3.8	53.5	63.6
[Mn ^{VII} (O) ₄] ⁻	0.12	9.5	-0.4	55.5	49.6	4.1	3.5	58.7	54.4
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	240	4.5	-13.7	34.5	59.5	17.7	-9.0	36.7	66.2
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	4.9	6.4	-9.2	20.0	60.8	28.9	-4.6	21.3	65.7
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	0.21	7.7	-10.0	53.6	55.7	1.5	-7.5	56.9	61.5
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	0.036	10.4	3.9	82.8	34.1	34.4	7.2	86.8	38.4
[Fe ^{IV} (O)(N4Py)] ²⁺	18	6.0	-5.8	65.0	38.0	19.1	1.5	69.0	46.4
[Fe ^{IV} (O)(BnTPEN)] ²⁺	100	4.9	-7.4	64.1	35.0	20.6	-1.2	66.7	43.0
[Fe ^{IV} (O)(^{Me} ₂ TACN-Py ₂)] ²⁺	7.4	6.5	-6.3	63.7	37.3	18.7	1.4	67.5	46.6
[Fe ^{IV} (O)(BP1)] ²⁺	1.1	7.6	-6.2	69.9	35.6	24.3	0.4	74.0	43.5
[Fe ^{IV} (O)(BP2)] ²⁺	40	5.4	-9.6	68.1	31.7	25.7	-3.2	71.5	40.0
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	125	4.8	-5.5	68.5	43.4	17.7	-3.8	71.8	47.5
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	0.01496	10.3	-3.3	7.6	85.8	55.3	0.8	7.2	93.7
[Mn ^{IV} (O)(N4Py)] ²⁺	3.6	6.9	-8.1	51.5	36.6	10.6	-3.0	55.1	43.7
[Co ^{IV} (O)(13-TMC)] ²⁺	0.083	7.3	-15.0	69.0	11.5	40.6	-11.0	74.1	16.7
[Fe ^{IV} (O)(13-TMC)] ²⁺	4.7	5.4	-19.0	78.3	17.6	42.9	-13.8	83.4	24.1
[Ru ^{VI} (O) ₂ (L)] ²⁺	7.45	6.1	0.11	85.5	22.1	44.9	2.8	89.4	26.5
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	22.5	6.1	-4.6	64.9	37.2	19.6	-1.0	66.2	42.7

^aSee Table S1 for references and experimental conditions.

Table S5. Kinetics, barrier heights, and thermodynamic parameters of reactivity with 1,4-cyclohexadiene

Oxo	k_2 (s ⁻¹) ^a	PCET Barrier (kcal/mol)	ΔG_{PCET} (kcal/mol)	ΔG_{PT} (kcal/mol)	ΔG_{ET} (kcal/mol)	$ \eta $ (kcal/mol)	ΔE_{PCET} (kcal/mol)	ΔE_{PT} (kcal/mol)	ΔE_{ET} (kcal/mol)
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	240	3.6	-19.2	64.8	26.5	27.1	-12.4	68.5	34.8
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	18	5.4	-12.6	64.6	36.4	19.9	-8.5	68.5	42.9
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	1.2	6.7	-10.6	61.6	44.7	12.0	-6.6	64.7	51.4
[Fe ^V (O)(TAML)] ⁻			-13.4	46.3	37.4	6.3	-10.4	50.3	41.8
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺			-9.8	75.3	34.0	29.2	-2.0	79.0	43.8
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	1.4	7.4	-12.8	54.2	43.8	7.4	-5.6	57.5	53.0
[Fe ^{IV} (O)(TMC)(OCOFCF ₃)] ⁺	1.2	7.5	-12.0	63.8	39.9	16.9	-4.8	67.2	49.7
[Fe ^{IV} (O)(TMCS)] ⁺			-11.8	47.3	47.3	0.038	-5.6	49.8	56.2
[Mn ^{IV} (O)(H ₃ buea)] ⁻			-2.6	34.7	59.6	17.6	1.8	36.6	66.3
[Fe ^{IV} (O)(TMP)]			-14.2	46.4	64.9	13.1	-9.7	51.3	70.5
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]			-12.1	23.0	71.5	34.3	-6.7	26.7	79.7
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺			-7.8	83.0	39.1	31.0	-6.1	85.9	42.7
[Fe ^{IV} (O)(tpfpp)]	9	6.7	-11.3	57.2	54.5	1.9	-7.3	60.6	60.6
[Mn ^{VII} (O) ₄] ⁻			-3.7	62.6	46.9	11.1	0.029	65.8	51.3
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺			-17	41.6	56.7	10.7	-12.5	43.8	63.2
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	1.3	7.8	-12.5	27.1	58.1	21.9	-8.1	28.4	62.6
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	0.096	8.6	-13.3	60.7	52.9	5.5	-11	64.0	58.5
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	0.015	11.5	0.63	89.9	31.4	41.4	3.7	93.9	35.4
[Fe ^{IV} (O)(N4Py)] ²⁺			-9.1	72.1	35.3	26.0	-2.0	76.0	43.4
[Fe ^{IV} (O)(BnTPEN)] ²⁺			-10.7	71.2	32.2	27.6	-4.7	73.8	40.0
[Fe ^{IV} (O)(^{Me} ₂ TACN-Py ₂)] ²⁺			-9.7	70.8	34.6	25.6	-2.1	74.6	43.6
[Fe ^{IV} (O)(BP1)] ²⁺			-9.5	77.0	32.9	31.2	-3.1	81.1	40.5
[Fe ^{IV} (O)(BP2)] ²⁺			-12.9	75.2	29.0	32.7	-6.7	78.5	37.0
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺			-8.8	75.6	40.7	24.7	-7.3	78.9	44.5
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	0.0159	10.8	-6.7	14.7	83.0	48.3	-2.7	14.3	90.7
[Mn ^{IV} (O)(N4Py)] ²⁺			-11.4	58.6	33.8	17.5	-6.5	62.2	40.7
[Co ^{IV} (O)(13-TMC)] ²⁺	0.037	8.1	-18.4	76.1	8.7	47.6	-14.5	81.1	13.7
[Fe ^{IV} (O)(13-TMC)] ²⁺	5.4	5.8	-22.3	85.4	14.8	50.0	-17.3	90.5	21.1
[Ru ^{VI} (O) ₂ (L)] ²⁺			-3.2	92.7	19.3	51.8	-0.72	96.5	23.5
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	240		-7.9	72.0	34.5	26.5	-4.5	73.3	39.7

^aSee Table S1 for references and experimental conditions.

Table S6. Kinetics, barrier heights, and thermodynamic parameters of reactivity with xanthene

Oxo	k_2 (s ⁻¹) ^a	PCET Barrier (kcal/mol)	ΔG_{PCET} (kcal/mol)	ΔG_{PT} (kcal/mol)	ΔG_{ET} (kcal/mol)	$ \eta $ (kcal/mol)	ΔE_{PCET} (kcal/mol)	ΔE_{PT} (kcal/mol)	ΔE_{ET} (kcal/mol)
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺			-18.7	57.0	21.0	25.4	-12.3	61.3	27.1
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺			-12.1	56.8	31.0	18.3	-8.4	61.3	35.3
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺			-10.1	53.8	39.2	10.3	-6.5	57.5	43.8
[Fe ^V (O)(TAML)] ⁻			-12.9	38.5	32.0	4.6	-10.3	43.1	34.2
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺			-9.3	67.4	28.6	27.5	-1.9	71.8	36.1
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	9.6	5.5	-12.2	46.4	38.4	5.7	-5.5	50.3	45.4
[Fe ^{IV} (O)(TMC)(OCOFCF ₃)] ⁺	7.6	5.6	-11.5	55.9	34.4	15.2	-4.7	60.0	42.1
[Fe ^{IV} (O)(TMCS)] ⁺			-11.3	39.4	41.9	1.7	-5.5	42.5	48.6
[Mn ^{IV} (O)(H ₃ buea)] ⁻			-2	26.8	54.2	19.3	1.8	29.3	58.6
[Fe ^{IV} (O)(TMP)]	4.3	5.5	-13.7	38.6	59.4	14.7	-9.6	44.1	62.8
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]			-11.5	15.1	66.1	36	-6.6	19.4	72.1
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺			-7.2	75.2	33.7	29.3	-6.0	78.6	35.1
[Fe ^{IV} (O)(tpfpp)]	14	5.4	-10.8	49.4	49.1	0.17	-7.3	53.3	53.0
[Mn ^{VII} (O) ₄] ⁻	0.56	8.6	-3.2	54.7	41.5	9.4	0.092	58.6	43.7
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	570	3.6	-16.5	33.7	51.3	12.4	-12.5	36.5	55.5
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	3.8	6.1	-12	19.2	52.6	23.6	-8.0	21.1	55.0
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	0.86	6.6	-12.8	52.8	47.4	3.8	-10.9	56.7	50.9
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	0.057	9.7	1.2	82.0	26.0	39.6	3.8	86.7	27.8
[Fe ^{IV} (O)(N4Py)] ²⁺			-8.5	64.3	29.9	24.3	-1.9	68.8	35.8
[Fe ^{IV} (O)(BnTPEN)] ²⁺			-10.2	63.4	26.8	25.8	-4.6	66.6	32.4
[Fe ^{IV} (O)(^{Me} 2TACN-Py ₂)] ²⁺			-9.1	63.0	29.2	23.9	-2.0	67.4	35.9
[Fe ^{IV} (O)(BP1)] ²⁺			-9	69.2	27.5	29.5	-3.0	73.8	32.8
[Fe ^{IV} (O)(BP2)] ²⁺			-12.4	67.4	23.6	31.0	-6.7	71.3	29.3
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	577	3.5	-8.2	67.7	35.3	22.9	-7.2	71.6	36.9
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	0.048	9.3	-6.1	6.9	77.6	50.0	-2.6	7.0	83.1
[Mn ^{IV} (O)(N4Py)] ²⁺			-10.9	50.7	28.4	15.8	-6.4	54.9	33.1
[Co ^{IV} (O)(13-TMC)] ²⁺	0.15	6.7	-17.9	68.3	3.2.0	46.0	-14.4	73.9	6.1
[Fe ^{IV} (O)(13-TMC)] ²⁺		4.5	-21.8	77.6	9.3.0	48.3	-17.3	83.3	13.5
[Ru ^{VI} (O) ₂ (L)] ²⁺	49.7	4.9	-2.6	84.8	13.9	50.1	-0.65	89.2	15.9
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	59	5.1	-7.4	64.2	29.1	24.8	-4.5	66.1	32.1

^aSee Table S1 for references and experimental conditions.

Table S7. Kinetics, barrier heights, and thermodynamic parameters of reactivity with fluorene

Oxo	k_2 (s ⁻¹) ^a	PCET Barrier (kcal/mol)	ΔG_{PCET} (kcal/mol)	ΔG_{PT} (kcal/mol)	ΔG_{ET} (kcal/mol)	$ \eta $ (kcal/mol)	ΔE_{PCET} (kcal/mol)	ΔE_{PT} (kcal/mol)	ΔE_{ET} (kcal/mol)
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺			-11.6	47.8	25.9	15.5	-5.1	51.1	32.0
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺			-5.0	47.7	35.8	8.4	-1.2	51.1	40.2
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺			-3.0	44.6	44.1	0.41	0.74	47.3	48.6
[Fe ^V (O)(TAML)] ⁻			-5.8	29.4	36.8	5.3	-3.1	32.9	39.0
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺			-2.2	58.3	33.4	17.6	5.3	61.6	41.0
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	0.15	7.8	-5.2	37.2	43.2	4.2	1.7	40.1	50.2
[Fe ^{IV} (O)(TMC)(OCOFCF ₃)] ⁺	0.051	8.4	-4.4	46.8	39.3	5.3	2.5	49.8	46.9
[Fe ^{IV} (O)(TMCS)] ⁺			-4.3	30.3	46.7	11.6	1.7	32.4	53.5
[Mn ^{IV} (O)(H ₃ buea)] ⁻			5.0	17.7	59.0	29.2	9.1	19.2	63.5
[Fe ^{IV} (O)(TMP)]	0.09	7.5	-6.6	29.5	64.3	24.6	-2.4	33.9	67.7
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	0.61	7.5	-4.5	6.1	70.9	45.9	0.64	9.3	76.9
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺			-0.2	66.1	38.5	19.5	1.2	68.5	39.9
[Fe ^{IV} (O)(tpfpp)]	2.3	6.5	-3.8	40.3	53.9	9.7	-0.023	43.2	57.8
[Mn ^{VII} (O) ₄] ⁻			3.8	45.7	46.3	0.45	7.3	48.4	48.6
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	28	5.4	-9.5	24.6	56.1	22.2	-5.2	26.4	60.4
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺			-4.9	10.1	57.5	33.5	-0.8	11.0	59.9
[Cr ^{IV} (O)(TMC)(Cl)] ⁺			-5.7	43.7	52.3	6.0	-3.7	46.6	55.7
[Ru ^{VI} (O) ₂ (TMC)] ²⁺			8.2	72.9	30.8	29.8	11.0	76.5	32.6
[Fe ^{IV} (O)(N ₄ Py)] ²⁺			-1.5	55.2	34.7	14.5	5.3	58.6	40.6
[Fe ^{IV} (O)(BnTPEN)] ²⁺			-3.1	54.3	31.6	16.0	2.6	56.4	37.2
[Fe ^{IV} (O)(^{Me} ₂ TACN-Py ₂)] ²⁺			-2.1	53.9	34.0	14.1	5.2	57.2	40.8
[Fe ^{IV} (O)(BP1)] ²⁺			-1.9	60.1	32.3	19.7	4.2	63.7	37.7
[Fe ^{IV} (O)(BP2)] ²⁺			-5.4	58.3	28.4	21.2	0.57	61.1	34.2
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	21.9	5.4	-1.2	58.6	40.1	13.1	-0.0089	61.5	41.7
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	0.00912	10.3	0.93	-2.2	82.4	59.8	4.6	-3.1	87.9
[Mn ^{IV} (O)(N ₄ Py)] ²⁺			-3.8	41.6	33.2	6.0	0.81	44.8	37.9
[Co ^{IV} (O)(13-TMC)] ²⁺	0.0064	8.2	-10.8	59.1	8.1	36.1	-7.2	63.7	10.9
[Fe ^{IV} (O)(13-TMC)] ²⁺			-14.7	68.5	14.2	38.4	-10.0	73.1	18.3
[Ru ^{VI} (O) ₂ (L)] ²⁺	1.58	7	4.4	75.7	18.7	40.3	6.6	79.1	20.7
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	1.32	7.4	-0.34	55.1	33.9	15.0	2.8	55.9	36.9

^aSee Table S1 for references and experimental conditions.

Detailed Statistics on DHA Regressions

In Table S8, we report statistics on the regressions with DHA reaction barriers from Table 1. We also give regressions with ΔG_{PCET}^2 and with electronic energies instead of free energies. While the regression against $\{\Delta E_{\text{PCET}}, \Delta E_{\text{PT}}, \Delta E_{\text{ET}}\}$ fits the data better than the regression against $\{\Delta G_{\text{PCET}}, \Delta G_{\text{PT}}, \Delta G_{\text{ET}}\}$, there are good theoretical reasons to use free energies rather than electronic energies for LFER analyses and we therefore limit our discussion to free energies.²² The table is followed by a detailed summary of each regression and a breakdown of the $\{\Delta G_{\text{PCET}}, \Delta G_{\text{PT}}, \Delta G_{\text{ET}}\}$ model for each data point.

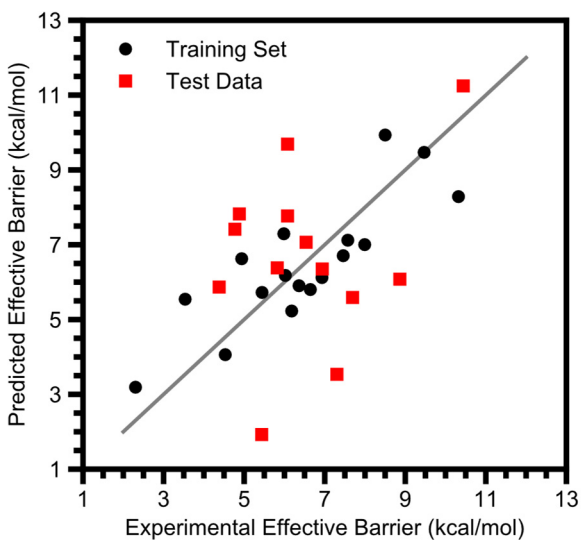
We report all the overall metrics as discussed in the methods section of the main text with more details specific to the parameters in each model and their corresponding coefficients. We report the correlation matrix of the parameters included in the model, their averages, and their standard deviations (all calculated with the training set). Within a linear regression, high correlation between two x-variables makes it difficult to untangle their effects on the y-variable, although the joint effect is unaffected.³⁸

For the coefficients, we report their values, their standard errors, 95% t-confidence intervals, and weighted coefficients. The coefficients' units are kcal/mol divided by the associated parameters' units. The standard errors do not directly inform on how reliable the coefficients are and are therefore scaled to give 95% t-confidence intervals. These rely on similar assumptions as the F-tests, and therefore have similar weaknesses.^{38,39} If the same analysis was performed on many different training sets – assuming the model is correctly formulated – one would expect to find the coefficients within the indicated interval 95% of the time (technically, this is the confidence in the method used to obtain the estimate of the coefficient, not in the estimate of the coefficient itself). If the interval contains zero, then there is no significant effect from the associated parameter and the coefficient and even its sign cannot be reliably interpreted. The weighted coefficients are the coefficients multiplied by the standard deviation of the associated parameter (within the training set). These can be used to compare the magnitude of disparate parameters' effects.⁴⁰

Table S8. Summary of statistics of regressions with DHA data

Parameter(s) Regressed with ΔG_{PCET}	R ²	MSE ^a	LOO ^b R ²	LOO ^b MSE ^a	5-Fold CV ^c MSE ^a	p-value ^d
ΔG_{PCET} only	0.70	1.18	0.60	1.57	1.49	< 0.001 ^f
%BV Steric Metrics	0.77	0.88	0.64	1.39	1.46	0.15
Oxo Spin Density	0.70	1.18	0.55	1.77	1.73	0.78
Spin Excitation	0.71	1.14	0.50	1.95	1.97	0.49
$ \eta $	0.73	1.06	0.53	1.82	1.76	0.22
$\Delta G_{\text{PT}}, \Delta G_{\text{ET}}$	0.86	0.57	0.71	1.14	1.34	0.0082 0.023 ^g 0.0038 ^h
ΔG_{PCET}^2	0.71	1.11	0.59	1.59	1.51	0.36
ΔE_{PCET} only ^e	0.62	1.47	0.52	1.89	1.90	< 0.001 ⁱ
$\Delta E_{\text{PCET}}, \Delta E_{\text{PT}}, \Delta E_{\text{ET}}$ ^e	0.86	0.53	0.75	0.96	1.16	0.0013 ^j

^aMean Squared Error, kcal² mol⁻². ^bLeave-One-Out. ^cCross Validation. ^dFrom an F-test where the null hypothesis is that only ΔG_{PCET} has an effect. ^e ΔG_{PCET} not included in the regression. ^fFrom an F-test where the null hypothesis is that ΔG_{PCET} has no effect. ^gFrom an F-test where the null hypothesis is that ΔG_{PT} has no effect. ^hFrom an F-test where the null hypothesis is that ΔG_{ET} has no effect. ⁱFrom an F-test where the null hypothesis is that ΔE_{PCET} has no effect. ^jFrom an F-test where the null hypothesis is that only ΔE_{PCET} has an effect.



Regression S1. DHA barriers against ΔG_{PCET} only.

['DHA ΔG_{PCET} '] Metrics:

Score on Training Data:	0.6967248832007887
MSE of Training Data:	1.1837466708175275
Score of LOO Cross Validation:	0.5971855224924804
MSE of LOO Cross Validation:	1.5722697652848394
MSE of 5-Fold Cross Validation:	1.49405736960365(0.04323619491372769)
F-Test p-value of final 1 variables:	3.078601862627206e-05

Correlation Matrix of x-values:

	DHA ΔG_{PCET}
DHA ΔG_{PCET}	1.0

['DHA ΔG_{PCET} '] Training Average:
[-7.77619718]

['DHA ΔG_{PCET} '] Training Deviation:
[4.05326542]

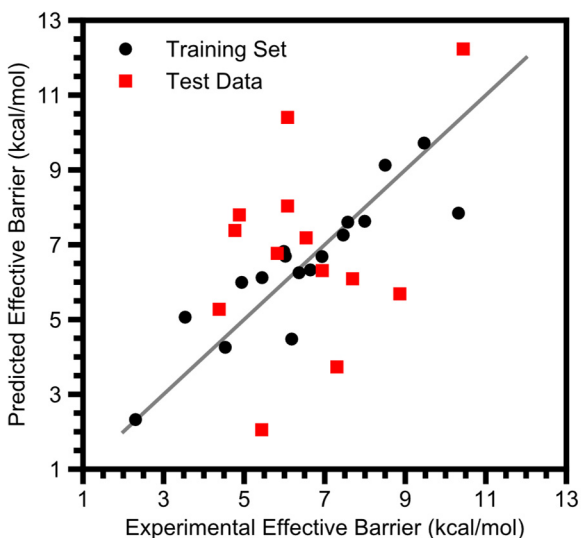
['DHA ΔG_{PCET} '] Coefficients:
[0.40685215]

['DHA ΔG_{PCET} '] Standard Error:
[0.06930726]

['DHA ΔG_{PCET} '] t-Test "Error":
[0.14772492]

['DHA ΔG_{PCET} '] Weighted Coefficients:
[1.64907974]

['DHA ΔG_{PCET} '] Intercept:
9.645819215174036



Regression S2. DHA barriers against ΔG_{PCET} and percent buried volume sterics.

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Metrics:

```
Score on Training Data:          0.7746125436672053
MSE of Training Data:           0.8797347236852846
Score of LOO Cross Validation:   0.644354460933599
MSE of LOO Cross Validation:    1.3881594616273243
MSE of 5-Fold Cross Validation: 1.46372512865656(0.059310929316259454)
F-Test p-value of final 2 variables: 0.14524602753892502
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	%BV Tot	%BV Dev
DHA ΔG_{PCET}	1.000000	-0.107404	0.230500
%BV Tot	-0.107404	1.000000	0.134191
%BV Dev	0.230500	0.134191	1.000000

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Training Average:
[-7.77619718 64.39411765 5.35367331]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Training Deviation:
[4.05326542 10.53891783 4.76681449]

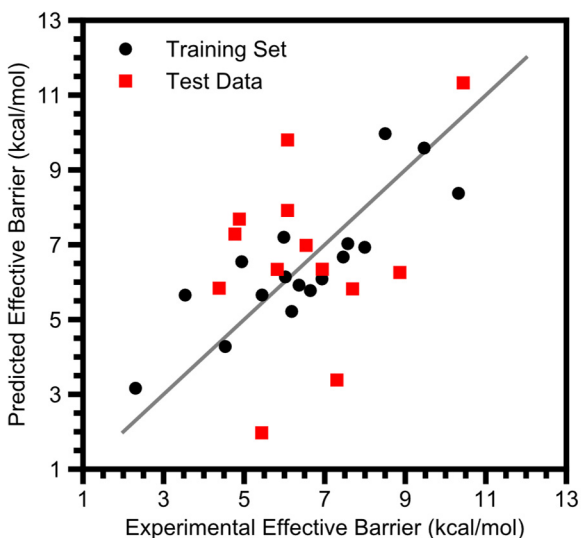
['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Coefficients:
[0.444406794 0.01827786 -0.11845869]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Standard Error:
[0.06664533 0.02516922 0.05685555]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] t-Test "Error":
[0.14397848 0.0543748 0.12282896]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Weighted Coefficients:
[1.79992522 0.19262889 -0.5646706]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Intercept:
9.392418865022623



Regression S3. DHA barriers against ΔG_{PCET} and the IBO spin density on the oxo ligand.

['DHA ΔG_{PCET} ', 'IBO Spin O'] Metrics:

```
Score on Training Data:          0.698551220951851
MSE of Training Data:           1.176618089826692
Score of LOO Cross Validation:   0.546795585374296
MSE of LOO Cross Validation:    1.7689523053359144
MSE of 5-Fold Cross Validation: 1.7301047476523321 (0.03545602037697516)
F-Test p-value of final 1 variables: 0.775139773791961
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	IBO Spin O
DHA ΔG_{PCET}	1.000000	-0.346171
IBO Spin O	-0.346171	1.000000

['DHA ΔG_{PCET} ', 'IBO Spin O'] Training Average:
[-7.77619718 0.55994471]

['DHA ΔG_{PCET} ', 'IBO Spin O'] Training Deviation:
[4.05326542 0.29315117]

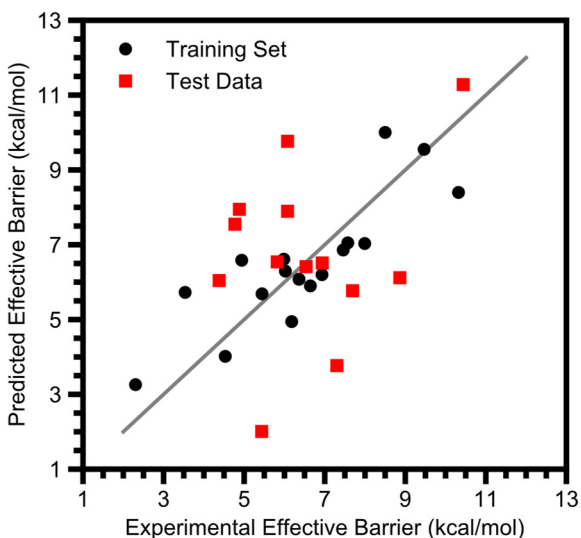
['DHA ΔG_{PCET} ', 'IBO Spin O'] Coefficients:
[0.39916608 -0.30699241]

['DHA ΔG_{PCET} ', 'IBO Spin O'] Standard Error:
[0.07623711 1.05409519]

['DHA ΔG_{PCET} ', 'IBO Spin O'] t-Test "Error":
[0.16351234 2.26080932]

['DHA ΔG_{PCET} ', 'IBO Spin O'] Weighted Coefficients:
[1.61792606 -0.08999518]

['DHA ΔG_{PCET} ', 'IBO Spin O'] Intercept:
9.757949587592675



Regression S4. DHA barriers against ΔG_{PCET} and the Spin Excitation Energy.

['DHA ΔG_{PCET} ', 'Spin Excitation'] Metrics:

```
Score on Training Data:          0.7072135314484478
MSE of Training Data:           1.1428072670986176
Score of LOO Cross Validation:   0.5009984749798582
MSE of LOO Cross Validation:    1.9477080751288274
MSE of 5-Fold Cross Validation:  1.970364948730487(0.0559990030724594)
F-Test p-value of final 1 variables: 0.49045257892652216
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	Spin Excitation
DHA ΔG_{PCET}	1.00000	-0.20409
Spin Excitation	-0.20409	1.00000

['DHA ΔG_{PCET} ', 'Spin Excitation'] Training Average:
[-7.77619718 14.58587927]

['DHA ΔG_{PCET} ', 'Spin Excitation'] Training Deviation:
[4.05326542 19.10348113]

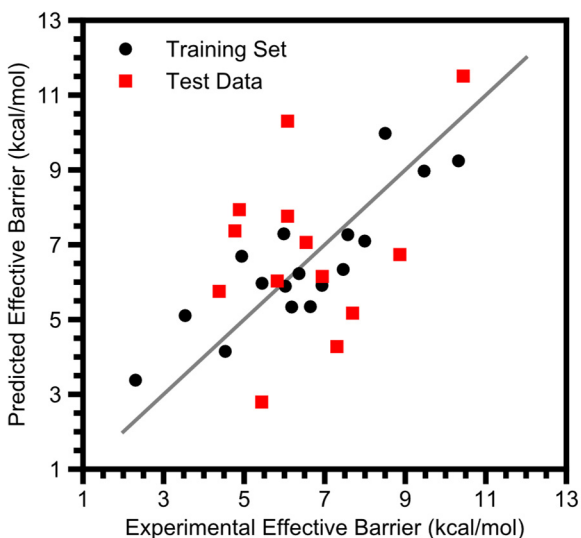
['DHA ΔG_{PCET} ', 'Spin Excitation'] Coefficients:
[0.39644513 -0.01081924]

['DHA ΔG_{PCET} ', 'Spin Excitation'] Standard Error:
[0.0720039 0.01527737]

['DHA ΔG_{PCET} ', 'Spin Excitation'] t-Test "Error":
[0.154433 0.03276669]

['DHA ΔG_{PCET} ', 'Spin Excitation'] Weighted Coefficients:
[1.60689734 -0.20668517]

['DHA ΔG_{PCET} ', 'Spin Excitation'] Intercept:
9.722700343793177



Regression S5. DHA barriers against ΔG_{PCET} and the magnitude of the asynchronicity.

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Metrics:

```
Score on Training Data:          0.7281325727412633
MSE of Training Data:           1.0611558419885931
Score of LOO Cross Validation:   0.5349640252644873
MSE of LOO Cross Validation:    1.815133376959526
MSE of 5-Fold Cross Validation: 1.7554887437479856(0.08293293544608828)
F-Test p-value of final 1 variables: 0.2241810808486162
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	DHA $ \eta $ (G)
DHA ΔG_{PCET}	1.000000	0.184231
DHA $ \eta $ (G)	0.184231	1.000000

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Training Average:
[-7.77619718 17.96727543]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Training Deviation:
[4.05326542 12.92730813]

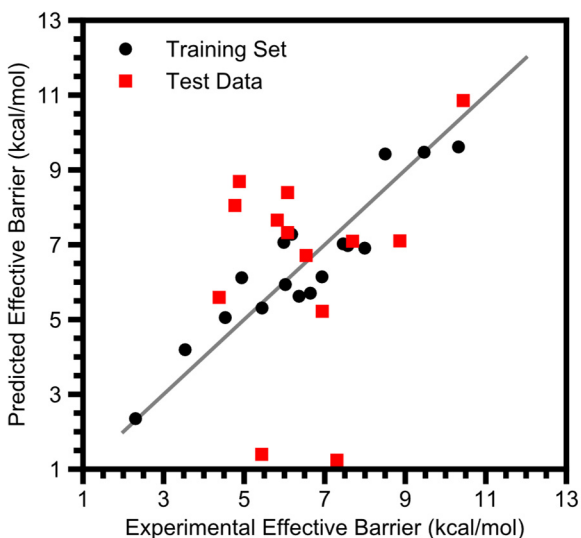
['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Coefficients:
[0.39066077 0.02755618]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Standard Error:
[0.06910646 0.02166784]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] t-Test "Error":
[0.14821863 0.04647289]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Weighted Coefficients:
[1.58345179 0.35622725]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Intercept:
9.024802368188036



Regression S6. DHA barriers against ΔG_{PCET} , ΔG_{PT} , and ΔG_{ET} .

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Metrics:

```
Score on Training Data:          0.8550607749306552
MSE of Training Data:          0.5657283293053714
Score of LOO Cross Validation:  0.708584021837019
MSE of LOO Cross Validation:    1.137457954395417
MSE of 5-Fold Cross Validation: 1.3430227389100244 (0.09649120302575805)
F-Test p-value of final 2 variables: 0.008237008538600432
F-Test p-value of 2nd to last variable (DHA  $\Delta G_{PT}$ ): 0.023223177281245677
F-Test p-value of final variable (DHA  $\Delta G_{ET}$ ): 0.00377509573731305
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	DHA ΔG_{PT}	DHA ΔG_{ET}
DHA ΔG_{PCET}	1.000000	-0.116636	0.300610
DHA ΔG_{PT}	-0.116636	1.000000	-0.886456
DHA ΔG_{ET}	0.300610	-0.886456	1.000000

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Training Average:
[-7.77619718 47.94811989 48.18969167]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Training Deviation:
[4.05326542 17.72475347 14.50071323]

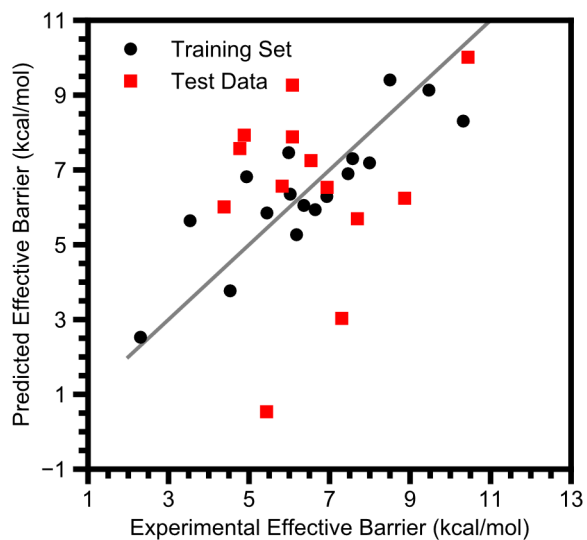
['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Coefficients:
[0.3120842 0.06952437 0.12109262]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Standard Error:
[0.05736941 0.02703542 0.03441251]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] t-Test "Error":
[0.12393907 0.05840647 0.07434371]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Weighted Coefficients:
[1.26496011 1.23230225 1.75592936]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Intercept:
-0.2600936876032849



Regression S7. DHA barriers against ΔG_{PCET} and ΔG_{PCET}^2 .

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Metrics:

```
Score on Training Data:          0.7149873903247832
MSE of Training Data:          1.112464258211542
Score of LOO Cross Validation:   0.5915803011130514
MSE of LOO Cross Validation:   1.5941481251619116
MSE of 5-Fold Cross Validation: 1.5101598742890083(0.056935040823286265)
F-Test p-value of final 1 variables: 0.3596321487917926
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	DHA ΔG_{PCET}^2
DHA ΔG_{PCET}	1.000000	-0.929028
DHA ΔG_{PCET}^2	-0.929028	1.000000

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Training Average:
[-7.77619718 76.89820308]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Training Deviation:
[4.05326542 62.99805804]

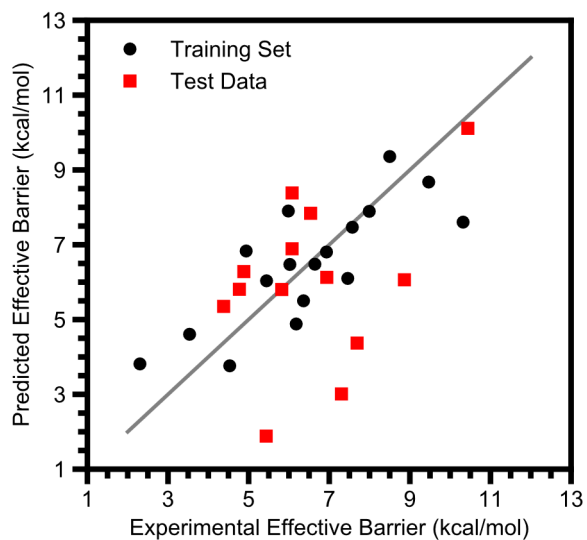
['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Coefficients:
[0.24146465 -0.01145385]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Standard Error:
[0.18795835 0.01209315]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] t-Test "Error":
[0.40313056 0.02593723]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Weighted Coefficients:
[0.97872033 -0.72157062]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Intercept:
9.240514307521131



Regression S8. DHA barriers against ΔE_{PCET} .

['DHA ΔE_{PCET} '] Metrics:

Score on Training Data:	0.6246046731001371
MSE of Training Data:	1.4652470441627932
Score of LOO Cross Validation:	0.5157469389983269
MSE of LOO Cross Validation:	1.8901417130553664
MSE of 5-Fold Cross Validation:	1.9017782503654304 (0.04647736834316938)
F-Test p-value of final 1 variables:	0.00015966818653256887

Correlation Matrix of x-values:

	DHA ΔE_{PCET}
DHA ΔE_{PCET}	1.0

['DHA ΔE_{PCET} '] Training Average:
[-2.08594867]

['DHA ΔE_{PCET} '] Training Deviation:
[3.99325888]

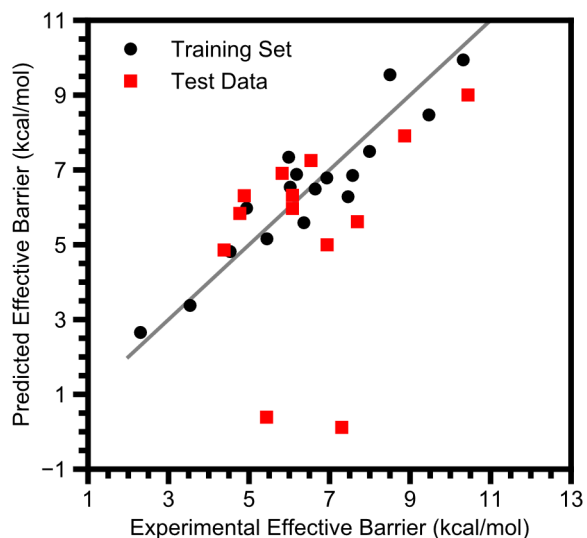
['DHA ΔE_{PCET} '] Coefficients:
[0.39100845]

['DHA ΔE_{PCET} '] Standard Error:
[0.07826766]

['DHA ΔE_{PCET} '] t-Test "Error":
[0.16682356]

['DHA ΔE_{PCET} '] Weighted Coefficients:
[1.56139797]

['DHA ΔE_{PCET} '] Intercept:
7.297680247312937



Regression S9. DHA barriers against ΔE_{PCET} , ΔE_{PT} , and ΔE_{ET} .

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Metrics:

```
Score on Training Data:           0.8642292420790744
MSE of Training Data:            0.5299418705349127
Score of LOO Cross Validation:    0.7546196643252872
MSE of LOO Cross Validation:    0.9577711435895295
MSE of 5-Fold Cross Validation:  1.162034462523503(0.0776391752517394)
F-Test p-value of final 2 variables: 0.0013460555172805089
```

Correlation Matrix of x-values:

	DHA ΔE_{PCET}	DHA ΔE_{PT}	DHA ΔE_{ET}
DHA ΔE_{PCET}	1.000000	0.093539	0.119751
DHA ΔE_{PT}	0.093539	1.000000	-0.868929
DHA ΔE_{ET}	0.119751	-0.868929	1.000000

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Training Average:
[-2.08594867 50.96221826 55.73635424]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Training Deviation:
[3.99325888 18.62129223 14.02559969]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Coefficients:
[0.32595791 0.04033659 0.11282918]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Standard Error:
[0.05562276 0.02392676 0.03185668]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] t-Test "Error":
[0.12016567 0.05169063 0.06882218]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Weighted Coefficients:
[1.30163433 0.75111934 1.58249696]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Intercept:
-1.1823410363409037

Table S9. Barrier heights predicted by the $\{\Delta G_{\text{PCET}}, \Delta G_{\text{PT}}, \Delta G_{\text{ET}}\}$ model and the contribution of each thermodynamic parameter

Oxo	Reference	$0.31 \times$ ΔG_{PCET} (kcal/mol)	$0.070 \times$ ΔG_{PT} (kcal/mol)	$0.12 \times$ ΔG_{ET} (kcal/mol)	Predicted Barrier ^a (kcal/mol)	Exp ^b Barrier (kcal/mol)
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	1	-5.0	4.0	3.6	2.4	2.3
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	2	-2.9	4.0	4.8	5.6	4.4
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	3	-2.3	3.8	5.7	7.0	7.5
[Fe ^V (O)(TAML)] ⁻	4	-3.1	2.7	4.9	4.2	3.5
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺	6	-2.0	4.7	4.5	6.9	8.0
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	6	-2.9	3.3	5.6	5.7	6.6
[Fe ^{IV} (O)(TMC)(OCOCF ₃)] ⁺	6	-2.7	3.9	5.2	6.1	6.9
[Fe ^{IV} (O)(TMCS)] ⁺	6	-2.7	2.8	6.0	5.9	6.0
[Mn ^{IV} (O)(H ₃ buea)] ⁻	9	0.2	1.9	7.5	9.4	8.5
[Fe ^{IV} (O)(TMP)]	11	-3.4	2.7	8.2	7.3	6.2
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	12	-2.7	1.1	9.0	7.1	8.9
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺	14	-1.4	5.3	5.0	8.7	4.9
[Fe ^{IV} (O)(tpfpp)]	15	-2.5	3.5	6.9	7.7	5.8
[Mn ^{VII} (O) ₄] ⁻	16	-0.14	3.9	6.0	9.5	9.5
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	18	-4.3	2.4	7.2	5.1	4.5
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	18	-2.9	1.4	7.4	5.6	6.4
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	19	-3.1	3.7	6.7	7.1	7.7
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	21	1.2	5.8	4.1	10.9	10.4
[Fe ^{IV} (O)(N4Py)] ²⁺	23	-1.8	4.5	4.6	7.1	6.0
[Fe ^{IV} (O)(BnTPEN)] ²⁺	23	-2.3	4.5	4.2	6.1	4.9
[Fe ^{IV} (O)(^{Me} c ² TACN-Py ₂)] ²⁺	23	-2.0	4.4	4.5	6.7	6.5
[Fe ^{IV} (O)(BP1)] ²⁺	23	-1.9	4.9	4.3	7.0	7.6
[Fe ^{IV} (O)(BP2)] ²⁺	23	-3.0	4.7	3.8	5.3	5.4
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	25	-1.7	4.8	5.3	8.0	4.8
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	26	-1.0	0.5	10.4	9.6	10.3
[Mn ^{IV} (O)(N4Py)] ²⁺	27	-2.5	3.6	4.4	5.2	6.9
[Co ^{IV} (O)(13-TMC)] ²⁺	28	-4.7	4.8	1.4	1.2	7.3
[Fe ^{IV} (O)(13-TMC)] ²⁺	29	-5.9	5.4	2.1	1.4	5.4
[Ru ^{VI} (O) ₂ (L)] ²⁺	30	0.03	6.0	2.6	8.4	6.1
[Ru ^{VI} (O) ₂ (F ₂₈ tpp)]	32	-1.4	4.5	4.5	7.3	6.1

^a $0.31\Delta G_{\text{PCET}} + 0.070\Delta G_{\text{PT}} + 0.12\Delta G_{\text{ET}} - 0.26$. ^bExperimental.

Entropy Adjustment to Reaction Barriers

As discussed in the main text, we subtracted from the experimental reaction barrier the loss of translational entropy upon metal oxo and substrate association. This correction is derived from the expression of the translational entropy of a chemical species of mass m and concentration C :⁴¹

$$TS_t = RT \ln \left(\left(\frac{2\pi m RT}{h^2} \right)^{\frac{3}{2}} C^{-1} \right) + \frac{5}{2} RT \quad (\text{S1})$$

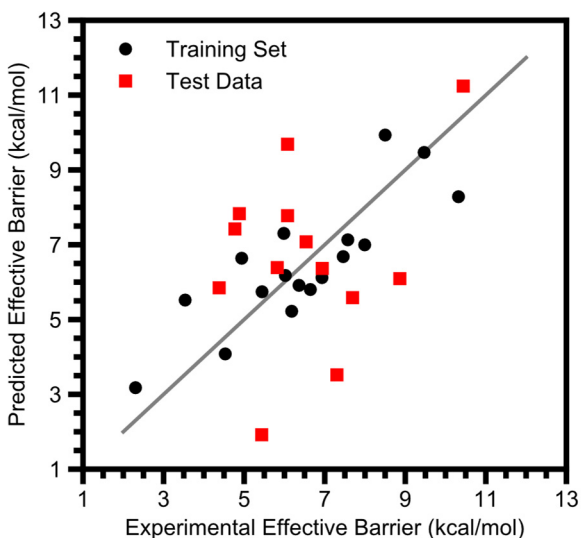
where RT is the thermal energy in kcal/mol and h is Plank's constant. With all species in the standard state of $C^\circ = 1 M$, the standard change in translational entropy upon association is:

$$\begin{aligned} (T\Delta S_t^\circ)_{assoc} = TS_{t,MO+CH} - (TS_{t,MO} - TS_{t,CH}) = RT \ln \left(\left(\frac{2\pi(m_{MO}+m_{CH})RT}{h^2} \right)^{\frac{3}{2}} C^{\circ-1} \right) + \frac{5}{2} RT - \\ \left(RT \ln \left(\left(\frac{2\pi m_{MO} RT}{h^2} \right)^{\frac{3}{2}} C^{\circ-1} \right) + \frac{5}{2} RT + RT \ln \left(\left(\frac{2\pi m_{CH} RT}{h^2} \right)^{\frac{3}{2}} C^{\circ-1} \right) + \frac{5}{2} RT \right) \quad (\text{S2}) \end{aligned}$$

in which the metal oxo is denoted as MO, the substrate as CH, and the associated complex as MO+CH. Simplifying this by combining the log terms via the identity $\ln a - \ln b - \ln c = -\ln \frac{bc}{a}$, canceling two of the $\frac{5}{2} RT$ terms, and factoring out RT gives:

$$(T\Delta S_t)_{assoc} = -RT \left[\ln \left(\left(\frac{2\pi \left(\frac{m_{Oxo} m_{Sub}}{m_{Oxo} + m_{Sub}} \right) RT}{h^2} \right)^{\frac{3}{2}} C^{\circ-1} \right) + \frac{5}{2} \right] \quad (\text{S3})$$

Combining the masses into $\mu = \frac{m_{Oxo} m_{Sub}}{m_{Oxo} + m_{Sub}}$ finishes the derivation of this expression as it appears in Equation 1 in the main text. We find this correction adequately accounts for the temperature dependence of the barriers; in Regression S10 we show that RT does not improve a fit to ΔG_{PCET} alone the fit. Inclusion of RT has a p -value of 0.97, barely affects the R^2 and MSE of the fit, and substantially worsens cross validation metrics.



Regression S10. DHA barriers against ΔG_{PCET} and RT .

['DHA ΔG_{PCET} ', 'kT'] Metrics:

```
Score on Training Data:          0.6967643666901857
MSE of Training Data:           1.1835925584405569
Score of LOO Cross Validation:   0.5227899514128529
MSE of LOO Cross Validation:    1.8626513518737027
MSE of 5-Fold Cross Validation: 1.868642947451995 (0.09296746191926707)
F-Test p-value of final 1 variables: 0.9665472615379543
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	kT
DHA ΔG_{PCET}	1.000000	0.575834
kT	0.575834	1.000000

['DHA ΔG_{PCET} ', 'kT'] Training Average:
[-7.77619718 0.55186587]

['DHA ΔG_{PCET} ', 'kT'] Training Deviation:
[4.05326542 0.04426339]

['DHA ΔG_{PCET} ', 'kT'] Coefficients:
[0.40469496 0.34304495]

['DHA ΔG_{PCET} ', 'kT'] Standard Error:
[0.08774231 8.03469455]

['DHA ΔG_{PCET} ', 'kT'] t-Test "Error":
[0.18818853 17.23270591]

['DHA ΔG_{PCET} ', 'kT'] Weighted Coefficients:
[1.64033608 0.01518433]

['DHA ΔG_{PCET} ', 'kT'] Intercept:
9.439729679880315

Effect of Solvent – Oxo Hydrogen Bonding on Regressions

Hydrogen bonding between protic solvents and the oxo ligand of metal oxo complexes likely results in raising the apparent barrier of PCET reactions,^{42,43} but we were unable to derive a reliable adjustment for this effect. Direct calculation of the equilibria between metal oxo complexes and solvent molecules was not feasible: DFT calculations of weak intermolecular interactions are unreliable,⁴⁴⁻⁴⁶ and even if largely electrostatic hydrogen bonds are an exception it would be difficult to determine the free energy of unbound solvent molecules in the variety of solvent mixtures which protic solvents appear in. We were, however, able to make a crude attempt at quantifying hydrogen bonding to demonstrate that our neglect of this effect does not affect our overall conclusions. Snelgrove et al.⁴² have shown that for hydrogen atom transfer reactions of O–H and N–H bonds the effect of hydrogen bonding to the solvent can be accounted for by means of Abraham’s hydrogen bonding parameters:^{33,47}

$$\log k^S = \log k^\circ + 8.3 \alpha \cdot \beta$$

where k^S is the rate in the presence of solvent hydrogen bonding, k° is the rate in the absence of solvent hydrogen bonding, α is Abraham’s hydrogen bond acidity of the substrate O–H or N–H bond, β is Abraham’s hydrogen bond basicity of the solvent, and all logarithms are base 10. This is very similar to a formula from Abraham for the equilibrium constant K of the formation of a hydrogen bond dimer between a donor with hydrogen bond acidity α and an acceptor with hydrogen bond basicity β (again with a common logarithm):⁴⁷

$$\log K = 7.354 \alpha \cdot \beta - 1.094$$

The similarity indicates that Snelgrove et al.’s expression is fundamentally related to the free energy of forming a hydrogen bonded dimer, and that it may be a good approximation for a more general situation than an O–H or N–H substrate donating a hydrogen bond to the solvent. However, the ability of protic solvents to form hydrogen bonds with each other renders it unclear if a simple application of the energy of dimer formation will apply as well to the case of hydrogen bonding to a protic solvent. It is further unclear how this formula’s applicability is affected by temperature changes, use of solvent mixtures, or the presence of electrolytes. The biggest hindrance to applying this formula, however, is that the Abraham hydrogen bond basicities of metal oxo complexes are not known. For all these reasons we are not confident that the use of this formula to adjust k_2 values for solvent hydrogen bonding will result in more accurate reaction barriers than neglect of this effect entirely. Nonetheless, we apply this formula as best we can to demonstrate that our results hold as well with or without an adjustment for hydrogen bonding.

We utilized the known β values of various carbon, nitrogen, phosphorus, and sulfur oxides to correlate the value of β with the DFT electronic energy of forming a dimer with water (calculated with the same level of theory as described in the main text, with the def2-TZVP basis on all atoms).^{47,48} The resulting correlation is shown in Figure S3 and the numerical data is given in Table S10. While the correlation is not spectacular ($r^2 = 0.61$), it allows us to come up with a reasonable estimate of β for each metal oxo complex with reported kinetics in a protic solvent via DFT calculations of the corresponding dimer between the metal oxo complex and water (calculated with the same level of theory as described in the main text, with the def2-TZVP basis on the water molecule).

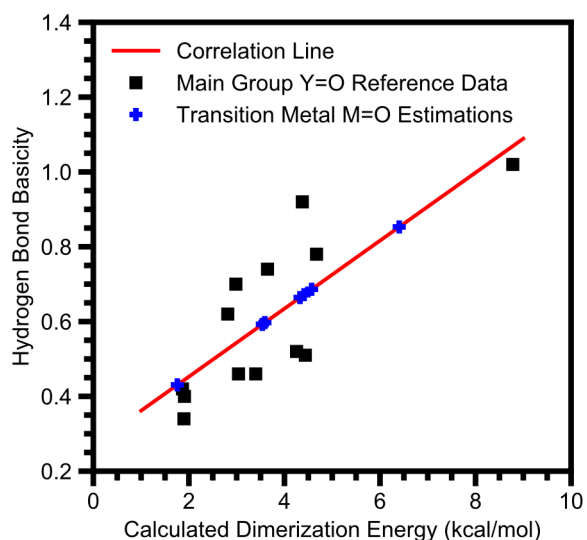


Figure S3. Correlation of main group oxides' hydrogen bond basicities and their calculated electronic energies of dimerization with water and the placement of relevant metal oxo complexes on the correlation line. The correlation coefficient r^2 is 0.61, and the regression equation is $y = 0.0909x + 0.2709$.

Table S10. Reference data used to construct the correlation between hydrogen bond basicity and electronic energy of dimerization and the resulting estimates of the hydrogen bond basicities of metal oxo complexes

Main Group Y=O or Transition Metal M=O	Calculated Electronic Energy of Dimerization with Water (kcal/mol)	Hydrogen Bond Basicity (Abraham Scale)
Acetone	1.91	0.40 ^a
Methyl Isopropyl Ketone	3.40	0.46 ^a
Benzophenone	3.04	0.46 ^a
Benzaldehyde	1.86	0.42 ^a
Acetophenone	4.44	0.51 ^a
Nitrobenzene	1.90	0.34 ^a
N,N-Dimethyl- ⁱ Butylamide	2.98	0.70 ^a
Triethyl Phosphine	8.78	1.02 ^a
Dimethyl Sulfoxide	4.67	0.78 ^a
N,N-Dimethyl-Methanesulfinamide	4.25	0.52 ^a
N,N-Dimethyl-Methanesulfonamide	3.65	0.74 ^a
Triphenyl Phosphite	2.81	0.62 ^a
Triphenyl Phosphine	4.37	0.92 ^a
[Fe ^{IV} (O)(TMC, MeCN)] ²⁺	1.76	0.43 ^d
[Fe ^{IV} (O)(TMC, N ₃)] ⁺	3.54 ^b	0.59 ^d
[Fe ^{IV} (O)(TMCS)] ⁺	4.33	0.66 ^d
[Mn ^V (O)(tf ₄ tmap, O)] ³⁺	4.57	0.69 ^d
[Mn ^{IV} (O)(tf ₄ tmap, OH)] ³⁺	6.40	0.85 ^d
[Mn ^{IV} (O)(Me ₂ EBC, O)]	4.41 ^c	0.67 ^d
[Mn ^{IV} (O)(N4Py)] ²⁺	3.59	0.60 ^d

^aReference 47. ^bThe conditions used in our analysis do not include a protic solvent, but an additional k_2 value is reported which was measured in a protic solvent mixture. ^cThis complex formed two hydrogen bonds upon dimerization, one for each of its oxo ligands and the water molecule's O-H bonds; the value given here is accordingly half the dimerization energy. ^dEstimated from the electronic dimerization energy.

With these estimates of hydrogen bond basicities in hand we were able to apply the formula of Snelgrove et al.⁴² to correct reaction barriers for solvent hydrogen bonding, giving as the overall formula for the reaction barrier:

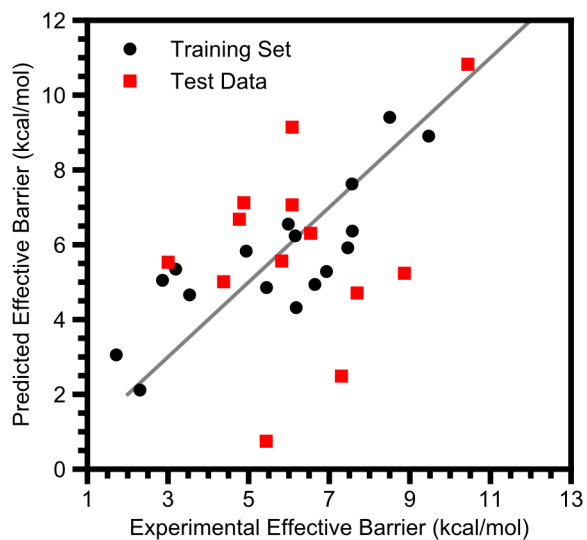
$$\Delta G_{PCET}^{\ddagger} = RT \ln \left(\frac{k_2 h}{n_{CH} n_O RT} \right) + (T\Delta S_t)_{assoc} - (1.4 \cdot 8.3) \alpha \cdot \beta \quad (S4)$$

where α is the hydrogen bond acidity of the solvent (0 for aprotic solvents), β is this derived hydrogen bond basicity of the metal oxo complex, and 1.4 is the conversion from common logarithm units to kcal/mol at room temperature (we assume there is no temperature dependence of the hydrogen bonding correction). This amounts to a reduction of ~2–3 kcal/mol in the reaction barrier for metal oxo complexes with $\alpha \neq 0$. Using these barriers we repeated the regressions summarized in Table S8, summarizing the new results in Table S11 with a detailed summary of each regression following. These regressions should be viewed as examining how our results are affected by an adjustment for hydrogen bonding, not as tests of distinct hypotheses. While the overall fits are slightly worse, our main result – that only ΔG_{PT} and ΔG_{ET} offer a significant improvement to the ΔG_{PCET} only fit – is unchanged upon this hydrogen bonding adjustment of the reaction barriers. The only notable differences are: (a) cross validation no longer gives evidence for a small, statistically insignificant steric effect, (b) that the Ru^{VI} oxo is not predicted as accurately,²¹ although its prediction is still off by less than 2 kcal/mol, and (c) that the Co^{III} oxo is now an outlier,¹² but not grossly so. Our finding that the same free energies explain the kinetics of the broader set of metal oxo complexes and this Co^{III} oxo complex remains valid.

Table S11. Summary of statistics of regressions with hydrogen bonding corrected DHA data

Parameter(s) Regressed with ΔG_{PCET}	R ²	MSE ^a	LOO ^b R ²	LOO ^b MSE ^a	5-Fold CV ^c MSE ^a	p-value ^d
ΔG_{PCET} only	0.66	1.65	0.59	2.00	2.02	< 0.001 ^f
%BV Steric Metrics	0.68	1.56	0.36	3.11	3.10	0.68
Oxo Spin Density	0.69	1.51	0.59	1.96	1.98	0.27
Spin Excitation	0.66	1.63	0.39	2.93	3.00	0.70
$ \eta $	0.67	1.60	0.55	2.18	2.15	0.53
$\Delta G_{PT}, \Delta G_{ET}$	0.80	0.94	0.71	1.40	1.54	0.027 0.0092 ^g 0.028 ^h
ΔG_{PCET}^2	0.66	1.63	0.53	2.25	2.23	0.69
ΔE_{PCET} only ^e	0.65	1.71	0.57	2.10	2.08	< 0.001 ⁱ
$\Delta E_{PCET}, \Delta E_{PT}, \Delta E_{ET}$ ^e	0.74	1.26	0.59	1.98	2.09	0.13 ^j

^aMean Squared Error, kcal² mol⁻². ^bLeave-One-Out. ^cCross Validation. ^dFrom an F-test where the null hypothesis is that only ΔG_{PCET} has an effect. ^e ΔG_{PCET} not included in the regression. ^fFrom an F-test where the null hypothesis is that ΔG_{PCET} has no effect. ^gFrom an F-test where the null hypothesis is that ΔG_{PT} has no effect. ^hFrom an F-test where the null hypothesis is that ΔG_{ET} has no effect. ⁱFrom an F-test where the null hypothesis is that ΔE_{PCET} has no effect. ^jFrom an F-test where the null hypothesis is that only ΔE_{PCET} has an effect.



Regression S11. H-Bond corrected DHA barriers against ΔG_{PCET} .

['DHA ΔG_{PCET} '] Metrics:

Score on Training Data:	0.6583716699943287
MSE of Training Data:	1.6502710857317893
Score of LOO Cross Validation:	0.5855573288938136
MSE of LOO Cross Validation:	2.0020083135629743
MSE of 5-Fold Cross Validation:	2.0163090946670144 (0.05795110828250081)
F-Test p-value of final 1 variables:	7.702231253337022e-05

Correlation Matrix of x-values:

	DHA ΔG_{PCET}
DHA ΔG_{PCET}	1.0

['DHA ΔG_{PCET} '] Training Average:
[-7.77619718]

['DHA ΔG_{PCET} '] Training Deviation:
[4.05326542]

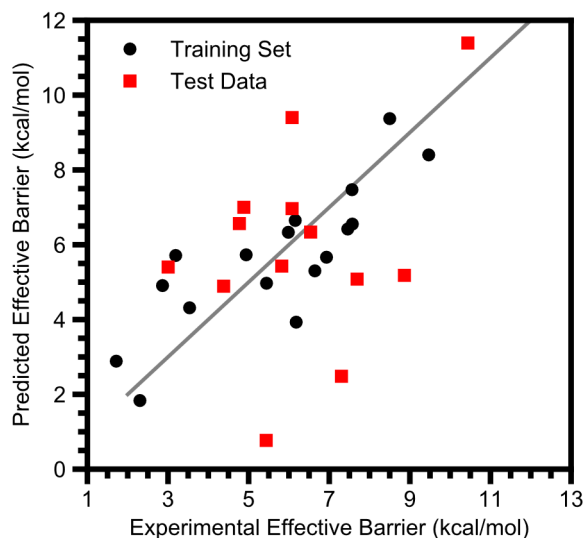
['DHA ΔG_{PCET} '] Coefficients:
[0.43997827]

['DHA ΔG_{PCET} '] Standard Error:
[0.08183272]

['DHA ΔG_{PCET} '] t-Test "Error":
[0.17442231]

['DHA ΔG_{PCET} '] Weighted Coefficients:
[1.78334872]

['DHA ΔG_{PCET} '] Intercept:
9.095284617394316



Regression S12. H-Bond adjusted DHA barriers against ΔG_{PCET} and percent buried volume sterics.

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Metrics:

```
Score on Training Data:          0.6780065083153538
MSE of Training Data:          1.555422962469681
Score of LOO Cross Validation:  0.3568563395708818
MSE of LOO Cross Validation:   3.106772165997647
MSE of 5-Fold Cross Validation: 3.0971664143020705 (0.07200841580974428)
F-Test p-value of final 2 variables: 0.6806218722701031
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	%BV Tot	%BV Dev
DHA ΔG_{PCET}	1.000000	-0.107404	0.230500
%BV Tot	-0.107404	1.000000	0.134191
%BV Dev	0.230500	0.134191	1.000000

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Training Average:
[-7.77619718 64.39411765 5.35367331]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Training Deviation:
[4.05326542 10.53891783 4.76681449]

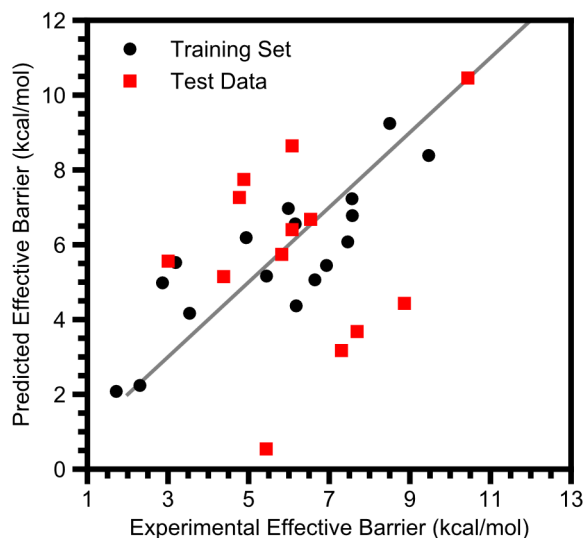
['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Coefficients:
[0.45769236 0.02716673 -0.03736001]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Standard Error:
[0.08861722 0.03346711 0.07559991]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] t-Test "Error":
[0.19144586 0.07230129 0.16332368]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Weighted Coefficients:
[1.85514862 0.28630793 -0.17808825]

['DHA ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Intercept:
7.683668572672475



Regression S13. H-Bond adjusted DHA barriers against ΔG_{PCET} and IBO spin density on the oxo ligand.

['DHA ΔG_{PCET} ', 'IBO Spin O'] Metrics:

```
Score on Training Data:          0.6880892431477332
MSE of Training Data:          1.5067172659640655
Score of LOO Cross Validation:  0.5948329610682959
MSE of LOO Cross Validation:    1.9572014101683484
MSE of 5-Fold Cross Validation: 1.9794617560199796 (0.05727008301927087)
F-Test p-value of final 1 variables: 0.26745197027806
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	IBO Spin O
DHA ΔG_{PCET}	1.000000	-0.346171
IBO Spin O	-0.346171	1.000000

['DHA ΔG_{PCET} ', 'IBO Spin O'] Training Average:
[-7.77619718 0.55994471]

['DHA ΔG_{PCET} ', 'IBO Spin O'] Training Deviation:
[4.05326542 0.29315117]

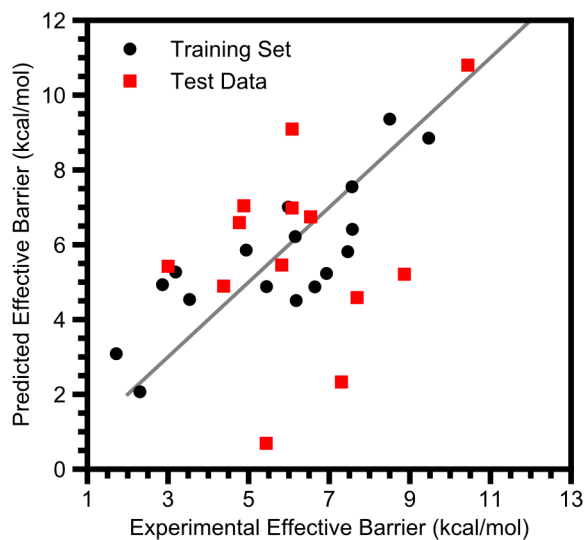
['DHA ΔG_{PCET} ', 'IBO Spin O'] Coefficients:
[0.47446962 1.37763277]

['DHA ΔG_{PCET} ', 'IBO Spin O'] Standard Error:
[0.08627094 1.19282835]

['DHA ΔG_{PCET} ', 'IBO Spin O'] t-Test "Error":
[0.18503277 2.55836236]

['DHA ΔG_{PCET} ', 'IBO Spin O'] Weighted Coefficients:
[1.92315131 0.40385466]

['DHA ΔG_{PCET} ', 'IBO Spin O'] Intercept:
8.592097982909333



Regression S14. H-Bond adjusted DHA barriers correction against ΔG_{PCET} and the spin excitation energy.

['DHA ΔG_{PCET} ', 'Spin Excitation'] Metrics:

```
Score on Training Data:          0.6622103027351723
MSE of Training Data:           1.6317281720897845
Score of LOO Cross Validation:   0.3927294822859495
MSE of LOO Cross Validation:    2.9334832289354793
MSE of 5-Fold Cross Validation:  3.0032229238497066 (0.09884773576992516)
F-Test p-value of final 1 variables: 0.6960080190817327
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	Spin Excitation
DHA ΔG_{PCET}	1.00000	-0.20409
Spin Excitation	-0.20409	1.00000

['DHA ΔG_{PCET} ', 'Spin Excitation'] Training Average:
[-7.77619718 14.58587927]

['DHA ΔG_{PCET} ', 'Spin Excitation'] Training Deviation:
[4.05326542 19.10348113]

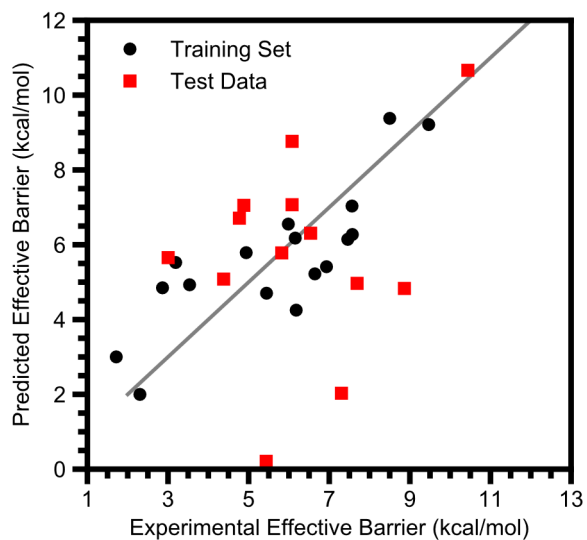
['DHA ΔG_{PCET} ', 'Spin Excitation'] Coefficients:
[0.44698225 0.0072814]

['DHA ΔG_{PCET} ', 'Spin Excitation'] Standard Error:
[0.08603861 0.01825517]

['DHA ΔG_{PCET} ', 'Spin Excitation'] t-Test "Error":
[0.18453447 0.03915345]

['DHA ΔG_{PCET} ', 'Spin Excitation'] Weighted Coefficients:
[1.81173768 0.13910013]

['DHA ΔG_{PCET} ', 'Spin Excitation'] Intercept:
9.043543240499048



Regression S15. H-Bond adjusted DHA barriers against ΔG_{PCET} and the magnitude of the asynchronicity.

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Metrics:

```
Score on Training Data:          0.6680402250602184
MSE of Training Data:          1.6035661275517157
Score of LOO Cross Validation:  0.5492930546538306
MSE of LOO Cross Validation:    2.1771866520289285
MSE of 5-Fold Cross Validation: 2.149580788555342(0.0830651883177897)
F-Test p-value of final 1 variables: 0.5334165382839267
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	DHA $ \eta $ (G)
DHA ΔG_{PCET}	1.000000	0.184231
DHA $ \eta $ (G)	0.184231	1.000000

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Training Average:
[-7.77619718 17.96727543]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Training Deviation:
[4.05326542 12.92730813]

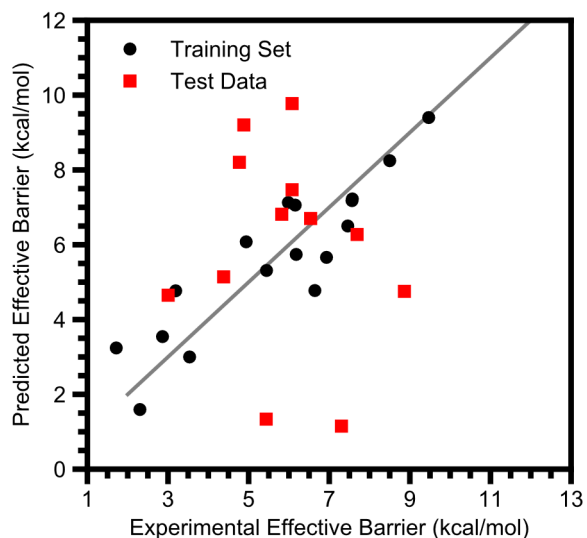
['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Coefficients:
[0.4499722 -0.01700872]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Standard Error:
[0.08495179 0.02663603]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] t-Test "Error":
[0.18220347 0.0571286]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Weighted Coefficients:
[1.82385677 -0.21987692]

['DHA ΔG_{PCET} ', 'DHA $|\eta|$ (G)'] Intercept:
9.478599679619604



Regression S16. H-Bond adjusted DHA barriers against ΔG_{PCET} , ΔG_{PT} , and ΔG_{ET} .

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Metrics:

Score on Training Data: 0.8044848580527584
 MSE of Training Data: 0.9444561742667039
 Score of LOO Cross Validation: 0.7106357878785099
 MSE of LOO Cross Validation: 1.397803842853806
 MSE of 5-Fold Cross Validation: 1.5386337886747041 (0.08094085043482879)
 F-Test p-value of final 2 variables: 0.026581064997124648
 F-Test p-value of 2nd to last variable (DHA ΔG_{PT}): 0.009188466064706025
 F-Test p-value of final variable (DHA ΔG_{ET}): 0.027671643184978723

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	DHA ΔG_{PT}	DHA ΔG_{ET}
DHA ΔG_{PCET}	1.000000	-0.116636	0.300610
DHA ΔG_{PT}	-0.116636	1.000000	-0.886456
DHA ΔG_{ET}	0.300610	-0.886456	1.000000

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Training Average:
 [-7.77619718 47.94811989 48.18969167]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Training Deviation:
 [4.05326542 17.72475347 14.50071323]

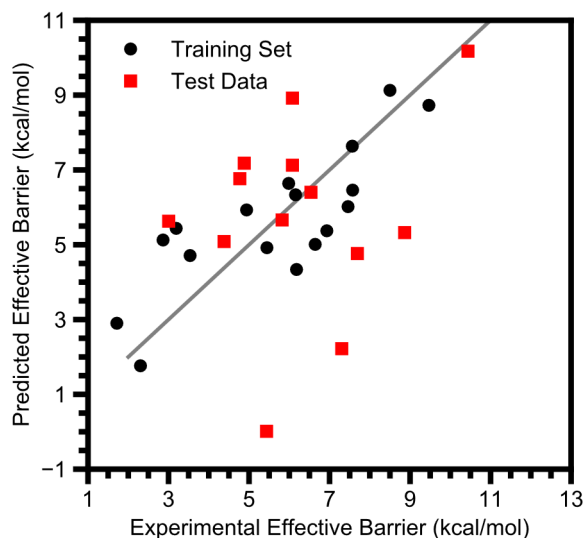
['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Coefficients:
 [0.37589886 0.10676076 0.11021676]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Standard Error:
 [0.07412544 0.03493173 0.04446347]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] t-Test "Error":
 [0.16013829 0.07546541 0.09605748]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Weighted Coefficients:
 [1.52361784 1.89230808 1.59822164]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PT} ', 'DHA ΔG_{ET} '] Intercept:
 -1.8332987921810613



Regression S17. H-Bond adjusted DHA barriers against ΔG_{PCET} and ΔG_{PCET}^2 .

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Metrics:

```
Score on Training Data:          0.6624878412462136
MSE of Training Data:          1.6303874935226972
Score of LOO Cross Validation:   0.5335369455694108
MSE of LOO Cross Validation:   2.2532981713669833
MSE of 5-Fold Cross Validation: 2.232966896805831(0.07882751337208369)
F-Test p-value of final 1 variables: 0.685715324703223
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	DHA ΔG_{PCET}^2
DHA ΔG_{PCET}	1.000000	-0.929028
DHA ΔG_{PCET}^2	-0.929028	1.000000

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Training Average:
[-7.77619718 76.89820308]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Training Deviation:
[4.05326542 62.99805804]

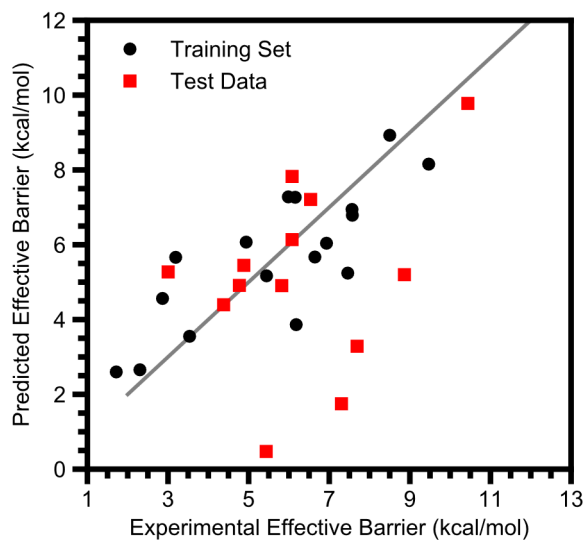
['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Coefficients:
[0.35262908 -0.00604934]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Standard Error:
[0.22754327 0.01464003]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] t-Test "Error":
[0.48803178 0.03139974]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Weighted Coefficients:
[1.42929925 -0.38109659]

['DHA ΔG_{PCET} ', 'DHA ΔG_{PCET}^2 '] Intercept:
8.881223350642781



Regression S18. H-Bond adjusted DHA barriers against ΔE_{PCET} .

['DHA ΔE_{PCET} '] Metrics:

Score on Training Data:	0.6454910010142754
MSE of Training Data:	1.7124924933718166
Score of LOO Cross Validation:	0.565956327438351
MSE of LOO Cross Validation:	2.0966929843360327
MSE of 5-Fold Cross Validation:	2.0816331006068287 (0.05733164762040685)
F-Test p-value of final 1 variables:	0.00010251166252062127

Correlation Matrix of x-values:

	DHA ΔE_{PCET}
DHA ΔE_{PCET}	1.0

['DHA ΔE_{PCET} '] Training Average:
[-2.08594867]

['DHA ΔE_{PCET} '] Training Deviation:
[3.99325888]

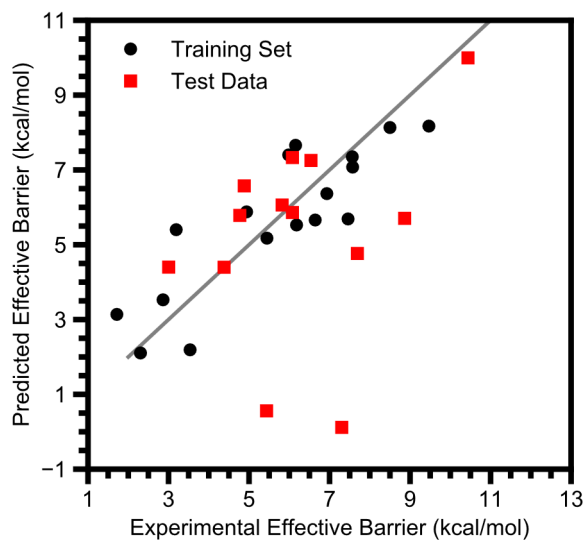
['DHA ΔE_{PCET} '] Coefficients:
[0.44219959]

['DHA ΔE_{PCET} '] Standard Error:
[0.08461381]

['DHA ΔE_{PCET} '] t-Test "Error":
[0.18035006]

['DHA ΔE_{PCET} '] Weighted Coefficients:
[1.76581744]

['DHA ΔE_{PCET} '] Intercept:
6.596332462651391



Regression S19. H-Bond adjusted DHA barriers ΔE_{PCET} , ΔE_{PT} , and ΔE_{ET} .

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Metrics:

```
Score on Training Data:          0.7398301329358178
MSE of Training Data:           1.2567775306795423
Score of LOO Cross Validation:   0.5909484679893019
MSE of LOO Cross Validation:    1.975965856930953
MSE of 5-Fold Cross Validation:  2.089103798214306(0.09558230895231092)
F-Test p-value of final 2 variables: 0.133842257174152
```

Correlation Matrix of x-values:

	DHA ΔE_{PCET}	DHA ΔE_{PT}	DHA ΔE_{ET}
DHA ΔE_{PCET}	1.000000	0.093539	0.119751
DHA ΔE_{PT}	0.093539	1.000000	-0.868929
DHA ΔE_{ET}	0.119751	-0.868929	1.000000

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Training Average:
[-2.08594867 50.96221826 55.73635424]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Training Deviation:
[3.99325888 18.62129223 14.02559969]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Coefficients:
[0.36471025 0.07661204 0.10478331]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Standard Error:
[0.08565794 0.03684674 0.04905865]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] t-Test "Error":
[0.18505273 0.07960254 0.10598478]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Weighted Coefficients:
[1.45638243 1.42661521 1.46964876]

['DHA ΔE_{PCET} ', 'DHA ΔE_{PT} ', 'DHA ΔE_{ET} '] Intercept:
-3.309865589515569

Further Discussion of Steric Parameters

There is little discussion in the literature about quantitative steric metrics for metal oxo mediated PCET, but in other systems such as asymmetric catalysis the nature of steric parameters is important.⁴⁹ Therefore, in addition to the percent buried volume (%BV) metric discussed in the main text we also determined distance and angle metrics (see Figure S4). These metrics ultimately do not fit the data any better than the %BV metrics.

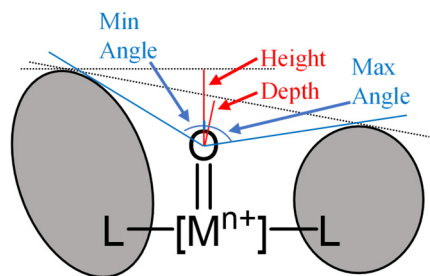


Figure S4. Illustration of distance and angle steric metrics.

Distance metrics were defined as how far from the oxo atom an infinitely wide flat substrate could approach without being encumbered by another atom in the complex. For this determination we used Bondi radii scaled by 1.17 with the Rowland-Taylor radii for hydrogen.^{50,51} The “height” as we defined it is the distance if the substrate is restricted to approaching along the metal-oxygen axis; that is, how much higher than the oxygen atom is there no steric bulk in any direction. The “depth” does not have this directionality restriction; it is the closest a substrate can approach along any direction with no steric encumberment perpendicular to its approach.

Angle metrics were based on cones with a vertex on the oxo atom and an axis along the M–O bond. We recorded the minimum angle of a cone which touches at least one other atom in the complex (using the same radii as with distance metrics) as well as the maximum angle of a cone in which at least one segment of the surface does not go through another atom.

After collecting these parameters, we analyzed the correlations between them to determine which were statistically distinct (Table S12). There were high correlations among many of them, such that it only took two parameters to convey most of the statistical information contained within this set of parameters. We used %BV sterics as the pair within the main text, for which we observed a small, statistically insignificant improvement to the ΔG_{PCET} fit (which disappears in the H-bonding correction discussed above). In Regression S20 we demonstrate that height and max angle perform worse; unlike %BV sterics, these metrics even behave poorly under cross validation. Overall, while we cannot decisively rule out a small correlation with %BV sterics there is no clear and irrefutable evidence for the influence of sterics on the reaction rates. This is surprising and demonstrates that oxo ligands are in general very unencumbered. However, it is chemically unfathomable that sterics have absolutely no influence on the reaction barrier; thus, the question of whether we observe a small effect or no effect is immaterial. Regardless, within our data set sterics are not as important as free energies in explaining and predicting reaction barriers.

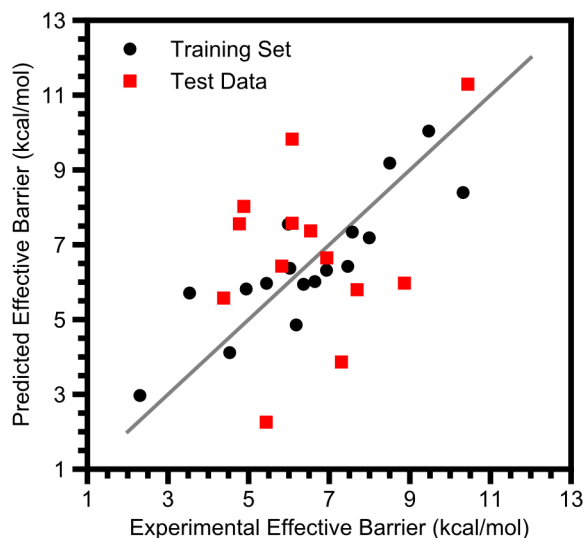
Table S12. Correlations between various steric metrics

	%BV Tot	%BV Dev	Height	Depth	Min Angle	Max Angle
%BV Tot	1	0.14236	0.33877	0.40745	-0.78889	-0.68510
%BV Dev	0.14236	1	0.64977	0.47271	-0.61376	0.01750
Height	0.33877	0.64977	1	0.90480	-0.75467	-0.09366
Depth	0.40745	0.47271	0.90480	1	-0.69931	-0.25180
Min Angle	-0.78889	-0.61376	-0.75467	-0.69931	1	0.41571
Max Angle	-0.68510	0.01750	-0.09366	-0.25180	0.41571	1

Table S13. Steric parameters considered in this study

Oxo	Total %BV	%BV Deviation	Height	Depth	Minimum Angle	Maximum Angle
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	66.3	10.4	3.43	2.57	31.0	81.3
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	68.0	10.5	3.42	2.84	31.1	86.3
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	79.6	3.2	3.40	3.4	29.5	52.1
[Fe ^V (O)(TAML)] ⁻	56.0	7.4	1.80	1.17	49.2	98.7
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺	74.1	2.0	1.70	1.70	44.8	61.0
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	74.1	1.9	1.70	1.70	44.7	61.0
[Fe ^{IV} (O)(TMC)(OCOCF ₃)] ⁺	74.2	1.8	1.73	1.73	44.1	61.4
[Fe ^{IV} (O)(TMCS)] ⁺	74.1	2.3	1.75	1.74	42.5	59.2
[Mn ^{IV} (O)(H ₃ buea)] ⁻	72.3	16.0	4.75	3.99	14.7	50.2
[Fe ^{IV} (O)(TMP)]	58.2	9.8	3.74	3.62	42.3	92.9
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	67.8	8.9	2.75	1.99	40.6	83.1
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺	58.1	5.6	1.49	1.15	52.2	88.5
[Fe ^{IV} (O)(tpfpp)]	52.4	0.15	2.16	2.14	65.3	91.6
[Mn ^{VII} (O) ₄] ⁻	35.2	1.1	0.00	0.00	101.3	101.3
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	55.3	0.43	2.36	2.36	63.3	84.8
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	53.1	0.23	2.24	2.23	64.8	88.9
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	75.0	2.1	1.74	1.74	44.3	59.9
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	73.1	2.0	1.75	1.73	43.8	74.0
[Fe ^{IV} (O)(N ₄ Py)] ²⁺	60.6	9.4	1.40	1.32	55.3	63.5
[Fe ^{IV} (O)(BnTPEN)] ²⁺	69.0	11.5	5.17	2.75	22.4	85.7
[Fe ^{IV} (O)(^{Me2} TACN-Py ₂)] ²⁺	63.8	4.7	1.26	1.26	61.5	65.9
[Fe ^{IV} (O)(BP1)] ²⁺	65.6	2.0	1.57	1.57	48.5	57.5
[Fe ^{IV} (O)(BP2)] ²⁺	64.5	1.5	1.58	1.51	48.0	70.5
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	58.8	5.5	1.73	1.21	46.2	88.5
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	62.5	10.2	1.72	1.38	46.6	106.2
[Mn ^{IV} (O)(N ₄ Py)] ²⁺	59.1	4.8	1.35	1.27	57.0	65.7
[Co ^{IV} (O)(13-TMC)] ²⁺	63.3	1.2	1.42	1.35	55.7	94.9
[Fe ^{IV} (O)(13-TMC)] ²⁺	66.7	1.1	1.57	1.49	52.4	92.2
[Ru ^{VI} (O) ₂ (L)] ²⁺	63.7	1.7	1.56	1.54	52.2	86.4
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	54.9	2.6	2.88	2.25	58.9	92.0

^aMultiplicity. ^bEnergy needed to access the lowest spin state of the oxo complex that is one multiplicity away from the multiplicity of the hydroxide; calculated at the ground spin state's optimized geometry.



Regression S20. DHA barriers against ΔG_{PCET} and the height, max angle steric metrics.

['DHA ΔG_{PCET} ', 'Height', 'Max Angle'] Metrics:

```
Score on Training Data:          0.7296160767550646
MSE of Training Data:          1.0553654132979189
Score of LOO Cross Validation:  0.4869671105616551
MSE of LOO Cross Validation:    2.0024754463934866
MSE of 5-Fold Cross Validation: 2.343099781826322(0.09930972506610071)
F-Test p-value of final 2 variables: 0.47417271859314414
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	Height	Max Angle
DHA ΔG_{PCET}	1.000000	-0.115239	-0.114024
Height	-0.115239	1.000000	-0.138121
Max Angle	-0.114024	-0.138121	1.000000

['DHA ΔG_{PCET} ', 'Height', 'Max Angle'] Training Average:

```
[-7.77619718  2.35675364  75.05752356]
```

['DHA ΔG_{PCET} ', 'Height', 'Max Angle'] Training Deviation:

```
[ 4.05326542  1.27930252  17.85106944]
```

['DHA ΔG_{PCET} ', 'Height', 'Max Angle'] Coefficients:

```
[ 0.39618155 -0.28333271 -0.00072724]
```

['DHA ΔG_{PCET} ', 'Height', 'Max Angle'] Standard Error:

```
[0.07139195 0.22689345 0.0162581 ]
```

['DHA ΔG_{PCET} ', 'Height', 'Max Angle'] t-Test "Error":

```
[0.15423294 0.4901735  0.03512348]
```

['DHA ΔG_{PCET} ', 'Height', 'Max Angle'] Weighted Coefficients:

```
[ 1.60582897 -0.36246825 -0.01298204]
```

['DHA ΔG_{PCET} ', 'Height', 'Max Angle'] Intercept:

```
10.28517288957433
```

Attempts to Determine Reorganization Parameters

A common theme in chemistry is that reaction barriers are in large part determined by the reorganization energy needed to deform to the transition state geometry without accounting for interaction between reactants; PCET chemistry is no exception to this. In one case, the deformation energy needed to reach a transition state geometry has been shown to correlate well with computed reaction barriers;⁵² in another case, the reorganization energy was the primary factor differentiating the reactivity between a Ru^{IV} oxo and a V^V oxo.⁵³ In light of both these studies and our hypothesis that anomalously low reorganization energies could contribute to the overestimation of Ru^{IV} oxo reaction barriers^{14,25} we have made several attempts to quantify reorganization and fit it to the data. Ultimately, no parameter examined demonstrated a significant effect.

The classical definition of reorganization energy is the energy needed to deform the products into the reactant geometry, or vice-versa, without the reaction actually occurring.^{54,55} We calculated a reorganization energy for the oxo complexes in just this manner, removing the hydroxide hydrogen from our optimized metal hydroxide structures and determining the energy of the metal oxo species at the resultant geometry (with the same level of theory as described in the main text). Wherever relevant, we checked multiple spin-states at this geometry and used the lowest energy obtained, regardless of the ground spin-state of the oxo. We performed a similar calculation for metal hydroxides by constraining the cartesian position of all oxo atoms and optimizing a hydrogen atom on top of this structure.

As alternative measurements of distortions, we used the predominant M–O stretching frequency in both the metal hydroxide and metal oxo complexes to determine the energies of stretching or compressing this specific bond into the other structure. The result heavily correlated with the change in the M–O bond distance, indicating similar information could be obtained without incorporating the vibrational frequency. Therefore, because mixing with other ligand vibrational modes made finding “stretching energies” for the non-oxo M–L bonds infeasible we instead tabulated the total change in M–L bond lengths.

The results of regressions with these parameters are given in Table S14. While the stretching energies and change in bond lengths offer some improvement to the fit, cross validation indicates this is mere overfitting and none of these regressions are statistically significant. Similarly, regressions along with the asynchronicity parameter (which is thought to work in concert with reorganization energy⁵⁶) do not provide a significant improvement.

Table S14. Summary of statistics on regressions with measures of deformation energy

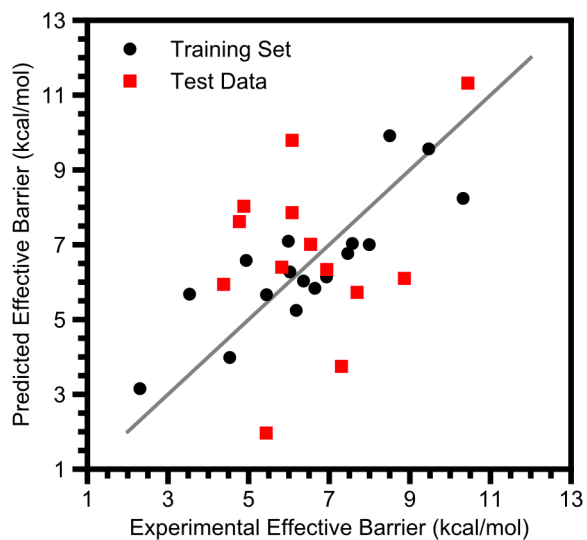
Parameter(s) Regressed with ΔG_{PCET}	R ²	MSE ^a	LOO ^b R ²	LOO ^b MSE ^a	5-Fold CV ^c MSE ^a	p-value ^d
ΔG_{PCET} only	0.70	1.18	0.60	1.57	1.49	< 0.001 ^e
Reorganization Energies	0.70	1.18	0.44	2.18	2.20	0.96
Stretching Energies	0.74	1.00	0.46	2.09	2.27	0.34
Bond Length Changes	0.75	0.97	0.47	2.07	2.01	0.27
Reorganization Energies, $ \eta $	0.75	0.97	0.48	2.03	2.12	0.48
Stretching Energies, $ \eta $	0.78	0.87	0.43	2.21	2.50	0.27
Bond Length Changes, $ \eta $	0.78	0.88	0.47	2.08	2.36	0.29

^aMean Squared Error, kcal² mol⁻². ^bLeave-One-Out. ^cCross Validation. ^dFrom an F-test where the null hypothesis is that only ΔG_{PCET} has an effect. ^eFrom an F-test where the null hypothesis is that ΔG_{PCET} has no effect.

Table S15. Reorganization parameters considered in this study

Oxo	Oxo Reorg. ^a	Hydroxide Reorg. ^a	Oxo Stretch ^b	Hydroxide Stretch ^b	M–O ΔLength ^c	ΣM–L ΔLength ^c
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	23.1	35.5	42.5	21.4	0.19	0.92
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	17.8	17.1	45.5	22.3	0.20	0.33
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	18.5	16.1	50.8	23.3	0.21	0.33
[Fe ^V (O)(TAML)] ⁻	13.6	15.7	48.2	21.4	0.20	0.0092
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺	21.0	22.7	41.8	20.0	0.19	0.58
[Fe ^{IV} (O)(TMC)(N ₃) ⁺	19.5	22.1	62.3	25.7	0.24	0.512
[Fe ^{IV} (O)(TMC)(OCOCF ₃) ⁺	20.1	23.3	59.6	25.0	0.23	0.47
[Fe ^{IV} (O)(TMCS)] ⁺	15.1	19.8	57.3	17.7	0.24	0.56
[Mn ^{IV} (O)(H ₃ buea)] ⁻	20.8	21.2	37.1	16.0	0.21	0.20
[Fe ^{IV} (O)(TMP)]	20.7	23.8	64.2	24.0	0.23	0.44
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	20.9	19.6	43.1	17.7	0.22	0.38
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺	8.5	8.6	24.5	13.7	0.16	-0.13
[Fe ^{IV} (O)(tpfpp)]	21.0	19.5	87.5	28.8	0.27	0.045
[Mn ^{VII} (O) ₄] ⁻	14.7	13.0	43.4	21.0	0.18	0.025
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	29.3	22.1	116.9	32.4	0.33	0.023
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	14.7	13.4	30.4	14.8	0.18	0.19
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	12.9	17.4	61.9	26.7	0.25	0.0060
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	14.6	13.9	43.9	20.5	0.19	-0.032
[Fe ^{IV} (O)(N4Py)] ²⁺	34.7	28.4	37.0	20.0	0.18	0.93
[Fe ^{IV} (O)(BnTPEN)] ²⁺	24.4	24.6	39.9	20.5	0.19	0.89
[Fe ^{IV} (O) ^(Me₂TACN-Py₂)] ²⁺	23.6	28.5	30.3	16.8	0.16	0.89
[Fe ^{IV} (O)(BP1)] ²⁺	26.2	28.7	33.8	18.6	0.17	0.89
[Fe ^{IV} (O)(BP2)] ²⁺	24.1	31.9	42.0	21.5	0.19	0.86
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	8.9	8.6	25.8	13.8	0.16	-0.13
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	22.8	26.2	62.6	21.2	0.25	0.20
[Mn ^{IV} (O)(N4Py)] ²⁺	22.9	21.5	22.6	11.9	0.14	0.63
[Co ^{IV} (O)(13-TMC)] ²⁺	10.1	11.6	5.7	4.8	0.084	0.41
[Fe ^{IV} (O)(13-TMC)] ²⁺	20.9	25.1	50.6	25.4	0.19	0.57
[Ru ^{VI} (O) ₂ (L)] ²⁺	13.9	13.3	44.1	21.3	0.19	-0.033
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	15.9	14.8	50.4	21.3	0.22	-0.032

^aReorganization; i.e. energy of the oxo at the hydroxide geometry or vice versa (kcal/mol). The position of the transferring H-atom was optimized for the hydroxide reorganization. ^bEnergy needed to distort the metal–oxygen bond of the oxo complex to its length in the hydroxide, or vice versa (kcal/mol); determined from frequency calculations. ^cThe change in the length of the metal–oxygen bond between the oxo complex and the hydroxide complex (Å). ^cThe sum of the change in the lengths of all metal–ligand bonds besides the metal–oxygen bond between the oxo complex and the hydroxide complex (Å).



Regression S21. DHA barriers against ΔG_{PCET} and the oxo reorganization energy.

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ '] Metrics:

Score on Training Data: 0.6985337405659753
 MSE of Training Data: 1.1766863194552986
 Score of LOO Cross Validation: 0.4413190508659992
 MSE of LOO Cross Validation: 2.1806494399090437
 MSE of 5-Fold Cross Validation: 2.1995049703717857 (0.06742190086236298)
 F-Test p-value of final 2 variables: 0.9618615594550874

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	Oxo λ	Hydroxide λ
DHA ΔG_{PCET}	1.000000	-0.113949	-0.336879
Oxo λ	-0.113949	1.000000	0.685471
Hydroxide λ	-0.336879	0.685471	1.000000

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ '] Training Average:
 [-7.77619718 21.37229441 22.86499201]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ '] Training Deviation:
 [4.05326542 5.37099513 6.03190216]

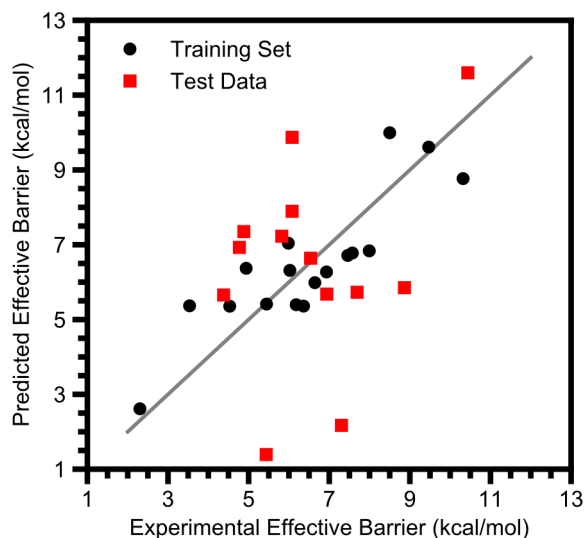
['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ '] Coefficients:
 [0.40306166 -0.0127441 -0.00372249]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ '] Standard Error:
 [0.08000681 0.07807801 0.07335822]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ '] t-Test "Error":
 [0.17284421 0.16867729 0.1584808]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ '] Weighted Coefficients:
 [1.6337159 -0.06844851 -0.0224537]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ '] Intercept:
 9.973829077770457



Regression S22. DHA barriers against ΔG_{PCET} and stretching energies of M–O(H) bonds.

```
['DHA  $\Delta G_{\text{PCET}}$ ', 'Oxo Stretch', 'Hydroxide Stretch'] Metrics:

Score on Training Data:                0.7429488443721649
MSE of Training Data:                  1.0033248125190048
Score of LOO Cross Validation:          0.46372208300228446
MSE of LOO Cross Validation:           2.09320568590959
MSE of 5-Fold Cross Validation:         2.266485644527874 (0.09874421962655447)
F-Test p-value of final 2 variables:    0.34134070652340187

Correlation Matrix of x-values:
          DHA  $\Delta G_{\text{PCET}}$   Oxo Stretch  Hydroxide Stretch
DHA  $\Delta G_{\text{PCET}}$           1.000000    -0.399234    -0.481905
Oxo Stretch          -0.399234     1.000000     0.865424
Hydroxide Stretch   -0.481905     0.865424     1.000000

['DHA  $\Delta G_{\text{PCET}}$ ', 'Oxo Stretch', 'Hydroxide Stretch'] Training Average:
[-7.77619718  51.16490969  21.37839275]

['DHA  $\Delta G_{\text{PCET}}$ ', 'Oxo Stretch', 'Hydroxide Stretch'] Training Deviation:
[ 4.05326542  19.44134649   3.86935373]

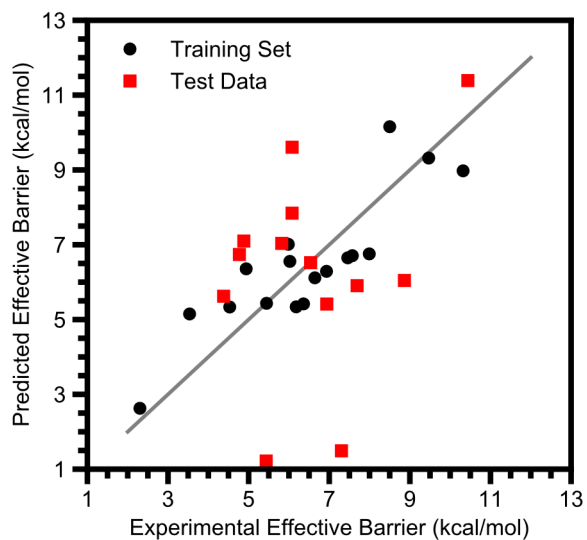
['DHA  $\Delta G_{\text{PCET}}$ ', 'Oxo Stretch', 'Hydroxide Stretch'] Coefficients:
[ 0.45176185  0.02455864 -0.00460389]

['DHA  $\Delta G_{\text{PCET}}$ ', 'Oxo Stretch', 'Hydroxide Stretch'] Standard Error:
[0.07828656  0.02854359  0.15006501]

['DHA  $\Delta G_{\text{PCET}}$ ', 'Oxo Stretch', 'Hydroxide Stretch'] t-Test "Error":
[0.16912782  0.06166468  0.32419574]

['DHA  $\Delta G_{\text{PCET}}$ ', 'Oxo Stretch', 'Hydroxide Stretch'] Weighted Coefficients:
[ 1.83111067  0.47745294 -0.01781408]

['DHA  $\Delta G_{\text{PCET}}$ ', 'Oxo Stretch', 'Hydroxide Stretch'] Intercept:
8.836929319321026
```



Regression S23. DHA barriers against ΔG_{PCET} and change in metal–ligand bond lengths.

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L'] Metrics:

```
Score on Training Data:           0.751448256020735
MSE of Training Data:           0.9701498183121323
Score of LOO Cross Validation:    0.46889535893792444
MSE of LOO Cross Validation:    2.073013300096122
MSE of 5-Fold Cross Validation:  2.0136398644927245 (0.07838159315728596)
F-Test p-value of final 2 variables: 0.27432806144440447
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	Δ Length M-O	Total Δ Length M-L
DHA ΔG_{PCET}	1.000000	-0.308863	-0.233562
Δ Length M-O	-0.308863	1.000000	-0.440362
Total Δ Length M-L	-0.233562	-0.440362	1.000000

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L'] Training Average:
[-7.77619718 0.2135339 0.47312783]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L'] Training Deviation:
[4.05326542 0.03836354 0.32487374]

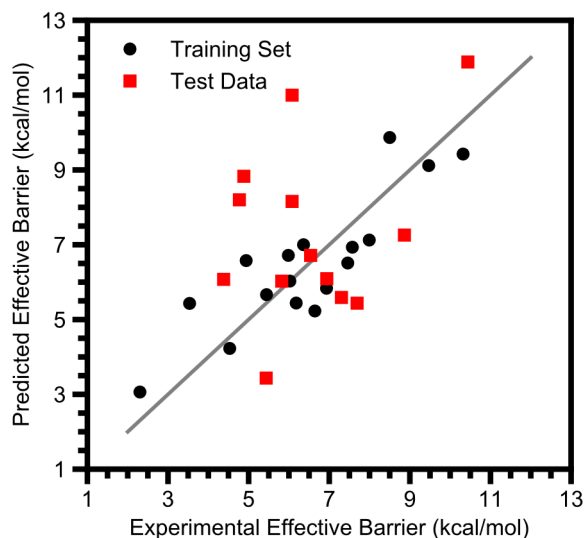
['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L'] Coefficients:
[0.44882346 13.36221923 0.15539224]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L'] Standard Error:
[0.07860524 8.99430283 1.03891916]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L'] t-Test "Error":
[0.1698163 19.43100991 2.24444839]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L'] Weighted Coefficients:
[1.8192006 0.51262207 0.05048286]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L'] Intercept:
7.045389227464227



Regression S24. DHA barriers against ΔG_{PCET} , reorganization, and the magnitude of the asynchronicity.

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ ', 'DHA $|\eta|$ (G)'] Metrics:

Score on Training Data: 0.7508389994578081
 MSE of Training Data: 0.9725278750272693
 Score of LOO Cross Validation: 0.47878455120218033
 MSE of LOO Cross Validation: 2.034413699365813
 MSE of 5-Fold Cross Validation: 2.1242747875853207 (0.07222199871900489)
 F-Test p-value of final 3 variables: 0.48404896214361404

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	Oxo λ	Hydroxide λ	DHA $ \eta $ (G)
DHA ΔG_{PCET}	1.000000	-0.113949	-0.336879	0.184231
Oxo λ	-0.113949	1.000000	0.685471	0.360767
Hydroxide λ	-0.336879	0.685471	1.000000	0.411410
DHA $ \eta $ (G)	0.184231	0.360767	0.411410	1.000000

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ ', 'DHA $|\eta|$ (G)'] Training Average:
 [-7.77619718 21.37229441 22.86499201 17.96727543]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ ', 'DHA $|\eta|$ (G)'] Training Deviation:
 [4.05326542 5.37099513 6.03190216 12.92730813]

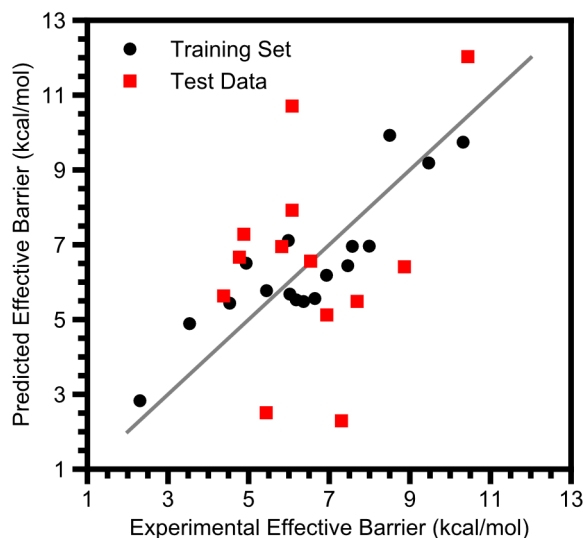
['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ ', 'DHA $|\eta|$ (G)'] Coefficients:
 [0.35613308 -0.01975543 -0.04662405 0.04146195]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ ', 'DHA $|\eta|$ (G)'] Standard Error:
 [0.08127479 0.07401256 0.0744917 0.02612321]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ ', 'DHA $|\eta|$ (G)'] t-Test "Error":
 [0.17708255 0.16125951 0.16230347 0.05691758]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ ', 'DHA $|\eta|$ (G)'] Weighted Coefficients:
 [1.44350191 -0.10610634 -0.28123169 0.53599146]

['DHA ΔG_{PCET} ', 'Oxo λ ', 'Hydroxide λ ', 'DHA $|\eta|$ (G)'] Intercept:
 9.994736811747302



Regression S25. DHA barriers against ΔG_{PCET} , stretching energies, and the magnitude of the asynchronicity.

['DHA ΔG_{PCET} ', 'Oxo Stretch', 'Hydroxide Stretch', 'DHA $|\eta|$ (G)'] Metrics:

```
Score on Training Data:          0.7778036840135025
MSE of Training Data:           0.8672790306468683
Score of LOO Cross Validation:   0.4336095053173339
MSE of LOO Cross Validation:    2.2107414203295503
MSE of 5-Fold Cross Validation: 2.4951787280872217 (0.09740659325306181)
F-Test p-value of final 3 variables: 0.27479651348982703
```

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	Oxo Stretch	Hydroxide Stretch	DHA $ \eta $ (G)
DHA ΔG_{PCET}	1.000000	-0.399234	-0.481905	0.184231
Oxo Stretch	-0.399234	1.000000	0.865424	-0.078940
Hydroxide Stretch	-0.481905	0.865424	1.000000	-0.241536
DHA $ \eta $ (G)	0.184231	-0.078940	-0.241536	1.000000

['DHA ΔG_{PCET} ', 'Oxo Stretch', 'Hydroxide Stretch', 'DHA $|\eta|$ (G)'] Training Average:
[-7.77619718 51.16490969 21.37839275 17.96727543]

['DHA ΔG_{PCET} ', 'Oxo Stretch', 'Hydroxide Stretch', 'DHA $|\eta|$ (G)'] Training
Deviation:
[4.05326542 19.44134649 3.86935373 12.92730813]

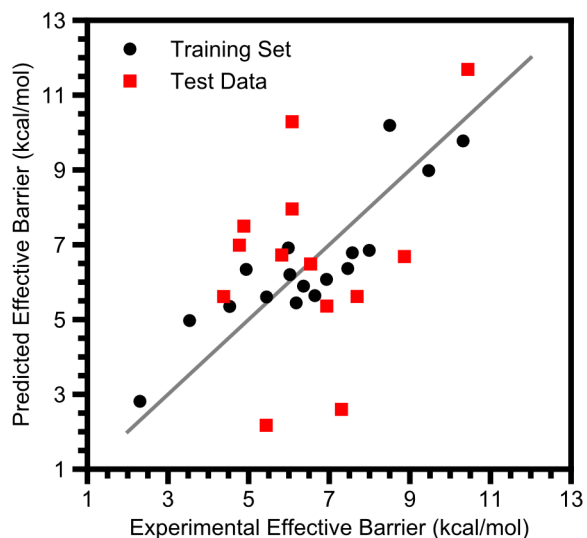
['DHA ΔG_{PCET} ', 'Oxo Stretch', 'Hydroxide Stretch', 'DHA $|\eta|$ (G)'] Coefficients:
[0.44430222 0.01412713 0.0616774 0.03059378]

['DHA ΔG_{PCET} ', 'Oxo Stretch', 'Hydroxide Stretch', 'DHA $|\eta|$ (G)'] Standard Error:
[0.07595257 0.02864889 0.15304247 0.02229869]

['DHA ΔG_{PCET} ', 'Oxo Stretch', 'Hydroxide Stretch', 'DHA $|\eta|$ (G)'] t-Test "Error":
[0.16548644 0.06242056 0.3334509 0.04858468]

['DHA ΔG_{PCET} ', 'Oxo Stretch', 'Hydroxide Stretch', 'DHA $|\eta|$ (G)'] Weighted
Coefficients:
[1.80087482 0.27465053 0.23865166 0.39549526]

['DHA ΔG_{PCET} ', 'Oxo Stretch', 'Hydroxide Stretch', 'DHA $|\eta|$ (G)'] Intercept:
7.3459742258465806



Regression S26. DHA barriers against ΔG_{PCET} , bond length changes, and the magnitude of the asynchronicity.

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L', 'DHA $|\eta|$ (G)'] Metrics:

Score on Training Data: 0.7754144322642288
 MSE of Training Data: 0.8766047835599248
 Score of LOO Cross Validation: 0.4683307976976163
 MSE of LOO Cross Validation: 2.075216901551265
 MSE of 5-Fold Cross Validation: 2.361928941102483 (0.0997562689075115)
 F-Test p-value of final 3 variables: 0.29022403136241515

Correlation Matrix of x-values:

	DHA ΔG_{PCET}	Δ Length M-O	Total Δ Length M-L	DHA $ \eta $ (G)
DHA ΔG_{PCET}	1.000000	-0.308863	-0.233562	0.184231
Δ Length M-O	-0.308863	1.000000	-0.440362	0.036738
Total Δ Length M-L	-0.233562	-0.440362	1.000000	0.117113
DHA $ \eta $ (G)	0.184231	0.036738	0.117113	1.000000

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L', 'DHA $|\eta|$ (G)'] Training Average:
 [-7.77619718 0.2135339 0.47312783 17.96727543]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L', 'DHA $|\eta|$ (G)'] Training
 Deviation:
 [4.05326542 0.03836354 0.32487374 12.92730813]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L', 'DHA $|\eta|$ (G)'] Coefficients:
 [0.42084833 10.92517568 -0.16992622 0.02512143]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L', 'DHA $|\eta|$ (G)'] Standard Error:
 [0.08160516 9.15568025 1.0673317 0.0221996]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L', 'DHA $|\eta|$ (G)'] t-Test "Error":
 [0.17780238 19.94851359 2.325516 0.04836878]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L', 'DHA $|\eta|$ (G)'] Weighted
 Coefficients:
 [1.70581 0.41912845 -0.05520457 0.32475242]

['DHA ΔG_{PCET} ', ' Δ Length M-O', 'Total Δ Length M-L', 'DHA $|\eta|$ (G)'] Intercept:
 7.050794199068996

Robustness of Results to Computational Methodology

Calculated free energies of reactions for transition metal complexes can depend greatly on the DFT functional used. This is particularly true for reactions which involve a transition from low-spin reactants to high-spin products, as is the case here.^{45,57} To confirm that our results are not an artifact of our computational methodology we recalculated the electronic energies with different computational methods at the O3LYP optimized geometries. These alternate methods were the B3LYP functional, the M06L functional, and O3LYP with the zeroth order regular approximation (ZORA) scalar relativistic correction. Importantly, the functionals tested incorporate varying amounts of Hartree Fock Exchange. Because M06L and ZORA are relatively sensitive to the integration grid used (per the ORCA manual),^{58,59} we used a finer integration grid than in our other calculations (Grid7/FinalGrid7, the finest grid setting available) and recalculated the O3LYP energies at this finer grid for comparison. As shown in Table S16 and the following regressions, we find ΔE_{PT} and ΔE_{ET} have significant contributions to reaction barriers regardless of the computational method used to calculate them.

Table S16. Summary of statistics on regressions with different computational methodology

Method	Parameter(s)	R ²	MSE ^a	LOO ^b R ²	LOO ^b MSE ^a	5-Fold CV ^c MSE ^a	p-value
O3LYP	ΔE_{PCET}	0.62	1.46	0.52	1.89	1.90	< 0.001 ^d
	$\Delta E_{PCET}, \Delta E_{PT}, \Delta E_{ET}$	0.87	0.52	0.76	0.95	1.15	0.001 ^e
B3LYP	ΔE_{PCET}	0.72	1.10	0.58	1.66	1.70	<0.001 ^d
	$\Delta E_{PCET}, \Delta E_{PT}, \Delta E_{ET}$	0.88	0.47	0.76	0.95	1.24	0.004 ^e
M06L	ΔE_{PCET}	0.65	1.37	0.54	1.81	1.94	< 0.001 ^d
	$\Delta E_{PCET}, \Delta E_{PT}, \Delta E_{ET}$	0.85	0.58	0.71	1.14	1.46	0.004 ^e
O3LYP-ZORA	ΔE_{PCET}	0.58	1.62	0.46	2.10	2.10	< 0.001 ^d
	$\Delta E_{PCET}, \Delta E_{PT}, \Delta E_{ET}$	0.85	0.59	0.75	0.99	1.21	0.001 ^e

^aMean Squared Error, kcal² mol⁻². ^bLeave-One-Out. ^cCross Validation. ^dFrom an F-test where the null hypothesis is that ΔG_{PCET} has no effect. ^eFrom an F-test where the null hypothesis is that ΔG_{PT} and ΔG_{ET} have no effect.

Table S17. ΔE_{PCET} computed with different computational methodologies

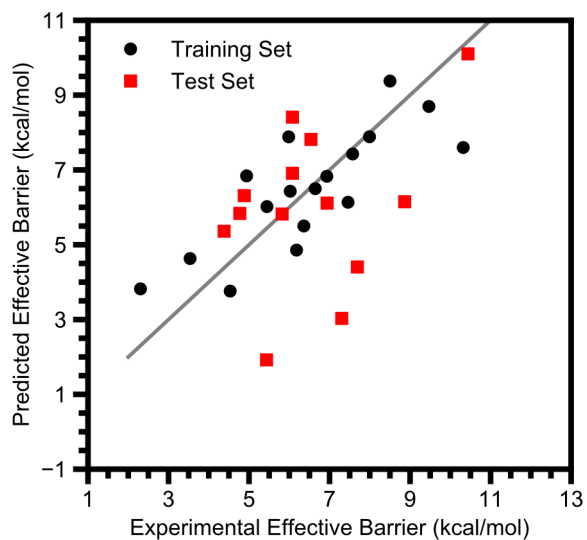
Oxo	O3LYP ΔE_{PCET}	B3LYP ΔE_{PCET}	M06L ΔE_{PCET}	O3LYP-ZORA ΔE_{PCET}
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	-9.0	-17.9	-15.7	-6.3
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	-5.0	-12.0	-7.9	-3.3
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	-3.0	-10.0	-5.7	-1.4
[Fe ^V (O)(TAML)] ⁻	-6.9	-14.2	-6.6	-5.2
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺	1.4	-6.9	-2.2	3.3
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	-2.1	-9.9	-5.2	-0.24
[Fe ^{IV} (O)(TMC)(OCOFCF ₃)] ⁺	-1.3	-9.0	-4.3	0.18
[Fe ^{IV} (O)(TMCS)] ⁺	-2.3	-10.2	-5.8	-0.67
[Mn ^{IV} (O)(H ₃ buea)] ⁻	5.2	-1.6	1.8	6.9
[Fe ^{IV} (O)(TMP)]	-6.3	-13.7	-14.1	-4.4
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	-3.0	-17.6	-6.0	0.41
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺	-2.6	-4.1	-1.7	-3.3
[Fe ^{IV} (O)(tpfpp)]	-3.8	-10.6	-3.1	-2.3
[Mn ^{VII} (O) ₄] ⁻	3.5	-5.5	8.2	5.6
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	-9.1	-19.6	-14.6	-7.0
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	-4.7	-9.6	-5.6	-1.8
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	-7.5	-14.0	-10.2	-5.9
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	7.1	0.88	7.4	5.6
[Fe ^{IV} (O)(N4Py)] ²⁺	1.4	-9.2	-6.4	4.3
[Fe ^{IV} (O)(BnTPEN)] ²⁺	-1.2	-10.9	-7.1	1.2
[Fe ^{IV} (O)(^{Me2} TACN-Py ₂)] ²⁺	1.3	-8.0	-4.9	3.7
[Fe ^{IV} (O)(BP1)] ²⁺	0.26	-9.8	-7.2	2.9
[Fe ^{IV} (O)(BP2)] ²⁺	-3.3	-12.5	-10.9	-0.71
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	-3.8	-5.1	-2.7	-4.6
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	0.70	-5.3	1.2	2.7
[Mn ^{IV} (O)(N4Py)] ²⁺	-3.1	-10.1	-5.4	-0.84
[Co ^{IV} (O)(13-TMC)] ²⁺	-11.0	-18.7	-10.7	-9.6
[Fe ^{IV} (O)(13-TMC)] ²⁺	-13.8	-21.2	-19.5	-12.4
[Ru ^{VI} (O) ₂ (L)] ²⁺	2.8	-3.6	4.3	1.2
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	-1.1	-7.2	-0.20	-2.4

Table S18. ΔE_{PT} computed with different computational methodologies

Oxo	O3LYP ΔE_{PT}	B3LYP ΔE_{PT}	M06L ΔE_{PT}	O3LYP-ZORA ΔE_{PT}
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	61.4	64.4	63.8	60.9
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	61.4	64.2	62.4	61.0
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	57.6	61.0	59.4	56.8
[Fe ^V (O)(TAML)] ⁻	43.2	38.3	45.0	44.7
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺	72.0	73.8	74.7	71.5
[Fe ^{IV} (O)(TMC)(N ₃) ⁺	50.5	53.4	54.4	50.0
[Fe ^{IV} (O)(TMC)(OCOCF ₃) ⁺	60.1	62.2	62.7	58.4
[Fe ^{IV} (O)(TMCS)] ⁺	42.7	45.7	46.1	42.3
[Mn ^{IV} (O)(H ₃ buca)] ⁻	29.5	31.4	27.9	28.8
[Fe ^{IV} (O)(TMP)]	44.2	41.9	45.5	44.7
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	19.5	21.2	22.1	21.7
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺	78.8	79.4	80.3	78.8
[Fe ^{IV} (O)(tpfpp)]	53.6	52.1	54.2	51.9
[Mn ^{VII} (O) ₄] ⁻	58.7	62.1	60.5	59.0
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	36.6	38.6	40.1	35.8
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	21.3	24.4	23.2	20.1
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	56.9	60.4	59.4	56.2
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	86.9	89.5	88.6	86.8
[Fe ^{IV} (O)(N4Py)] ²⁺	68.9	69.7	71.6	68.5
[Fe ^{IV} (O)(BnTPEN)] ²⁺	66.7	68.1	69.3	66.1
[Fe ^{IV} (O)(^{Me} 2TACN-Py ₂)] ²⁺	67.5	68.8	70.2	67.0
[Fe ^{IV} (O)(BP1)] ²⁺	74.0	75.1	76.8	73.6
[Fe ^{IV} (O)(BP2)] ²⁺	71.4	72.9	74.0	70.9
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	71.8	72.7	74.1	71.9
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	7.1	10.2	10.0	6.4.0
[Mn ^{IV} (O)(N4Py)] ²⁺	55.1	57.3	56.7	54.4
[Co ^{IV} (O)(13-TMC)] ²⁺	74.0	76.5	75.1	73.9
[Fe ^{IV} (O)(13-TMC)] ²⁺	83.4	86.2	84.5	83.1
[Ru ^{VI} (O) ₂ (L)] ²⁺	89.3	92.9	90.0	88.9
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	66.3	69.9	67.3	61.9

Table S19. ΔE_{ET} computed with different computational methodologies

Oxo	O3LYP ΔE_{ET}	B3LYP ΔE_{ET}	M06L ΔE_{ET}	O3LYP-ZORA ΔE_{ET}
[Fe ^{IV} (O)(Me ₃ NTB)(MeCN)] ²⁺	37.8	29.3	27.1	41.1
[Fe ^{IV} (O)(TMG ₂ dien)(MeCN)] ²⁺	45.9	39.4	39.7	48.4
[Fe ^{IV} (O)(TMG ₃ tren)] ²⁺	54.4	47.9	48.9	56.8
[Fe ^V (O)(TAML)] ⁻	44.8	37.4	42.2	46.6
[Fe ^{IV} (O)(TMC)(MeCN)] ²⁺	46.7	40.3	41.4	49.2
[Fe ^{IV} (O)(TMC)(N ₃)] ⁺	56.0	49.9	50.1	58.4
[Fe ^{IV} (O)(TMC)(OCOCF ₃)] ⁺	52.7	47.2	48.0	55.7
[Fe ^{IV} (O)(TMCS)] ⁺	59.2	52.5	52.9	61.3
[Mn ^{IV} (O)(H ₃ buca)] ⁻	69.2	64.5	66.0	72.2
[Fe ^{IV} (O)(TMP)]	73.5	75.1	69.7	73.6
[Co ^{III} (O)(PhB ^{tBu} Im ₃)]	82.8	74.8	74.6	85.6
[Ru ^{IV} (O)(H ⁺ TPA)(bpy)] ³⁺	45.8	48.8	41.5	45.9
[Fe ^{IV} (O)(tpfpp)]	63.6	65.2	59.6	66.0
[Mn ^{VII} (O) ₄] ⁻	54.4	44	55.4	56.3
[Mn ^V (O) ₂ (tf ₄ tmap)] ³⁺	66.2	87.1	61.7	67.9
[Mn ^{IV} (O)(OH)(tf ₄ tmap)] ³⁺	65.7	67.9	60.4	67.6
[Cr ^{IV} (O)(TMC)(Cl)] ⁺	61.5	56.4	56.7	63.8
[Ru ^{VI} (O) ₂ (TMC)] ²⁺	38.5	33.1	35.1	37.5
[Fe ^{IV} (O)(N4Py)] ²⁺	46.4	36.4	34.9	49.9
[Fe ^{IV} (O)(BnTPEN)] ²⁺	42.9	34.7	34.6	46.1
[Fe ^{IV} (O)(^{Me} 2TACN-Py ₂)] ²⁺	46.5	37.9	36.7	49.4
[Fe ^{IV} (O)(BP1)] ²⁺	43.3	33.9	32.2	46.5
[Fe ^{IV} (O)(BP2)] ²⁺	40.0	31.6	28.9	43.3
[Ru ^{IV} (O)(bpy) ₂ (py)] ²⁺	47.6	51.1	43.7	47.7
[Mn ^{IV} (O) ₂ (Me ₂ EBC)]	93.7	87.4	89.3	95.6
[Mn ^{IV} (O)(N4Py)] ²⁺	43.7	37.2	37.0	47.1
[Co ^{IV} (O)(13-TMC)] ²⁺	16.8	9.3	13.9	18.8
[Fe ^{IV} (O)(13-TMC)] ²⁺	24.2	17.5	16.2	26.3
[Ru ^{VI} (O) ₂ (L)] ²⁺	26.5	20.8	24	25.4
[Ru ^{VI} (O) ₂ (F ₂₈ -tpp)]	42.7	38.1	39	45.6



Regression S27. DHA barriers against O3LYP's ΔE_{PCET} .

['O3LYP ΔE_{PCET} '] Metrics:

Score on Training Data:	0.6248135531191439
MSE of Training Data:	1.4644317414445578
Score of LOO Cross Validation:	0.5155711219123456
MSE of LOO Cross Validation:	1.8908279641807464
MSE of 5-Fold Cross Validation:	1.9028770862454243 (0.04693830813373367)
F-Test p-value of final 1 variables:	0.0001589808441718743

Correlation Matrix of x-values:

	O3LYP ΔE_{PCET}
O3LYP ΔE_{PCET}	1.0

['O3LYP ΔE_{PCET} '] Training Average:
[-2.1557534]

['O3LYP ΔE_{PCET} '] Training Deviation:
[3.99653951]

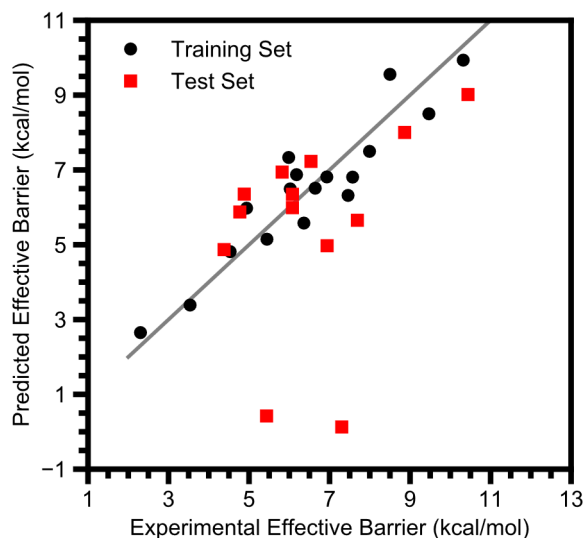
['O3LYP ΔE_{PCET} '] Coefficients:
[0.39075281]

['O3LYP ΔE_{PCET} '] Standard Error:
[0.07818165]

['O3LYP ΔE_{PCET} '] t-Test "Error":
[0.16664024]

['O3LYP ΔE_{PCET} '] Weighted Coefficients:
[1.56165903]

['O3LYP ΔE_{PCET} '] Intercept:
7.3244233791333135



Regression S28. DHA barriers against O3LYP's ΔE_{PCET} , ΔE_{PT} , and ΔE_{ET} .

['O3LYP ΔE_{PCET} ', 'O3LYP ΔE_{PT} ', 'O3LYP ΔE_{ET} '] Metrics:

Score on Training Data: 0.8661041977336073
 MSE of Training Data: 0.522623523624661
 Score of LOO Cross Validation: 0.7561336561488596
 MSE of LOO Cross Validation: 0.951861714554554
 MSE of 5-Fold Cross Validation: 1.154890730587609 (0.07663350650334944)
 F-Test p-value of final 2 variables: 0.0012341809272257143

Correlation Matrix of x-values:

	O3LYP ΔE_{PCET}	O3LYP ΔE_{PT}	O3LYP ΔE_{ET}
O3LYP ΔE_{PCET}	1.000000	0.092458	0.118059
O3LYP ΔE_{PT}	0.092458	1.000000	-0.869440
O3LYP ΔE_{ET}	0.118059	-0.869440	1.000000

['O3LYP ΔE_{PCET} ', 'O3LYP ΔE_{PT} ', 'O3LYP ΔE_{ET} '] Training Average:
 [-2.1557534 50.94173114 55.69690677]

['O3LYP ΔE_{PCET} ', 'O3LYP ΔE_{PT} ', 'O3LYP ΔE_{ET} '] Training Deviation:
 [3.99653951 18.63116025 14.02743234]

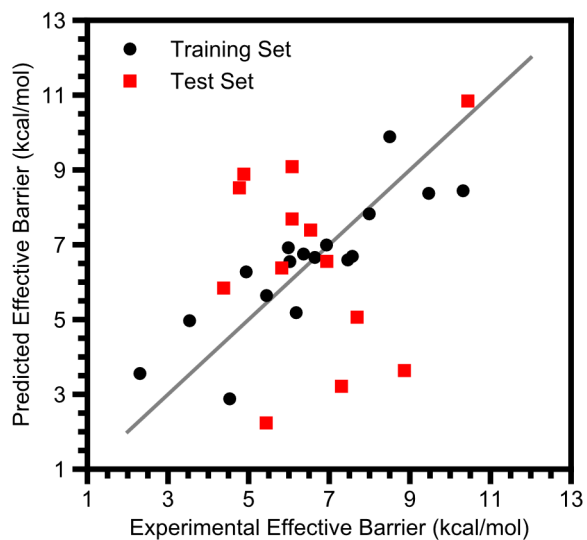
['O3LYP ΔE_{PCET} ', 'O3LYP ΔE_{PT} ', 'O3LYP ΔE_{ET} '] Coefficients:
 [0.32591958 0.04105499 0.11375599]

['O3LYP ΔE_{PCET} ', 'O3LYP ΔE_{PT} ', 'O3LYP ΔE_{ET} '] Standard Error:
 [0.05506456 0.02374144 0.03161931]

['O3LYP ΔE_{PCET} ', 'O3LYP ΔE_{PT} ', 'O3LYP ΔE_{ET} '] t-Test "Error":
 [0.11895975 0.05129026 0.06830937]

['O3LYP ΔE_{PCET} ', 'O3LYP ΔE_{PT} ', 'O3LYP ΔE_{ET} '] Weighted Coefficients:
 [1.30255047 0.76490212 1.59570441]

['O3LYP ΔE_{PCET} ', 'O3LYP ΔE_{PT} ', 'O3LYP ΔE_{ET} '] Intercept:
 -1.2426099746813781



Regression S29. DHA barriers against B3LYP's ΔE_{PCET} .

['B3LYP ΔE_{PCET}] Metrics:

Score on Training Data:	0.7185873128148237
MSE of Training Data:	1.0984130023493341
Score of LOO Cross Validation:	0.5752474491511528
MSE of LOO Cross Validation:	1.6578986871562655
MSE of 5-Fold Cross Validation:	1.7027161796546295 (0.07407851365423393)
F-Test p-value of final 1 variables:	1.733634882372659e-05

Correlation Matrix of x-values:

	B3LYP ΔE_{PCET}
B3LYP ΔE_{PCET}	1.0

['B3LYP ΔE_{PCET}] Training Average:
[-10.33181066]

['B3LYP ΔE_{PCET}] Training Deviation:
[4.30591229]

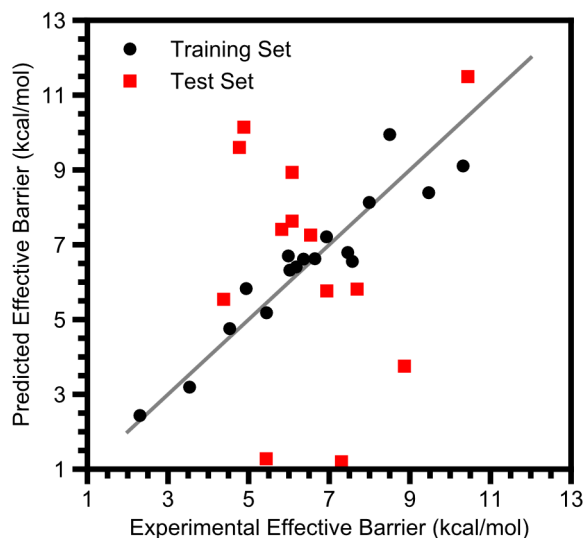
['B3LYP ΔE_{PCET}] Coefficients:
[0.38894267]

['B3LYP ΔE_{PCET}] Standard Error:
[0.06284519]

['B3LYP ΔE_{PCET}] t-Test "Error":
[0.13395135]

['B3LYP ΔE_{PCET}] Weighted Coefficients:
[1.67475302]

['B3LYP ΔE_{PCET}] Intercept:
10.500538700135094



Regression S30. DHA barriers against B3LYP's ΔE_{PCET} , ΔE_{PT} , and ΔE_{ET} .

['B3LYP ΔE_{PCET} ', 'B3LYP ΔE_{PT} ', 'B3LYP ΔE_{ET} '] Metrics:

Score on Training Data: 0.8784702014938369
 MSE of Training Data: 0.4743564058440075
 Score of LOO Cross Validation: 0.7572853874456303
 MSE of LOO Cross Validation: 0.947366264671894
 MSE of 5-Fold Cross Validation: 1.2363937155719087 (0.09772669492501583)
 F-Test p-value of final 2 variables: 0.004262890528072938

Correlation Matrix of x-values:

	B3LYP ΔE_{PCET}	B3LYP ΔE_{PT}	B3LYP ΔE_{ET}
B3LYP ΔE_{PCET}	1.000000	-0.127181	0.046790
B3LYP ΔE_{PT}	-0.127181	1.000000	-0.826294
B3LYP ΔE_{ET}	0.046790	-0.826294	1.000000

['B3LYP ΔE_{PCET} ', 'B3LYP ΔE_{PT} ', 'B3LYP ΔE_{ET} '] Training Average:

[-10.33181066 52.5454078 50.98919915]

['B3LYP ΔE_{PCET} ', 'B3LYP ΔE_{PT} ', 'B3LYP ΔE_{ET} '] Training Deviation:

[4.30591229 18.62901372 18.26010309]

['B3LYP ΔE_{PCET} ', 'B3LYP ΔE_{PT} ', 'B3LYP ΔE_{ET} '] Coefficients:

[0.40163668 0.04998103 0.07462551]

['B3LYP ΔE_{PCET} ', 'B3LYP ΔE_{PT} ', 'B3LYP ΔE_{ET} '] Standard Error:

[0.04497118 0.01843489 0.01867506]

['B3LYP ΔE_{PCET} ', 'B3LYP ΔE_{PT} ', 'B3LYP ΔE_{ET} '] t-Test "Error":

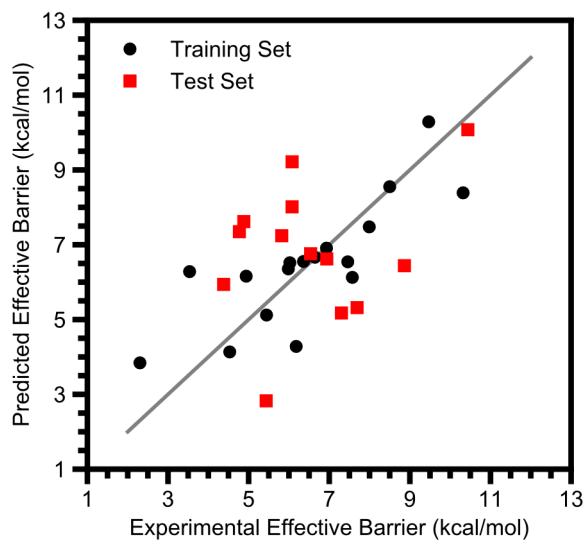
[0.09715433 0.03982616 0.04034501]

['B3LYP ΔE_{PCET} ', 'B3LYP ΔE_{PT} ', 'B3LYP ΔE_{ET} '] Weighted Coefficients:

[1.72941233 0.93109722 1.36266952]

['B3LYP ΔE_{PCET} ', 'B3LYP ΔE_{PT} ', 'B3LYP ΔE_{ET} '] Intercept:

4.200322441694215



Regression S31. DHA barriers against M06L's ΔE_{PCET} .

['M06L ΔE_{PCET}] Metrics:

Score on Training Data:	0.6489813916645575
MSE of Training Data:	1.3700995762444375
Score of LOO Cross Validation:	0.53623765519843
MSE of LOO Cross Validation:	1.810162131016007
MSE of 5-Fold Cross Validation:	1.943021323080626 (0.07769574536680626)
F-Test p-value of final 1 variables:	9.496453767954272e-05

Correlation Matrix of x-values:

	M06L ΔE_{PCET}
M06L ΔE_{PCET}	1.0

['M06L ΔE_{PCET}] Training Average:
[-5.8857926]

['M06L ΔE_{PCET}] Training Deviation:
[5.90685145]

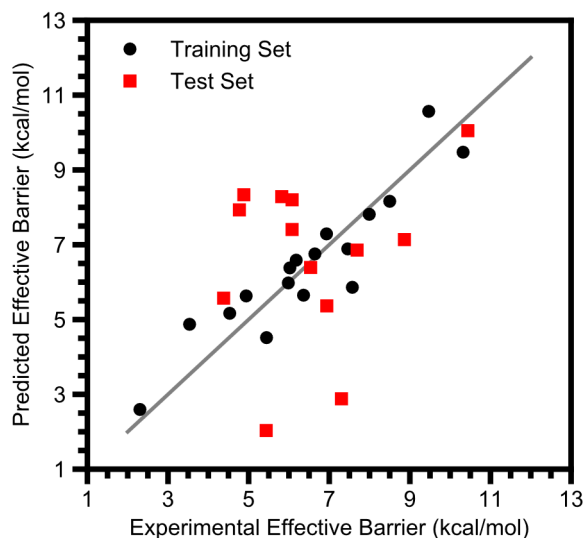
['M06L ΔE_{PCET}] Coefficients:
[0.26944558]

['M06L ΔE_{PCET}] Standard Error:
[0.05116517]

['M06L ΔE_{PCET}] t-Test "Error":
[0.10905597]

['M06L ΔE_{PCET}] Weighted Coefficients:
[1.59157503]

['M06L ΔE_{PCET}] Intercept:
8.067957508683563



Regression S32. DHA barriers against M06L's ΔE_{PCET} , ΔE_{PT} , and ΔE_{ET} .

```
['M06L  $\Delta E_{PCET}$ ', 'M06L  $\Delta E_{PT}$ ', 'M06L  $\Delta E_{ET}$ '] Metrics:

Score on Training Data:                0.8510495458264639
MSE of Training Data:                  0.5813850015311927
Score of LOO Cross Validation:          0.7071919877823828
MSE of LOO Cross Validation:           1.1428913565658008
MSE of 5-Fold Cross Validation:         1.4555347084599448 (0.09713878607647679)
F-Test p-value of final 2 variables:    0.0038029971170726595

Correlation Matrix of x-values:
           M06L  $\Delta E_{PCET}$   M06L  $\Delta E_{PT}$   M06L  $\Delta E_{ET}$ 
M06L  $\Delta E_{PCET}$       1.000000    -0.207271    0.353413
M06L  $\Delta E_{PT}$        -0.207271     1.000000   -0.867418
M06L  $\Delta E_{ET}$         0.353413    -0.867418     1.000000

['M06L  $\Delta E_{PCET}$ ', 'M06L  $\Delta E_{PT}$ ', 'M06L  $\Delta E_{ET}$ '] Training Average:
[-5.8857926  53.24122039  49.62308161]

['M06L  $\Delta E_{PCET}$ ', 'M06L  $\Delta E_{PT}$ ', 'M06L  $\Delta E_{ET}$ '] Training Deviation:
[ 5.90685145 18.94195623 16.00741272]

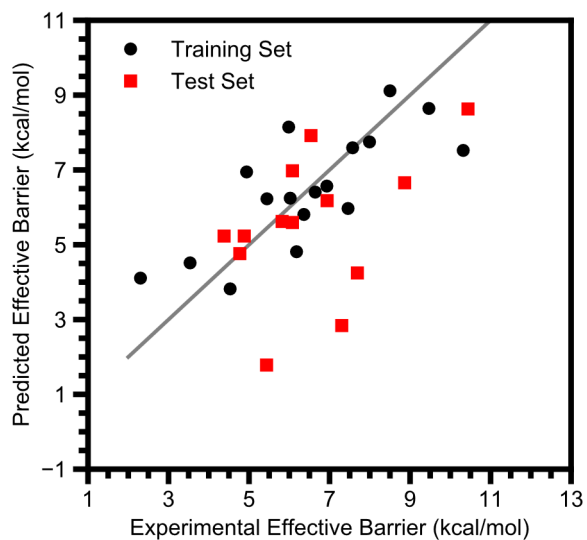
['M06L  $\Delta E_{PCET}$ ', 'M06L  $\Delta E_{PT}$ ', 'M06L  $\Delta E_{ET}$ '] Coefficients:
[0.20521987 0.0711776 0.116457 ]

['M06L  $\Delta E_{PCET}$ ', 'M06L  $\Delta E_{PT}$ ', 'M06L  $\Delta E_{ET}$ '] Standard Error:
[0.03917302 0.02296595 0.02842  ]

['M06L  $\Delta E_{PCET}$ ', 'M06L  $\Delta E_{PT}$ ', 'M06L  $\Delta E_{ET}$ '] t-Test "Error":
[0.08462816 0.04961491 0.06139768]

['M06L  $\Delta E_{PCET}$ ', 'M06L  $\Delta E_{PT}$ ', 'M06L  $\Delta E_{ET}$ '] Weighted Coefficients:
[1.21220329 1.34824305 1.86417519]

['M06L  $\Delta E_{PCET}$ ', 'M06L  $\Delta E_{PT}$ ', 'M06L  $\Delta E_{ET}$ '] Intercept:
-1.8785991938222475
```



Regression S33. DHA barriers against O3LYP-ZORA's ΔE_{PCET} .

['ZORA ΔE_{PCET} '] Metrics:

Score on Training Data:	0.5837879956450376
MSE of Training Data:	1.6245631349823895
Score of LOO Cross Validation:	0.4632551558748629
MSE of LOO Cross Validation:	2.095028200853886
MSE of 5-Fold Cross Validation:	2.100418828317726 (0.04913667840929494)
F-Test p-value of final 1 variables:	0.000356141781854169

Correlation Matrix of x-values:

	ZORA ΔE_{PCET}
ZORA ΔE_{PCET}	1.0

['ZORA ΔE_{PCET} '] Training Average:
[-0.04816983]

['ZORA ΔE_{PCET} '] Training Deviation:
[3.95594462]

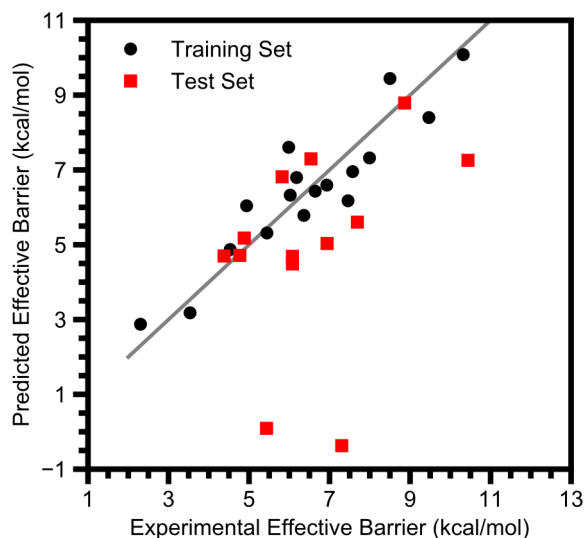
['ZORA ΔE_{PCET} '] Coefficients:
[0.38158243]

['ZORA ΔE_{PCET} '] Standard Error:
[0.08319026]

['ZORA ΔE_{PCET} '] t-Test "Error":
[0.17731583]

['ZORA ΔE_{PCET} '] Weighted Coefficients:
[1.50951897]

['ZORA ΔE_{PCET} '] Intercept:
6.500437449829684



Regression S34. DHA barriers against O3LYP-ZORA's ΔE_{PCET} , ΔE_{PT} , and ΔE_{ET} .

['ZORA ΔE_{PCET} ', 'ZORA ΔE_{PT} ', 'ZORA ΔE_{ET} '] Metrics:

Score on Training Data: 0.849900635628982
 MSE of Training Data: 0.585869440069017
 Score of LOO Cross Validation: 0.7468405586771689
 MSE of LOO Cross Validation: 0.9881346317321933
 MSE of 5-Fold Cross Validation: 1.20988798980493(0.07486597934720962)
 F-Test p-value of final 2 variables: 0.0013210450640702698

Correlation Matrix of x-values:

	ZORA ΔE_{PCET}	ZORA ΔE_{PT}	ZORA ΔE_{ET}
ZORA ΔE_{PCET}	1.000000	0.115023	0.106737
ZORA ΔE_{PT}	0.115023	1.000000	-0.872438
ZORA ΔE_{ET}	0.106737	-0.872438	1.000000

['ZORA ΔE_{PCET} ', 'ZORA ΔE_{PT} ', 'ZORA ΔE_{ET} '] Training Average:
 [-4.81698302e-02 5.05000651e+01 5.81283061e+01]

['ZORA ΔE_{PCET} ', 'ZORA ΔE_{PT} ', 'ZORA ΔE_{ET} '] Training Deviation:
 [3.95594462 18.67471947 13.55389964]

['ZORA ΔE_{PCET} ', 'ZORA ΔE_{PT} ', 'ZORA ΔE_{ET} '] Coefficients:
 [0.31228114 0.04369815 0.12462006]

['ZORA ΔE_{PCET} ', 'ZORA ΔE_{PT} ', 'ZORA ΔE_{ET} '] Standard Error:
 [0.05972849 0.02574095 0.0354332]

['ZORA ΔE_{PCET} ', 'ZORA ΔE_{PT} ', 'ZORA ΔE_{ET} '] t-Test "Error":
 [0.12903556 0.05560993 0.07654877]

['ZORA ΔE_{PCET} ', 'ZORA ΔE_{PT} ', 'ZORA ΔE_{ET} '] Weighted Coefficients:
 [1.23536689 0.81605065 1.68908777]

['ZORA ΔE_{PCET} ', 'ZORA ΔE_{PT} ', 'ZORA ΔE_{ET} '] Intercept:
 -2.9536129994751716

Analysis of Ru Oxo Kinetics with Several Substrates

Due to the overestimation reaction barriers for Ru oxo complexes, we have investigated whether free energies other than ΔG_{PCET} have an effect on the kinetics of $[\text{Ru}^{\text{IV}}(\text{O})(\text{bpy})_2(\text{py})]^{2+}$ with several substrates. The experimental data is from two reports from Mayer and coworkers.^{25,60} The determination of barrier heights and computational methodology were the same as for the data on multiple oxo complexes.

Table S20. Summary of data for regressions with the Ru^{IV} oxo data

Substrate	Corr. ^a	k_2 (mol s ⁻¹)	PCET Barrier (kcal/mol)	ΔG_{PCET} (kcal/mol)	ΔG_{PCET} (kcal/mol)	ΔG_{PCET} (kcal/mol)
9,10-Dihydroanthracene	2	125 ^e	4.77	-5.48	68.5	43.4
Ethylbenzene	2	0.022 ^e	10.22	2.90	82.8	51.7
Isopropylbenzene	2	0.033 ^e	9.90	1.29	85.1	53.9
Toluene	1	0.0064 ^e	10.65	8.69	83.5	53.8
Xanthene	1	577 ^e	3.46	-8.24	67.7	35.3
Fluorene	1	21.9 ^e	5.44	-1.21	58.6	40.1
AcrH ₂ ^b	1	5,700 ^f	2.11	-11.4	70.5	19.5
BNAH ^c	1	70,000 ^f	0.457	-12.1	88.1	19.3
Indene	1	10.8 ^e	6.11	-2.61	54.5	40.0
Cyclohexene	1 ^c	0.92 ^e	7.81	-4.94	84.5	41.5

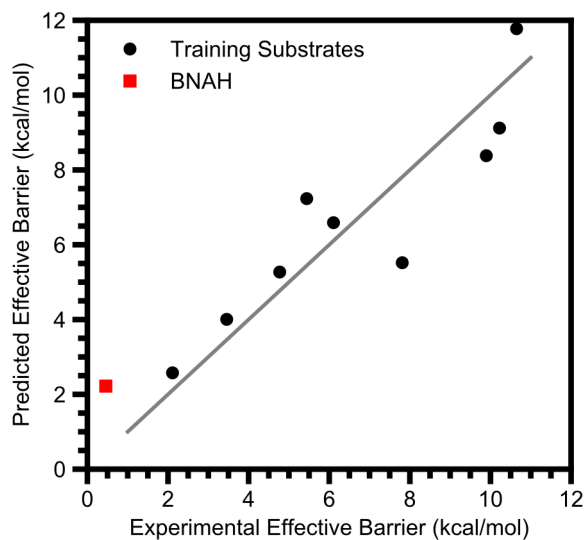
^aStoichiometric correction to the rate. ^b10-Methyl-9,10-dihydroacridine. ^c*N*-Benzyl-1,4-dihydronicotinamide. ^dCyclohexenone is the only observed product, which we take to imply a 1:1 reaction stoichiometry. ^eReference 25. ^fReference 60.

We find that ΔG_{PT} and ΔG_{ET} improve the fit to all substrates except *N*-benzyl-1,4-dihydronicotinamide (BNAH). It is unclear why BNAH does not fit the trend, as it is thought to react via the same PCET mechanism as the other substrates. Nonetheless there does not seem to be a broader issue with hydridic C–H bonds because 10-methyl-9,10-dihydroacridine (AcrH₂) fits well. The coefficients of the fits with ΔG_{PT} and ΔG_{ET} are similar to those seen in the fit with DHA (ΔG_{PCET} has a coefficient ~ 0.3 ; ΔG_{PT} and ΔG_{ET} have a coefficients ~ 0.1), which reinforces the conclusion that we are observing the same trends in both data sets.

Table S21. Summary of statistics on regressions with the Ru^{IV} oxo data

Parameter(s) Regressed with	R ²	MSE ^a	LOO ^b R ²	LOO ^b MSE ^a	5-Fold CV ^c MSE ^a	<i>p</i> -value
ΔG_{PCET} only	0.81	1.58	0.69	2.61	2.77	<0.001 ^d
ΔG_{PCET} , ΔG_{ET} , and ΔG_{PT}	0.94	0.48	0.79	1.79	2.18	0.051 ^e

^aMean Squared Error, kcal² mol⁻². ^bLeave-One-Out. ^cCross Validation. ^dFrom an F-test where the null hypothesis is that ΔG_{PCET} has no effect. ^eFrom an F-test where the null hypothesis is that ΔG_{PT} and ΔG_{ET} have no effect.



Regression S35. Ru^{IV} oxo barriers against ΔG_{PCET} .

[' ΔG_{PCET} '] Metrics:

Score on Training Data:	0.8141313040751759
MSE of Training Data:	1.5840108561567379
Score of LOO Cross Validation:	0.6935554692619883
MSE of LOO Cross Validation:	2.6115826609941655
MSE of 5-Fold Cross Validation:	2.769340429340532 (0.09523255744448217)
F-Test p-value of final 1 variables:	0.0008715558586384065

Correlation Matrix of x-values:

	ΔG_{PCET}
ΔG_{PCET}	1.0

[' ΔG_{PCET} '] Training Average:
[-2.32885283]

[' ΔG_{PCET} '] Training Deviation:
[5.73889131]

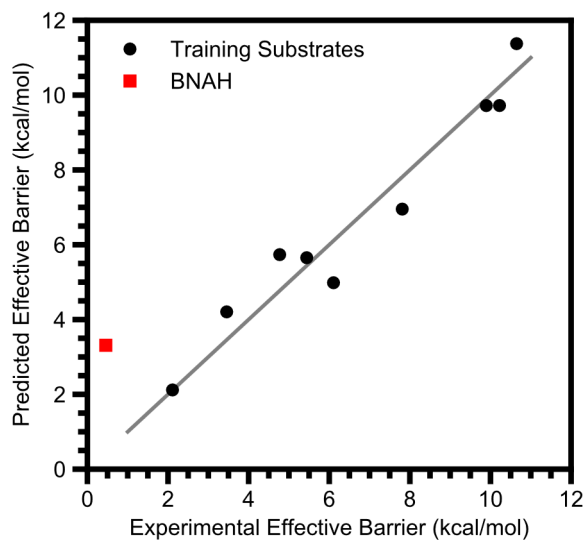
[' ΔG_{PCET} '] Coefficients:
[0.4589815]

[' ΔG_{PCET} '] Standard Error:
[0.08288998]

[' ΔG_{PCET} '] t-Test "Error":
[0.19600367]

[' ΔG_{PCET} '] Weighted Coefficients:
[2.63404493]

[' ΔG_{PCET} '] Intercept:
7.787390135961275



Regression S36. Ru^{IV} oxo barriers against ΔG_{PCET} , ΔG_{PT} , and ΔG_{ET} .

[' ΔG_{PCET} ', ' ΔG_{PT} ', ' ΔG_{ET} '] Metrics:

```
Score on Training Data:                0.9433272836504076
MSE of Training Data:                 0.48297642321627954
Score of LOO Cross Validation:         0.789763533352954
MSE of LOO Cross Validation:         1.7916779577753412
MSE of 5-Fold Cross Validation:       2.1772658070507824(0.09820218535610042)
F-Test p-value of final 2 variables:   0.0513356946380471
```

Correlation Matrix of x-values:

	ΔG_{PCET}	ΔG_{PT}	ΔG_{ET}
ΔG_{PCET}	1.000000	0.418868	0.876863
ΔG_{PT}	0.418868	1.000000	0.501120
ΔG_{ET}	0.876863	0.501120	1.000000

[' ΔG_{PCET} ', ' ΔG_{PT} ', ' ΔG_{ET} '] Training Average:

[-2.32885283 72.85902939 42.13973614]

[' ΔG_{PCET} ', ' ΔG_{PT} ', ' ΔG_{ET} '] Training Deviation:

[5.73889131 10.9865912 10.20429223]

[' ΔG_{PCET} ', ' ΔG_{PT} ', ' ΔG_{ET} '] Coefficients:

[0.24144858 0.07967059 0.09854522]

[' ΔG_{PCET} ', ' ΔG_{PT} ', ' ΔG_{ET} '] Standard Error:

[0.11278959 0.0327295 0.06656052]

[' ΔG_{PCET} ', ' ΔG_{PT} ', ' ΔG_{ET} '] t-Test "Error":

[0.28993488 0.08413386 0.17109926]

[' ΔG_{PCET} ', ' ΔG_{PT} ', ' ΔG_{ET} '] Weighted Coefficients:

[1.38564716 0.87530822 1.00558426]

[' ΔG_{PCET} ', ' ΔG_{PT} ', ' ΔG_{ET} '] Intercept:

-2.676603704473255

Summary of Statistics on Regressions on the Co^{III} Oxo Data

Table S23 gives a summary of the regressions performed on the Co^{III} oxo complex. We reiterate the previously reported trend with ΔG_{PT} and lack of a trend with ΔG_{PCET} .¹² We also detail how the addition of ΔG_{PCET} to the regression with ΔG_{PT} is significant and demonstrate that addition of neither the substrates' %BV sterics nor ΔG_{ET} improve the fit further. The substrate 1,1,3,3-tetraphenylpropene was excluded from this analysis due to its relatively large steric hinderance.

Table S22. Summary of data for regressions with the Co^{II} oxo data

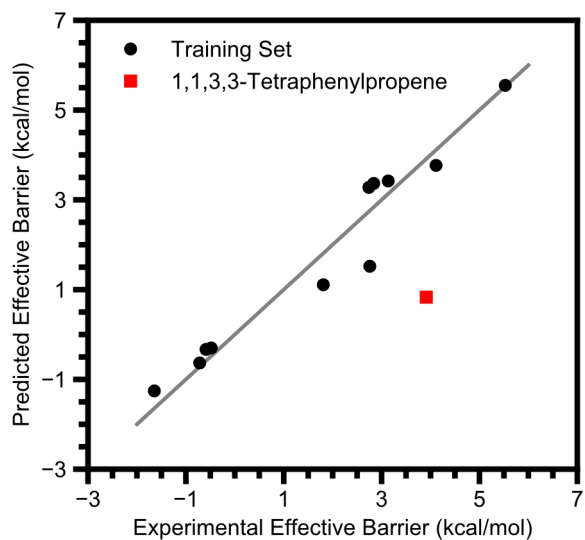
Substrate	k_2 (mol/s) ^a	PCET Barrier (kcal/mol)	ΔG_{PCET} (kcal/mol)	ΔG_{PT} (kcal/mol)	ΔG_{ET} (kcal/mol)	%BV ^b
9,10-Dihydroanthracene	0.0584 ^c	3.1	-6.7	29.5	94.8	47.4
Fluorene	0.61	1.8	-3.3	19.3	90.5	43.2
1,3-Cyclohexadiene	0.0027 ^c	5.5	-11.8	38.9	82.8	41.9
9-(<i>p</i> -CF ₃ Ph)Fluorene	112	-1.6	-9.9	8.8	91.9	57.6
9-(<i>p</i> -MeOPh)Fluorene	17.6	-0.48	-11.1	13.0	84.6	57.8
9-(<i>p</i> -MePh)Fluorene	22.4	-0.59	-10.7	12.9	88.8	57.7
3-Methylxanthene	0.088	2.8	-11.2	29.2	82.3	46.0
Diphenylmethane	0.012	4.1	-2.4	31.0	99.4	48.2
9-Phenylfluorene	29.6	-0.72	-10.3	11.6	90.0	57.7
9- <i>tert</i> -Butylfluorene	0.088	2.8	-5.2	21.1	89.0	61.5
1,1,3,3-Tetraphenylpropene	0.008	2.7	-12.5	18.0	88.1	73.5
Xanthene	0.1128	3.1	-10.4	28.9	85.3	45.8

^aReference 12. ^bPercent buried volume of a sphere around the reactive hydrogen atom. ^cCorrected by a stoichiometric factor of 2.

Table S23. Summary of statistics on regressions with the Co^{III} oxo data

Parameter(s) Regressed with	R ²	MSE ^a	LOO ^b R ²	LOO ^b MSE ^a	5-Fold CV ^c MSE ^a	<i>p</i> -value
ΔG_{PT} only	0.94	0.28	0.93	0.36	0.39	< 0.001 ^d
ΔG_{PCET} only	0.09	4.39	-0.32	6.35	6.37	0.37 ^e
ΔG_{PT} and ΔG_{PCET}	0.97	0.13	0.94	0.27	0.29	0.017 ^e
ΔG_{PT} , ΔG_{PCET} , and %BV Sterics	0.98	0.10	0.83	0.80	0.80	0.21 ^f
ΔG_{PT} and ΔG_{ET}	0.95	0.25	0.93	0.36	0.52	0.41 ^g
ΔG_{PT} , ΔG_{PCET} , and ΔG_{ET}	0.98	0.08	0.95	0.23	0.29	0.072 ^g

^aMean Squared Error, kcal² mol⁻². ^bLeave-One-Out. ^cCross Validation. ^dFrom an F-test where the null hypothesis is that ΔG_{PT} has no effect. ^eFrom an F-test where the null hypothesis is that ΔG_{PCET} has no effect. ^fFrom an F-test where the null hypothesis is that %BV Sterics has no effect. ^gFrom an F-test where the null hypothesis is that ΔG_{ET} has no effect.



Regression S37. Co^{III} oxo barriers against ΔG_{PT} .

[' ΔG_{PT} '] Metrics:

Score on Training Data:	0.9424632998739368
MSE of Training Data:	0.27729834873004827
Score of LOO Cross Validation:	0.9252474025325068
MSE of LOO Cross Validation:	0.36027043253438246
MSE of 5-Fold Cross Validation:	0.38974742022611514 (0.011222596536024027)
F-Test p-value of final 1 variables:	6.966522436702149e-07

Correlation Matrix of x-values:

	ΔG_{PT}
ΔG_{PT}	1.0

[' ΔG_{PT} '] Training Average:
[22.19752727]

[' ΔG_{PT} '] Training Deviation:
[9.42668502]

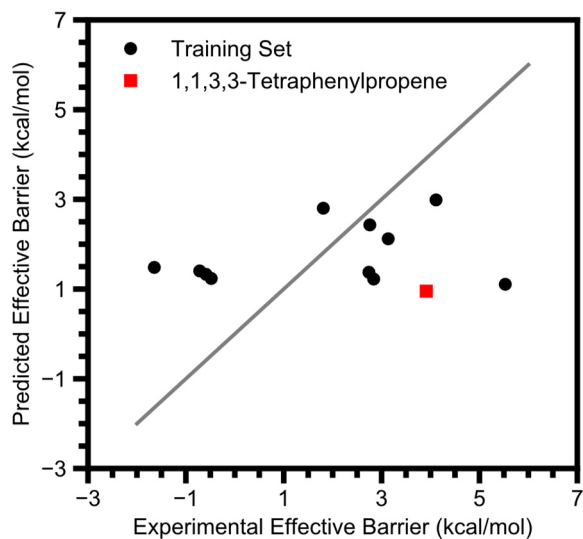
[' ΔG_{PT} '] Coefficients:
[0.22608638]

[' ΔG_{PT} '] Standard Error:
[0.01862059]

[' ΔG_{PT} '] t-Test "Error":
[0.0421227]

[' ΔG_{PT} '] Weighted Coefficients:
[2.13124506]

[' ΔG_{PT} '] Intercept:
-3.246666603888153



Regression S38. Co^{III} oxo barriers against ΔG_{PCET} .

[' ΔG_{PCET} '] Metrics:

Score on Training Data:	0.08862503668507471
MSE of Training Data:	4.392375159635855
Score of LOO Cross Validation:	-0.31700265884710466
MSE of LOO Cross Validation:	6.34729940666087
MSE of 5-Fold Cross Validation:	6.37119453049353 (0.09952217793998655)
F-Test p-value of final 1 variables:	0.3739434558155724

Correlation Matrix of x-values:

	ΔG_{PCET}
ΔG_{PCET}	1.0

[' ΔG_{PCET} '] Training Average:

[-8.45470682]

[' ΔG_{PCET} '] Training Deviation:

[3.26244406]

[' ΔG_{PCET} '] Coefficients:

[0.20032553]

[' ΔG_{PCET} '] Standard Error:

[0.21413388]

[' ΔG_{PCET} '] t-Test "Error":

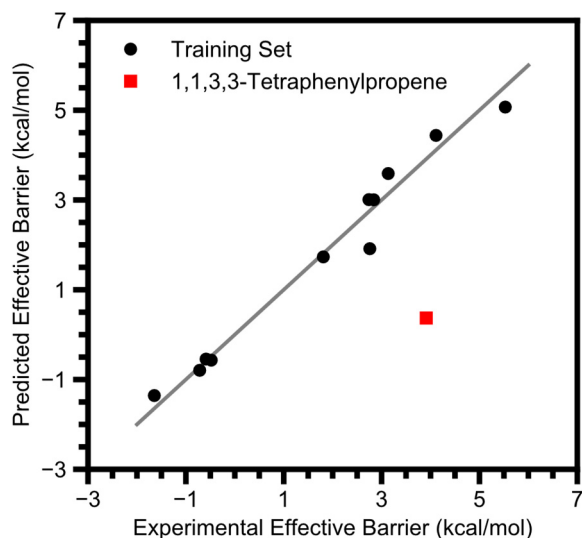
[0.48440449]

[' ΔG_{PCET} '] Weighted Coefficients:

[0.65355084]

[' ΔG_{PCET} '] Intercept:

3.465585563988545



Regression S39. Co^{III} oxo barriers against ΔG_{PT} and ΔG_{PCET} .

[' ΔG_{PT} ', ' ΔG_{PCET} '] Metrics:

Score on Training Data: 0.9728720534806891
 MSE of Training Data: 0.13074324314324676
 Score of LOO Cross Validation: 0.943560930601589
 MSE of LOO Cross Validation: 0.2720083131940089
 MSE of 5-Fold Cross Validation: 0.2929711051982866 (0.01173660654476484)
 F-Test p-value of final 1 variables: 0.01721332594582059

Correlation Matrix of x-values:

	ΔG_{PT}	ΔG_{PCET}
ΔG_{PT}	1.000000	0.128517
ΔG_{PCET}	0.128517	1.000000

[' ΔG_{PT} ', ' ΔG_{PCET} '] Training Average:

[22.19752727 -8.45470682]

[' ΔG_{PT} ', ' ΔG_{PCET} '] Training Deviation:

[9.42668502 3.26244406]

[' ΔG_{PT} ', ' ΔG_{PCET} '] Coefficients:

[0.22082357 0.11832428]

[' ΔG_{PT} ', ' ΔG_{PCET} '] Standard Error:

[0.01367484 0.03951282]

[' ΔG_{PT} ', ' ΔG_{PCET} '] t-Test "Error":

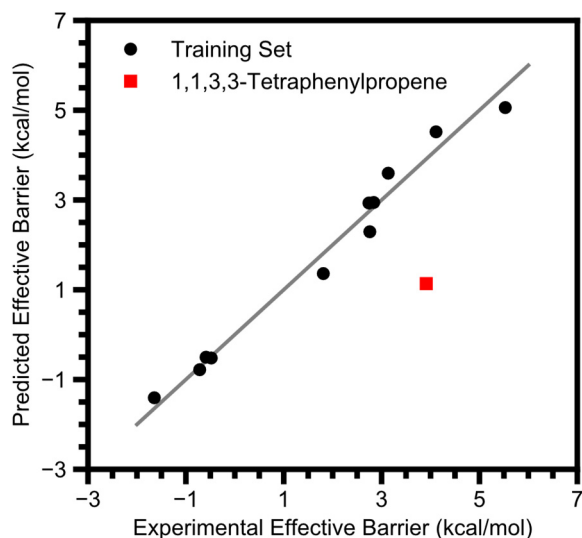
[0.03153423 0.09111673]

[' ΔG_{PT} ', ' ΔG_{PCET} '] Weighted Coefficients:

[2.08163428 0.38602634]

[' ΔG_{PT} ', ' ΔG_{PCET} '] Intercept:

-2.129448313216325



Regression S40. Co^{III} oxo barriers against ΔG_{PT} , ΔG_{PCET} , and substrates' percent buried volume sterics.

[' ΔG_{PT} ', ' ΔG_{PCET} ', '%BV'] Metrics:

```
Score on Training Data:          0.9785995318612503
MSE of Training Data:          0.10313963894215689
Score of LOO Cross Validation:  0.8335055335504782
MSE of LOO Cross Validation:   0.8024207248241055
MSE of 5-Fold Cross Validation: 0.8002864721214152 (0.03212409826687691)
F-Test p-value of final 1 variables: 0.21338614672251444
```

Correlation Matrix of x-values:

	ΔG_{PT}	ΔG_{PCET}	%BV
ΔG_{PT}	1.000000	0.128517	-0.777256
ΔG_{PCET}	0.128517	1.000000	-0.121393
%BV	-0.777256	-0.121393	1.000000

[' ΔG_{PT} ', ' ΔG_{PCET} ', '%BV'] Training Average:
[22.19752727 -8.45470682 51.34545455]

[' ΔG_{PT} ', ' ΔG_{PCET} ', '%BV'] Training Deviation:
[9.42668502 3.26244406 6.77567355]

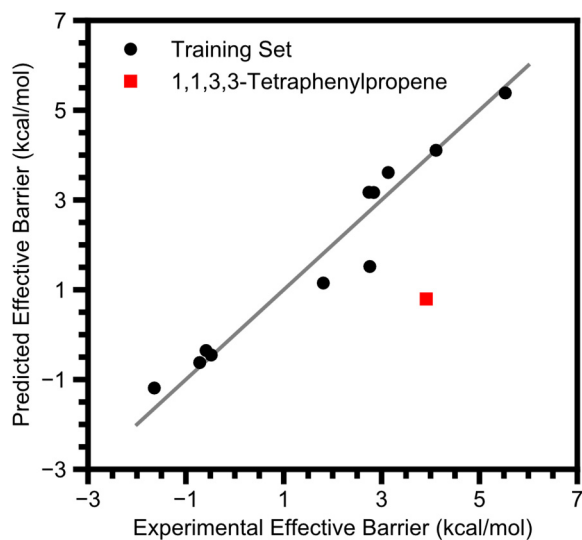
[' ΔG_{PT} ', ' ΔG_{PCET} ', '%BV'] Coefficients:
[0.24253036 0.120095 0.03899516]

[' ΔG_{PT} ', ' ΔG_{PCET} ', '%BV'] Standard Error:
[0.02049641 0.03754008 0.02848994]

[' ΔG_{PT} ', ' ΔG_{PCET} ', '%BV'] t-Test "Error":
[0.0484663 0.08876819 0.06736801]

[' ΔG_{PT} ', ' ΔG_{PCET} ', '%BV'] Weighted Coefficients:
[2.2862573 0.39180322 0.26421845]

[' ΔG_{PT} ', ' ΔG_{PCET} ', '%BV'] Intercept:
-4.598538368410885



Regression S41. Co^{III} oxo barriers against ΔG_{PT} and ΔG_{ET} .

[' ΔG_{PT} ', ' ΔG_{ET} '] Metrics:

Score on Training Data: 0.9473851700776209
 MSE of Training Data: 0.2535773762523971
 Score of LOO Cross Validation: 0.9257014183495356
 MSE of LOO Cross Validation: 0.35808230154870657
 MSE of 5-Fold Cross Validation: 0.5218007751115226 (0.09976949819374094)
 F-Test p-value of final 1 variables: 0.4121834589527267

Correlation Matrix of x-values:

	ΔG_{PT}	ΔG_{ET}
ΔG_{PT}	1.000000	-0.106709
ΔG_{ET}	-0.106709	1.000000

[' ΔG_{PT} ', ' ΔG_{ET} '] Training Average:

[22.19752727 89.03654545]

[' ΔG_{PT} ', ' ΔG_{ET} '] Training Deviation:

[9.42668502 4.97130331]

[' ΔG_{PT} ', ' ΔG_{ET} '] Coefficients:

[0.22783984 0.03115895]

[' ΔG_{PT} ', ' ΔG_{ET} '] Standard Error:

[0.01899495 0.0360186]

[' ΔG_{PT} ', ' ΔG_{ET} '] t-Test "Error":

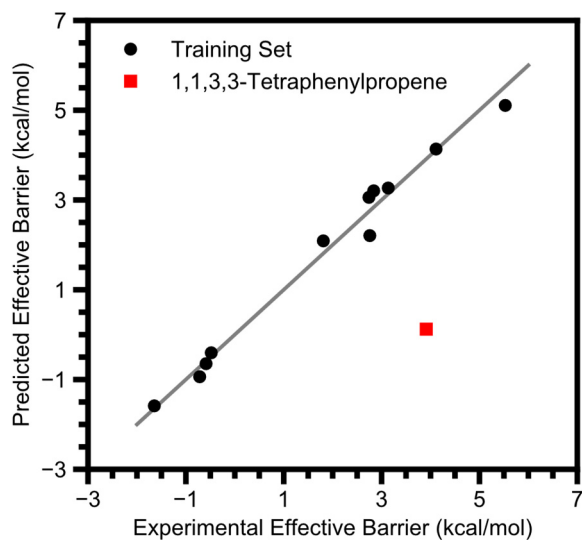
[0.04380243 0.08305904]

[' ΔG_{PT} ', ' ΔG_{ET} '] Weighted Coefficients:

[2.14777439 0.15490058]

[' ΔG_{PT} ', ' ΔG_{ET} '] Intercept:

-6.059874252255053



Regression S42. Co^{III} oxo barriers against ΔG_{PT} , ΔG_{PCET} , and ΔG_{ET} .

[' ΔG_{PT} ', ' ΔG_{PCET} ', ' ΔG_{ET} '] Metrics:

```
Score on Training Data:          0.9834815349371753
MSE of Training Data:          0.07961080624089117
Score of LOO Cross Validation:  0.9532389621068799
MSE of LOO Cross Validation:    0.2253650029330011
MSE of 5-Fold Cross Validation: 0.29298124182750607(0.036112502254110106)
F-Test p-value of final 1 variables: 0.0716825286335695
```

Correlation Matrix of x-values:

	ΔG_{PT}	ΔG_{PCET}	ΔG_{ET}
ΔG_{PT}	1.000000	0.128517	-0.106709
ΔG_{PCET}	0.128517	1.000000	0.750813
ΔG_{ET}	-0.106709	0.750813	1.000000

[' ΔG_{PT} ', ' ΔG_{PCET} ', ' ΔG_{ET} '] Training Average:
[22.19752727 -8.45470682 89.03654545]

[' ΔG_{PT} ', ' ΔG_{PCET} ', ' ΔG_{ET} '] Training Deviation:
[9.42668502 3.26244406 4.97130331]

[' ΔG_{PT} ', ' ΔG_{PCET} ', ' ΔG_{ET} '] Coefficients:
[0.21293067 0.20413059 -0.07243803]

[' ΔG_{PT} ', ' ΔG_{PCET} ', ' ΔG_{ET} '] Standard Error:
[0.01199958 0.05219299 0.03416295]

[' ΔG_{PT} ', ' ΔG_{PCET} ', ' ΔG_{ET} '] t-Test "Error":
[0.02837449 0.12341681 0.08078254]

[' ΔG_{PT} ', ' ΔG_{PCET} ', ' ΔG_{ET} '] Weighted Coefficients:
[2.00723035 0.66596465 -0.3601114]

[' ΔG_{PT} ', ' ΔG_{PCET} ', ' ΔG_{ET} '] Intercept:
5.2208535130795175

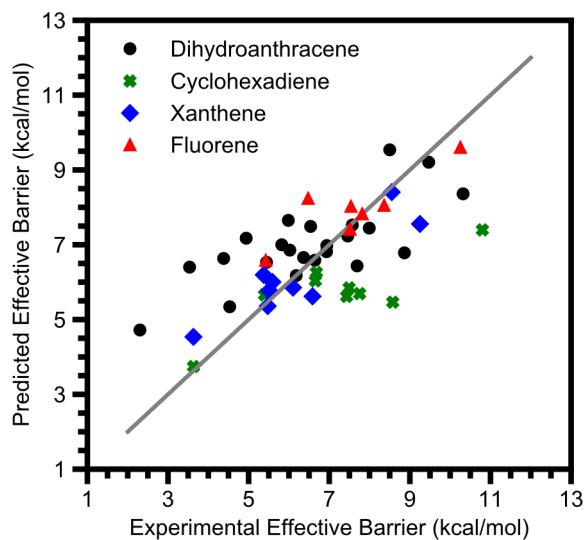
Regressions of Metal Oxo Complexes with Multiple Substrates

Table S24 gives details on the regressions between multiple substrates' barriers for reactivity with several metal oxo species. Most of the parameters we analyze do not change between substrate to substrate (the exceptions being the free energies), so we were wary of giving too much weight to metal oxo complexes which had k_2 values reported for an unusually large number of substrates. For that reason we limited our analysis to the substrates which have the largest number of k_2 values reported with metal oxo complexes in our data set: 9,10-dihydroanthracene (DHA), 1,4-cyclohexadiene (CHD), xanthene (Xth), and fluorene (Fl). Due to the same concern with extra weight being given to specific metal oxo complexes we only report the overall R^2 and MSE of the fit along with a modified LOO R^2 and MSE. This modification is that we did not leave out one individual data point at a time to predict with all other data points; instead we left out all data for a given metal oxo complex and predicted them with the rest of the metal oxo complexes' data. Ultimately, the results from this analysis cohere with what is seen for that regressions to only DHA data: when compared to the fit to only ΔG_{PCET} , only ΔG_{PT} and ΔG_{ET} show a convincing effect. The data used in these regressions is given in Table S3 (data relating to spin), Table S4 (data relating to reactivity with DHA), Table S6 (data related to reactivity with 1,4-cyclohexadiene (CHD)), Table S7 (data related to reactivity with fluorene), (data related to reactivity with xanthene), and Table S13 (steric parameters).

Table S24. Summary of statistics on regressions with multiple substrates and multiple metal oxo complexes

Parameter(s) Regressed with ΔG_{PCET}	R^2	MSE ^a	LOO ^b R^2	LOO ^b MSE ^a
ΔG_{PCET} only	0.45	1.79	0.36	2.10
%BV Sterics	0.48	1.71	0.28	2.37
Oxo Spin Density	0.53	1.55	0.37	2.08
Spin Excitation	0.50	1.66	0.39	2.01
$ \eta $	0.50	1.63	0.30	2.30
$\Delta G_{\text{PT}}, \Delta G_{\text{ET}}$	0.64	1.18	0.50	1.64

^aMean Squared Error, kcal² mol⁻². ^bLeave-One-Out.



Regression S43. Multiple substrates' reaction barriers against ΔG_{PCET} .

['Sub ΔG_{PCET} '] Metrics:

Score on Training Data:	0.45487429395449097
MSE of Training Data:	1.7936813739581947
Score of LOO Cross Validation:	0.3623252595400116
MSE of LOO Cross Validation:	2.0982046744851544

Correlation Matrix of x-values:

	Sub ΔG_{PCET}
Sub ΔG_{PCET}	1.0

['Sub ΔG_{PCET} '] Training Average:
[-8.86079851]

['Sub ΔG_{PCET} '] Training Deviation:
[4.20784163]

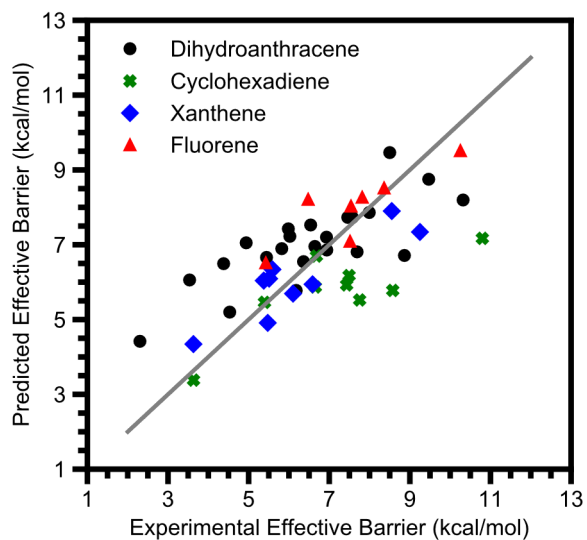
['Sub ΔG_{PCET} '] Coefficients:
[0.29074391]

['Sub ΔG_{PCET} '] Standard Error:
[0.04692825]

['Sub ΔG_{PCET} '] t-Test "Error":
[0.09446167]

['Sub ΔG_{PCET} '] Weighted Coefficients:
[1.22340434]

['Sub ΔG_{PCET} '] Intercept:
9.3326501024694



Regression S44. Multiple substrates' reaction barriers against ΔG_{PCET} and percent buried volume sterics.

['Sub ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Metrics:

Score on Training Data: 0.48027058057784117
 MSE of Training Data: 1.710117444063089
 Score of LOO Cross Validation: 0.2785190099479361
 MSE of LOO Cross Validation: 2.373960719829397

Correlation Matrix of x-values:

	Sub ΔG_{PCET}	%BV Tot	%BV Dev
Sub ΔG_{PCET}	1.000000	-0.155632	0.192876
%BV Tot	-0.155632	1.000000	0.155131
%BV Dev	0.192876	0.155131	1.000000

['Sub ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Training Average:

[-8.86079851 63.96875 4.65175846]

['Sub ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Training Deviation:

[4.20784163 10.24309028 4.35809801]

['Sub ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Coefficients:

[0.30887955 0.02627491 -0.04095496]

['Sub ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Standard Error:

[0.04864807 0.01984959 0.04696706]

['Sub ΔG_{PCET} ', '%BV Tot', '%BV Dev'] t-Test "Error":

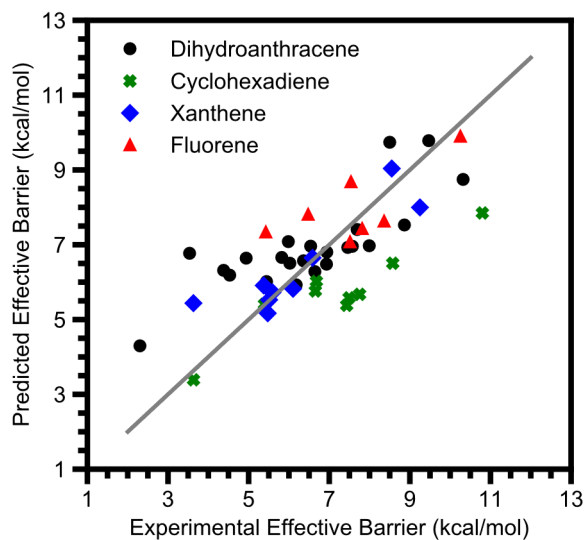
[0.09804374 0.04000422 0.09465589]

['Sub ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Weighted Coefficients:

[1.29971621 0.26913631 -0.17848572]

['Sub ΔG_{PCET} ', '%BV Tot', '%BV Dev'] Intercept:

8.003085518073675



Regression S45. Multiple substrates' reaction barriers against ΔG_{PCET} and IBO spin density on the oxo ligand.

['Sub ΔG_{PCET} ', 'IBO Spin O'] Metrics:

Score on Training Data:	0.5287385429894587
MSE of Training Data:	1.5506384827018973
Score of LOO Cross Validation:	0.36879954216229527
MSE of LOO Cross Validation:	2.076901697904626

Correlation Matrix of x-values:

	Sub ΔG_{PCET}	IBO Spin O
Sub ΔG_{PCET}	1.000000	-0.170138
IBO Spin O	-0.170138	1.000000

['Sub ΔG_{PCET} ', 'IBO Spin O'] Training Average:
 [-8.86079851 0.48515917]

['Sub ΔG_{PCET} ', 'IBO Spin O'] Training Deviation:
 [4.20784163 0.32509068]

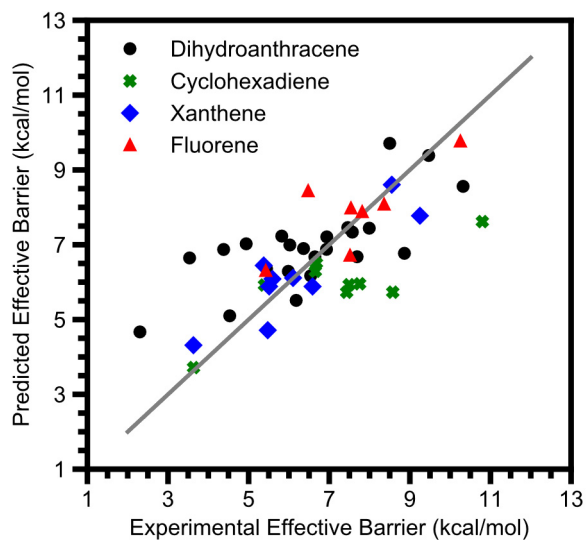
['Sub ΔG_{PCET} ', 'IBO Spin O'] Coefficients:
 [0.27051544 -1.53891806]

['Sub ΔG_{PCET} ', 'IBO Spin O'] Standard Error:
 [0.04476805 0.57945946]

['Sub ΔG_{PCET} ', 'IBO Spin O'] t-Test "Error":
 [0.09016748 1.16709126]

['Sub ΔG_{PCET} ', 'IBO Spin O'] Weighted Coefficients:
 [1.13828612 -0.50028792]

['Sub ΔG_{PCET} ', 'IBO Spin O'] Intercept:
 9.900029869312357



Regression S46. Multiple substrates' reaction barriers against ΔG_{PCET} and the spin excitation energy.

['Sub ΔG_{PCET} ', 'Spin Excitation'] Metrics:

```
Score on Training Data:          0.49613389580124573
MSE of Training Data:           1.6579207989041966
Score of LOO Cross Validation:   0.39044592960659175
MSE of LOO Cross Validation:    2.0056764345539455
```

Correlation Matrix of x-values:

	Sub ΔG_{PCET}	Spin Excitation
Sub ΔG_{PCET}	1.000000	-0.077451
Spin Excitation	-0.077451	1.000000

['Sub ΔG_{PCET} ', 'Spin Excitation'] Training Average:
[-8.86079851 11.34056619]

['Sub ΔG_{PCET} ', 'Spin Excitation'] Training Deviation:
[4.20784163 17.66873331]

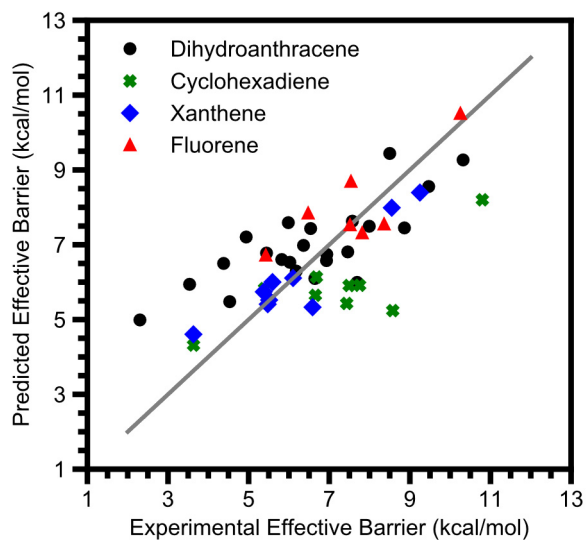
['Sub ΔG_{PCET} ', 'Spin Excitation'] Coefficients:
[0.28394156 -0.02091645]

['Sub ΔG_{PCET} ', 'Spin Excitation'] Standard Error:
[0.04575333 0.01089624]

['Sub ΔG_{PCET} ', 'Spin Excitation'] t-Test "Error":
[0.09215195 0.02194616]

['Sub ΔG_{PCET} ', 'Spin Excitation'] Weighted Coefficients:
[1.1947811 -0.36956713]

['Sub ΔG_{PCET} ', 'Spin Excitation'] Intercept:
9.509580161062551



Regression S47. Multiple substrates' reaction barriers against ΔG_{PCET} and the magnitude of the asynchronicity.

['Sub ΔG_{PCET} ', 'Sub $|\eta|$ (G)'] Metrics:

Score on Training Data: 0.5041455584938033
 MSE of Training Data: 1.6315592276432798
 Score of LOO Cross Validation: 0.2998360096801256
 MSE of LOO Cross Validation: 2.3038192736560474

Correlation Matrix of x-values:

	Sub ΔG_{PCET}	Sub $ \eta $ (G)
Sub ΔG_{PCET}	1.000000	0.298842
Sub $ \eta $ (G)	0.298842	1.000000

['Sub ΔG_{PCET} ', 'Sub $|\eta|$ (G)'] Training Average:
 [-8.86079851 17.97838265]

['Sub ΔG_{PCET} ', 'Sub $|\eta|$ (G)'] Training Deviation:
 [4.20784163 14.68415922]

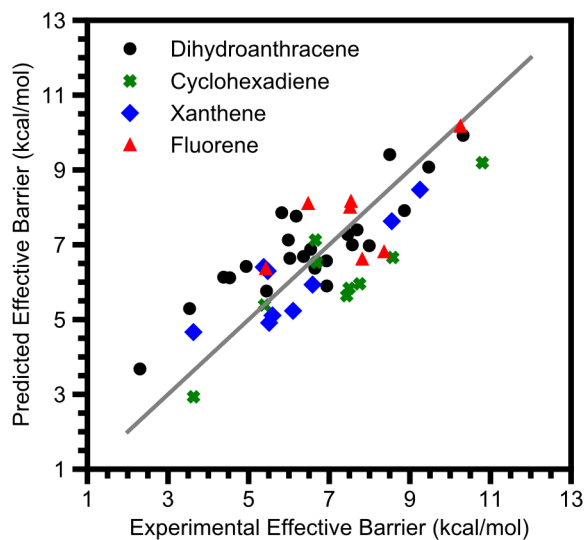
['Sub ΔG_{PCET} ', 'Sub $|\eta|$ (G)'] Coefficients:
 [0.26077867 0.02873333]

['Sub ΔG_{PCET} ', 'Sub $|\eta|$ (G)'] Standard Error:
 [0.04741871 0.01358814]

['Sub ΔG_{PCET} ', 'Sub $|\eta|$ (G)'] t-Test "Error":
 [0.09550618 0.02736792]

['Sub ΔG_{PCET} ', 'Sub $|\eta|$ (G)'] Weighted Coefficients:
 [1.09731536 0.42192485]

['Sub ΔG_{PCET} ', 'Sub $|\eta|$ (G)'] Intercept:
 8.550555292333174



Regression S48. Multiple substrates' reaction barriers against ΔG_{PCET} , ΔG_{PT} , and ΔG_{ET} .

['Sub ΔG_{PCET} ', 'Sub ΔG_{PT} ', 'Sub ΔG_{ET} '] Metrics:

Score on Training Data: 0.6424983850662855
 MSE of Training Data: 1.1763231503396485
 Score of LOO Cross Validation: 0.5010163972835706
 MSE of LOO Cross Validation: 1.6418554182588772

Correlation Matrix of x-values:

	Sub ΔG_{PCET}	Sub ΔG_{PT}	Sub ΔG_{ET}
Sub ΔG_{PCET}	1.000000	-0.308508	0.359117
Sub ΔG_{PT}	-0.308508	1.000000	-0.860287
Sub ΔG_{ET}	0.359117	-0.860287	1.000000

['Sub ΔG_{PCET} ', 'Sub ΔG_{PT} ', 'Sub ΔG_{ET} '] Training Average:
 [-8.86079851 44.08376701 50.44489208]

['Sub ΔG_{PCET} ', 'Sub ΔG_{PT} ', 'Sub ΔG_{ET} '] Training Deviation:
 [4.20784163 18.89575872 14.48110578]

['Sub ΔG_{PCET} ', 'Sub ΔG_{PT} ', 'Sub ΔG_{ET} '] Coefficients:
 [0.2286421 0.04120077 0.09643366]

['Sub ΔG_{PCET} ', 'Sub ΔG_{PT} ', 'Sub ΔG_{ET} '] Standard Error:
 [0.04163513 0.01697321 0.02257307]

['Sub ΔG_{PCET} ', 'Sub ΔG_{PT} ', 'Sub ΔG_{ET} '] t-Test "Error":
 [0.08391008 0.03420727 0.04549303]

['Sub ΔG_{PCET} ', 'Sub ΔG_{PT} ', 'Sub ΔG_{ET} '] Weighted Coefficients:
 [0.96208973 0.77851978 1.39646609]

['Sub ΔG_{PCET} ', 'Sub ΔG_{PT} ', 'Sub ΔG_{ET} '] Intercept:
 2.1015075758414623

Availability of Data and Python Scripts

The data folder accompanying this supplementary information contains csv files with all the analyzed parameters and python scripts for running the regression output. It also contains the optimized geometries and ORCA output files of the relevant frequency calculations. Instructions for downloading the software needed to run the python script can be found at <https://www.scipy.org/install.html> and <https://www.python.org/downloads/>.

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