Supporting Information
Modeling the Roles of Rigidity and Dopants in Single-Atom Methane-to-Methanol Catalysts

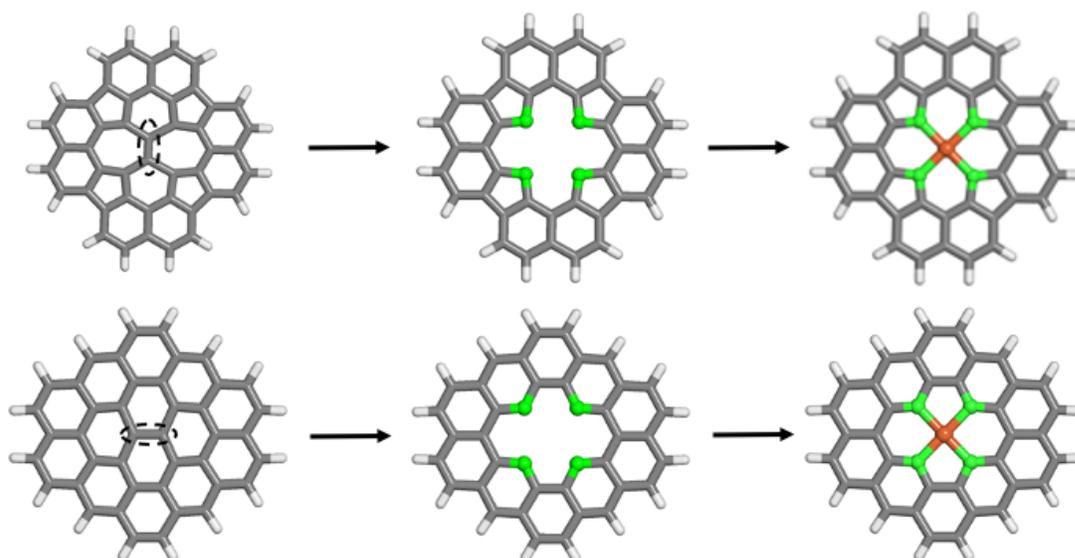Haojun Jia[1,2], Aditya Nandy[1,2], Mingjie Liu[1], and Heather J. Kulik[1,*]

[1]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

[2]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

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Figure S1. Creation of a divacancy in 5- and 6-membered ring graphene flakes (top and bottom respectively). The two carbon atoms annotated with a dashed circle are removed to create a vacancy (left). The four nearest carbon atoms to this region are replaced by dopant atoms (middle). Finally, the Fe atom is embedded in the middle of the divacancy to complete the SAC model (right).

Table S1. Total energies (in Ha) for LS and IS N-doped 5- and 6-membered ring SACs and intermediates.

system	spin state	resting state energy (Ha)	oxo energy (Ha)	hydroxyl energy (Ha)	methanol energy (Ha)
5-membered Fe-N-C	LS	-1874.8439	-1949.9342	-1950.6178	-1990.4720
	IS	-1874.9148	-1949.9961	-1950.6391	-1990.5272
6-membered Fe-N-C	LS	-1721.9736	-1797.0657	-1797.7547	-1837.6396
	IS	-1722.0352	-1797.1170	-1797.7630	-1837.5627

Table S2. Spin splitting energy (in kcal/mol) for LS and IS N-doped 5- and 6-membered ring SACs.

| system	ΔE_{I-L} spin splitting energy (kcal/mol)			
	resting state	oxo	hydroxyl	methanol
5-membered Fe-N-C	-44.49	-38.87	-13.35	-34.68
6-membered Fe-N-C	-38.63	-32.19	-5.21	-38.63

Table S3. Reaction energetics (in kcal/mol) for LS and IS N-doped 5- and 6-membered ring SACs.

system	spin state	ΔE(oxo) (kcal/mol)	ΔE(HAT) (kcal/mol)	ΔE(rebound) (kcal/mol)	ΔE(release) (kcal/mol)
5-membered Fe-N-C	LS	-12.69	-3.42	-39.76	19.02
	IS	-7.07	22.09	-61.09	9.21
6-membered Fe-N-C	LS	-13.83	-6.79	-59.05	42.81
	IS	-7.30	20.17	-72.82	23.17

Table S4. Spin states and charges for 5- and 6-membered ring SAC models, 14-membered macrocyclic Fe complexes, and transition-metal complexes with different coordinating atoms (N, O, P and S). For all SAC models, the spin states of other catalytic intermediates are also indicated. Systems that were not explicitly studied in this work are indicated with "--". In all instances, we treat iron as Fe(II) and add it with a net charge of +2.

system	resting state spin state	metal oxo spin state	metal hydroxyl spin state	metal methanol spin state	system charge
5-membered ring SAC					
Fe-N-C	singlet	singlet	doublet	singlet	-2
Fe-O-C	singlet	singlet	doublet	singlet	+2
Fe-P-C	singlet	singlet	doublet	singlet	-2
Fe-S-C	singlet	singlet	doublet	singlet	+2
6-membered ring SAC					
Fe-N-C	singlet	singlet	doublet	singlet	+2
Fe-O-C	singlet	singlet	doublet	singlet	+2
Fe-P-C	singlet	singlet	doublet	singlet	+2
Fe-S-C	singlet	singlet	doublet	singlet	+2
14-membered macrocycle					
Fe-N-C	singlet	--	--	--	+2
Fe-O-C	singlet	--	--	--	+2
Fe-P-C	singlet	--	--	--	+2
Fe-S-C	singlet	--	--	--	+2
TMC					
Fe(pyridine)$_6$	singlet	--	--	--	+2
Fe(4H-pyran)$_6$	singlet	--	--	--	+2
Fe(phosphinine)$_6$	singlet	--	--	--	+2
Fe(4H-thiopyran)$_6$	singlet	--	--	--	+2
Fe(pyrrole)$_6$	singlet	--	--	--	-4
Fe(furan)$_6$	singlet	--	--	--	+2
Fe(pospholide)$_6$	singlet	--	--	--	-4
Fe(thiophene)$_6$	singlet	--	--	--	+2
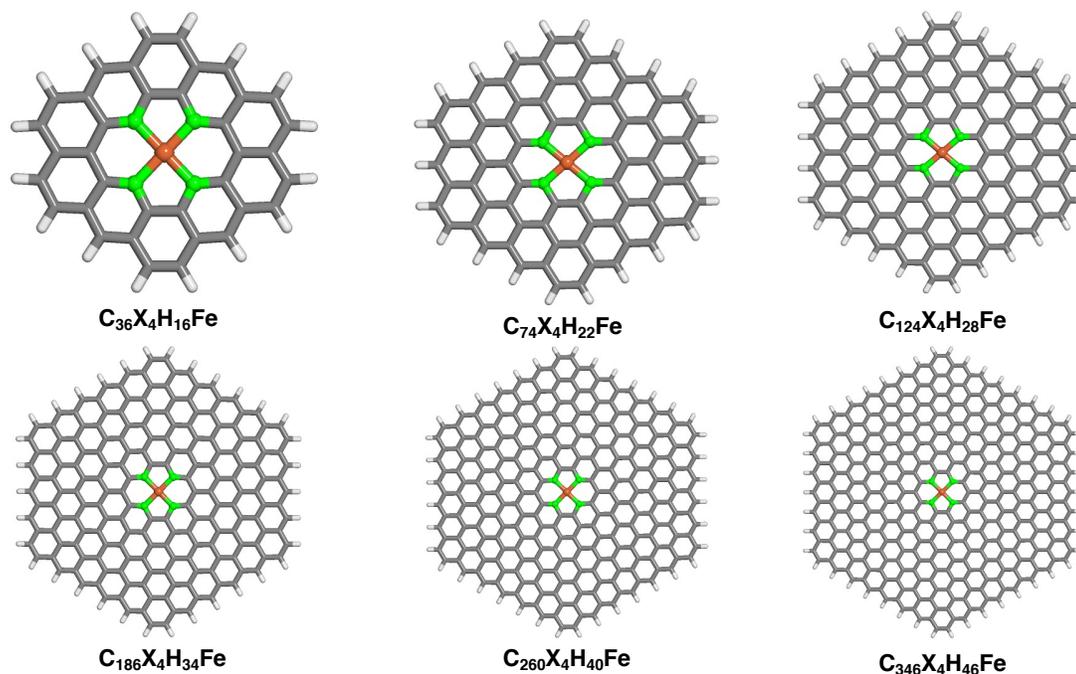
Figure S2. Atomic structures of increasingly large SACs with different coordinating atoms shown in green (X = N, O, P or S). The representative structures are shown in ball-and-stick representation colored as follows: Fe in brown, C in gray, and H in white.

The structures shown are: $C_{36}X_4H_{16}Fe$, $C_{74}X_4H_{22}Fe$, $C_{124}X_4H_{28}Fe$, $C_{186}X_4H_{34}Fe$, $C_{260}X_4H_{40}Fe$, $C_{346}X_4H_{46}Fe$
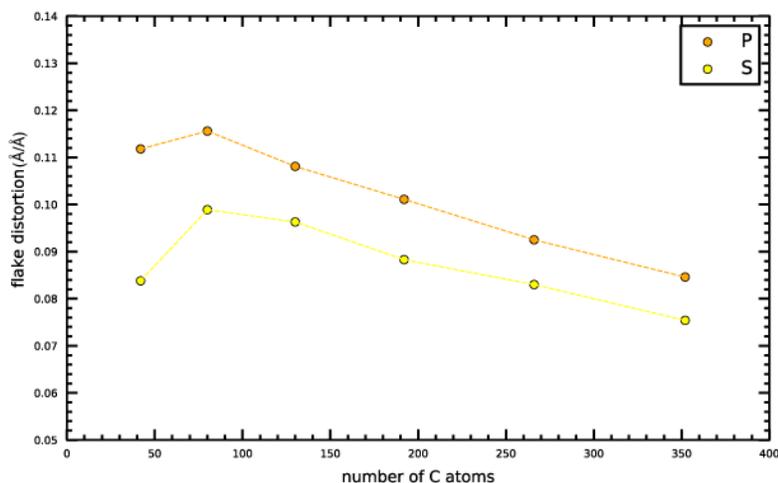
Figure S3. Normalized flake distortion of increasingly large P- and S-coordinating SACs with full geometry optimization. Distortion is quantified by measuring the distance of the center of mass from the initial planar SAC geometry after dividing the size of corresponding flake. Here, the number of C atoms refers to all atoms in the flake prior to insertion of the vacancy and placement of the dopants and iron.

Table S5. Out-of-plane distortion of increasingly large SACs with P- and S-coordinating atoms for full geometry optimization as quantified by distance of the center of mass from the initial planar SAC geometry. All distances are in units of Å.

system	out-of-plane distortion X=P	out-of-plane distortion X=S
$C_{36}X_4H_{16}Fe$	1.52	1.14
$C_{74}X_4H_{22}Fe$	2.07	1.77
$C_{124}X_4H_{28}Fe$	2.39	2.13
$C_{186}X_4H_{34}Fe$	2.67	2.33
$C_{260}X_4H_{40}Fe$	2.84	2.55
$C_{346}X_4H_{46}Fe$	2.96	2.64
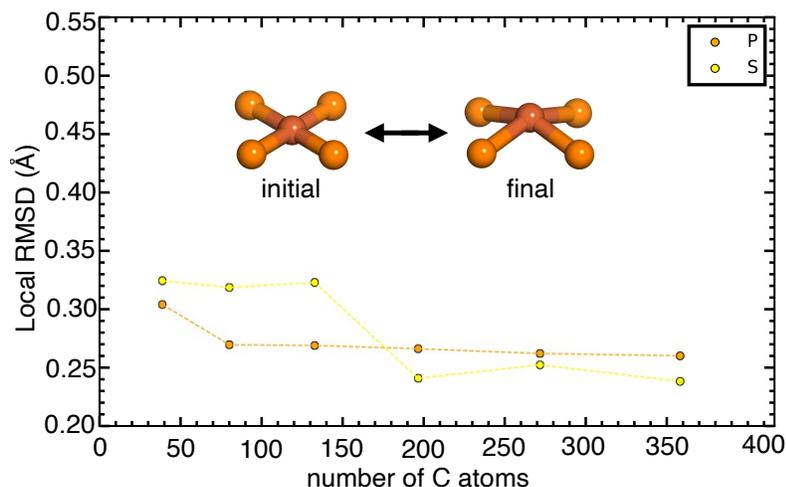
Figure S4. Local root-mean-square deviation (RMSD) of the metal and four coordinating atoms of increasingly large P- and S-coordinating SACs as quantified by the difference between the initial planar and the fully optimized distorted structures. Here, the number of C atoms refers to all atoms in the flake prior to insertion of the vacancy and placement of the dopants and iron.

Table S6. Average metal–ligand bond lengths of increasingly large SACs with different coordinating atoms (N, O, P and S). All distances are in units of Å.

system	bond length X=N	bond length X=O	bond length X=P	bond length X=S
$C_{36}X_4H_{16}Fe$	1.92	1.90	2.15	2.21
$C_{74}X_4H_{22}Fe$	1.90	1.90	2.07	2.10
$C_{124}X_4H_{28}Fe$	1.91	1.89	2.07	2.11
$C_{186}X_4H_{34}Fe$	1.91	1.90	2.07	2.09
$C_{260}X_4H_{40}Fe$	1.88	1.89	2.06	2.10
$C_{346}X_4H_{46}Fe$	1.87	1.90	2.06	2.09

5-membered ring		6-membered ring	

P-coordinated SAC	S-coordinated SAC	P-coordinated SAC	S-coordinated SAC
θ= 3.9 degree	θ= -11.1 degree	θ= 19.3 degree	θ= -3.3 degree
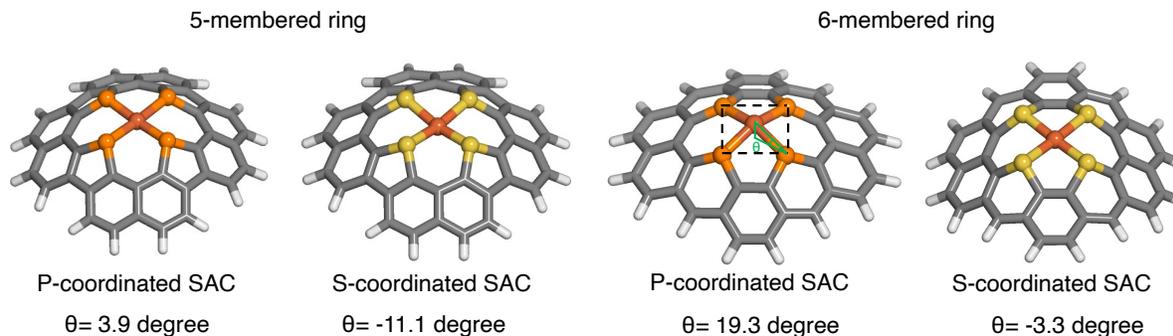
Figure S5. The metal dihedral angle, θ, is the dihedral angle between the Fe metal and the plane formed by any 3 of the 4 coordinating atoms. This angle is shown schematically in the P-coordinated 5-membered ring SAC. A negative value for this angle indicates that metal lies below the coordinating atom plane.

Table S7. Average metal–ligand bond lengths (BLs, in Å) of 5- and 6-membered SAC models, 14-membered macrocyclic complexes, and mononuclear transition-metal complex analogues with and without constraints out of the plane (i.e., the z-axis, for the 5-membered and 6-memebered SAC only). Results are shown for cases where all coordinating atoms are one of four elements (N, O, P and S). Systems that were not constrained and have no result are indicated as "--".

system	full geometry optimization average M-L BL (Å)	constrained z-axis average M-L BL (Å)
5-membered ring SAC		
Fe-N-C	1.97	1.97
Fe-O-C	1.99	1.99
Fe-P-C	2.19	1.95
Fe-S-C	2.15	1.97
6-membered ring SAC		
Fe-N-C	1.92	1.92
Fe-O-C	1.89	1.89
Fe-P-C	2.15	2.01
Fe-S-C	2.21	1.94
14-membered macrocycle		
Fe-N-C	1.84	--
Fe-O-C	1.87	--
Fe-P-C	2.09	--
Fe-S-C	2.13	--
octahedral transition metal complex		
Fe(pyridine)$_6$	2.11	--
Fe(4H-pyran)$_6$	2.17	--
Fe(phosphinine)$_6$	2.25	--
Fe(4H-thiopyran)$_6$	2.38	--
Fe(pyrrole)$_6$	2.11	--
Fe(furan)$_6$	2.03	--
Fe(phospholide)$_6$	2.33	--
Fe(thiophene)$_6$	2.38	--

5-membered ring

6-membered ring

N-coordinated SAC
θ= 0 degree

N-coordinated SAC-oxo
θ= 10.8 degree

N-coordinated SAC
θ= 0 degree

N-coordinated SAC-oxo
θ= 11.2 degree

N-coordinated SAC-hydroxyl
θ= 8.9 degree

N-coordinated SAC-methanol
θ= 4.1 degree

N-coordinated SAC-hydroxyl
θ= 7.0 degree

N-coordinated SAC-methanol
θ= 4.2 degree

O-coordinated SAC
θ= 0 degree

O-coordinated SAC-oxo
θ= 8.0 degree

O-coordinated SAC
θ= 0 degree

O-coordinated SAC-oxo
θ= 7.2 degree

O-coordinated SAC-hydroxyl
θ= 8.5 degree

O-coordinated SAC-methanol
θ= 5.5 degree

O-coordinated SAC-hydroxyl
θ= 5.7 degree

O-coordinated SAC-methanol
θ= 8.2 degree

Figure S6. The metal dihedral angle, θ (labeled on the N-coordinating 5-membered ring oxo intermediate structure), is the dihedral angle between the Fe metal and the plane formed by 3 coordinating atoms. We annotate this angle for each intermediate (resting state, oxo, hydroxyl, methanol) in the radical rebound mechanism for conversion of methane to methanol.

Table S8. The average dopant–dopant distance (in Å) for 5- and 6-membered SAC models with different coordinating atoms (N, O, P and S).

system	dopant-dopant distance (Å)
5-membered ring SAC	
Fe-N-C	2.80
Fe-O-C	2.80
Fe-P-C	3.10
Fe-S-C	3.11
6-membered ring SAC	
Fe-N-C	2.63
Fe-O-C	2.78
Fe-P-C	2.95
Fe-S-C	3.13

Table S9. Covalent radii of X bonds (in Å). The low-spin (LS) Fe covalent radius is estimated to be 1.42 Å[1].

X	X radius (Å)
N	0.71
O	0.66
P	1.07
S	1.05

Table S10. Relative metal−ligand bond length, d_{rel}(Fe−X), of 5- and 6-membered ring SAC models, 14-membered macrocyclic Fe complexes and mononuclear transition-metal complex analogues with different coordinating atoms (N, O, P and S). All relative bond lengths are unitless because they are the ratios of the bond length to the sum of the covalent radii of the substituent atoms.

system	d_{rel}(Fe–X)
5-membered ring SAC	
Fe-N-C	0.93
Fe-O-C	0.95
Fe-P-C	0.88
Fe-S-C	0.87
6-membered ring SAC	
Fe-N-C	0.90
Fe-O-C	0.91
Fe-P-C	0.87
Fe-S-C	0.89
14-membered macrocycle	
Fe-N-C	0.86
Fe-O-C	0.90
Fe-P-C	0.84
Fe-S-C	0.86
octahedral transition metal complex	
Fe(pyridine)$_6$	0.99
Fe(4H-pyran)$_6$	1.04
Fe(phosphinine)$_6$	0.90
Fe(4H-thiopyran)$_6$	0.96
Fe(pyrrole)$_6$	0.99
Fe(furan)$_6$	0.97
Fe(phospholide)$_6$	0.94
Fe(thiophene)$_6$	0.96

Table S11. Complexation energies (in eV) of 5- and 6-membered ring SAC models and 14-membered macrocyclic Fe complexes with different coordinating atoms (N, O, P and S) and constraint conditions.

system	full geometry optimization complexation energy (eV)	constrained z-axis complexation energy (eV)	difference between full and constrained (eV)
5-membered ring SAC			
Fe-N-C	-38.08	-38.09	0.01
Fe-O-C	-31.18	-31.18	0.00
Fe-P-C	-33.54	-32.17	-1.37
Fe-S-C	-32.63	-32.03	-0.60
6-membered ring SAC			
Fe-N-C	-37.37	-37.58	0.20
Fe-O-C	-28.60	-28.75	0.14
Fe-P-C	-33.64	-32.10	-1.54
Fe-S-C	-31.39	-29.84	-1.55
14-membered macrocycle			
Fe-N-C	-38.24	--	--
Fe-O-C	-28.10	--	--
Fe-P-C	-33.39	--	--
Fe-S-C	-29.14	--	--

Table S12. Comparison of Mulliken spin density on the metal for each intermediate.

system	resting state Mulliken spin density	metal oxo Mulliken spin density	metal hydroxyl Mulliken spin density	metal methanol Mulliken spin density
5-membered ring SAC				
Fe-N-C	0.00	0.00	0.989	0.00
Fe-O-C	0.00	0.00	0.814	0.00
Fe-P-C	0.00	0.00	0.975	0.00
Fe-S-C	0.00	0.00	0.893	0.00
6-membered ring SAC				
Fe-N-C	0.00	0.00	0.952	0.00
Fe-O-C	0.00	0.00	1.034	0.00
Fe-P-C	0.00	0.00	0.955	0.00
Fe-S-C	0.00	0.00	0.986	0.00

Table S13. The natural charges and Fe $3d$ orbital populations for 5- and 6-membered SACs with different coordinating atoms (N, O, P and S).

system	natural charge	NBO $3d$ orbital population
5-membered ring SACs		
Fe-N-C	0.87457	6.74
Fe-O-C	0.98444	6.64
Fe-P-C	0.35333	7.26
Fe-S-C	0.59156	7.07
6-membered ring SACs		
Fe-N-C	1.03059	6.71
Fe-O-C	0.56377	7.05
Fe-P-C	0.36083	7.24
Fe-S-C	0.58992	7.07

Table S14. The flake oxidation energy (in eV) (i.e., the energy for oxo formation) for 5- and 6-membered flakes with different coordinating atoms (N, O, P and S) and no metal present. The favorable oxo formation on the P-containing flake is due to formation of a μ-oxo that cannot form when a metal is present. All other oxidation energies are less favorable than the equivalent metal-oxo formation.

| system	flake oxidation energy (eV)
5-membered ring flakes	
N-C	-0.40
O-C	2.95
P-C	-2.61
S-C	-0.23
6-membered ring flakes	
N-C	0.52
O-C	2.50
P-C	-5.77
S-C	-0.62
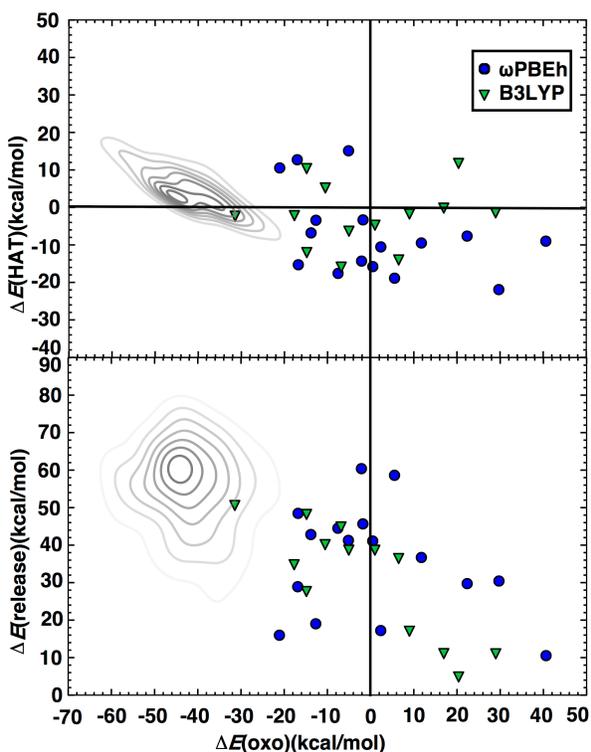
Figure S7. ΔE(oxo) vs ΔE(HAT) (top) and ΔE(oxo) vs ΔE(release) (bottom) reaction energies (in kcal/mol) of representative TMCs from prior work[2] computed with B3LYP/LACVP* compared to SAC reaction energies computed with ωPBEh/LACVP*, as reported in the main text, (circles) and B3LYP/LACVP* single-point energies (triangles) on the SAC models. For a subset of O-, P- and S-doped SACs in this work, the B3LYP single-point energy calculations did not converge. The TMCs from prior work are the full LS Fe(II) subset from the square pyramidal constrained (SQ) set of Ref. 2. The TMC KDEs are colored in gray and shown as contour lines with decreasing saturation in 7 evenly spaced levels. Although a different functional is employed, the energy range sampled on SACs is comparable with changing functional.
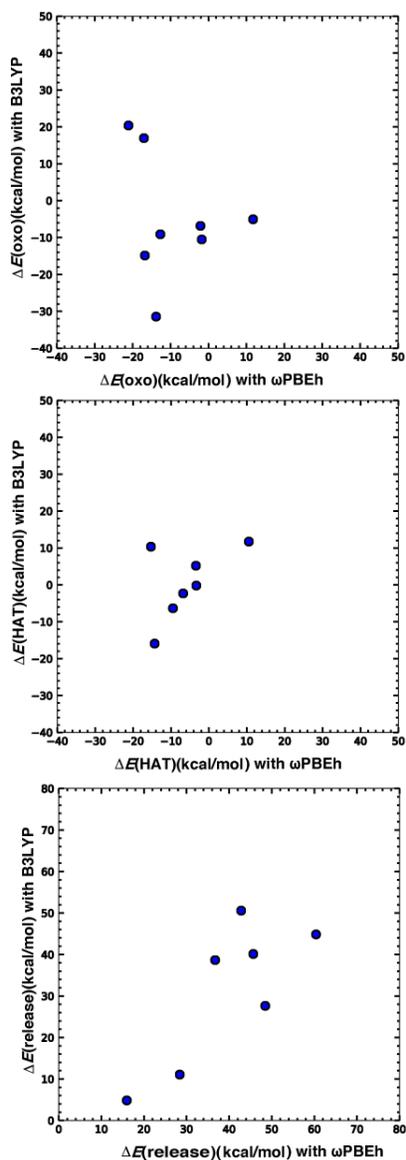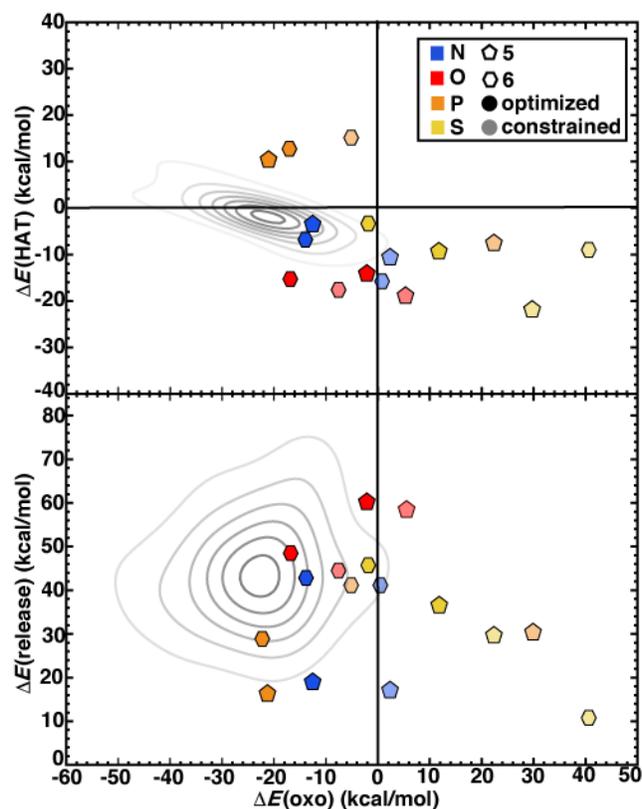
Figure S8. Parity plot of SAC reaction energies (ΔE(oxo), ΔE(HAT) and ΔE(release)) between the ωPBEh and B3LYP functionals with the LACVP* basis set in kcal/mol. The B3LYP/LACVP* energies are evaluated as single-point energies on the ωPBEh structures.
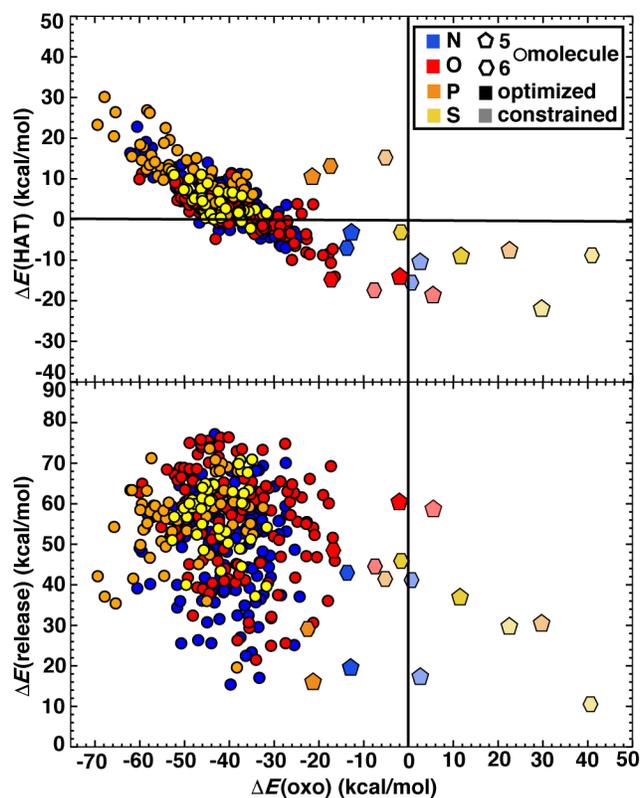
Figure S9. ΔE(oxo) vs ΔE(HAT) (top) and ΔE(oxo) vs ΔE(release) (bottom) reaction energies (in kcal/mol) of representative transition-metal complexes (TMCs) from prior work[2] compared to 5- (pentagon symbols) and 6-membered (hexagon symbols) ring SAC systems. Both TMCs and SACs are colored by the metal-coordinating atoms in the ligands, as indicated in inset legend. The TMCs are from the all LS Fe(II) in the square pyramidal constrained (SQ) set in Ref. 2. For the complexes containing multiple coordinating atom elements, the symbol is colored by the heavier coordinating atom. The SACs are further distinguished by full geometry optimization (opaque) and constrained z-axis optimization (translucent).
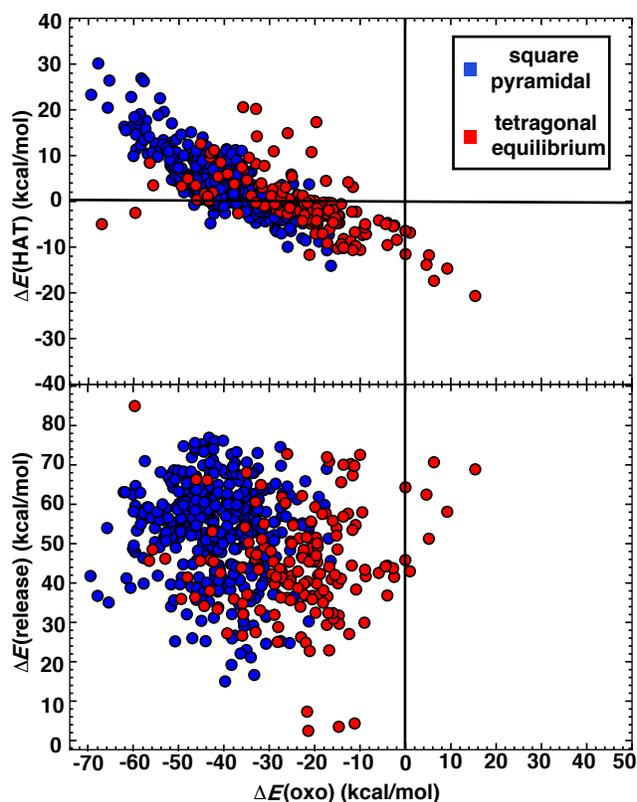
Figure S10. ΔE(oxo) vs ΔE(HAT) (top) and ΔE(oxo) vs ΔE(release) (bottom) reaction energies (in kcal/mol) of 80 homoleptic LS Fe(II) molecular complexes from the SQ data set in Ref.[2] relative to 5- (pentagon) and 6-membered (hexagon) ring SAC systems. Both TMCs and SACs are colored by metal-coordinating atoms as indicated in inset legend. The TMCs are from the all LS Fe(II) in the square pyramidal constrained (SQ) set in Ref. 2. Representative structures of a O-doped 6-membered ring graphene flake SAC with bond length of 1.9 Å and $Fe(II)(OH_2)_4$-oxo with an out-of-plane distortion angle of 10° and bond length of 2.2 Å are shown in inset. The SACs are further distinguished by full geometry optimization (opaque) and constrained z-axis optimization (translucent).
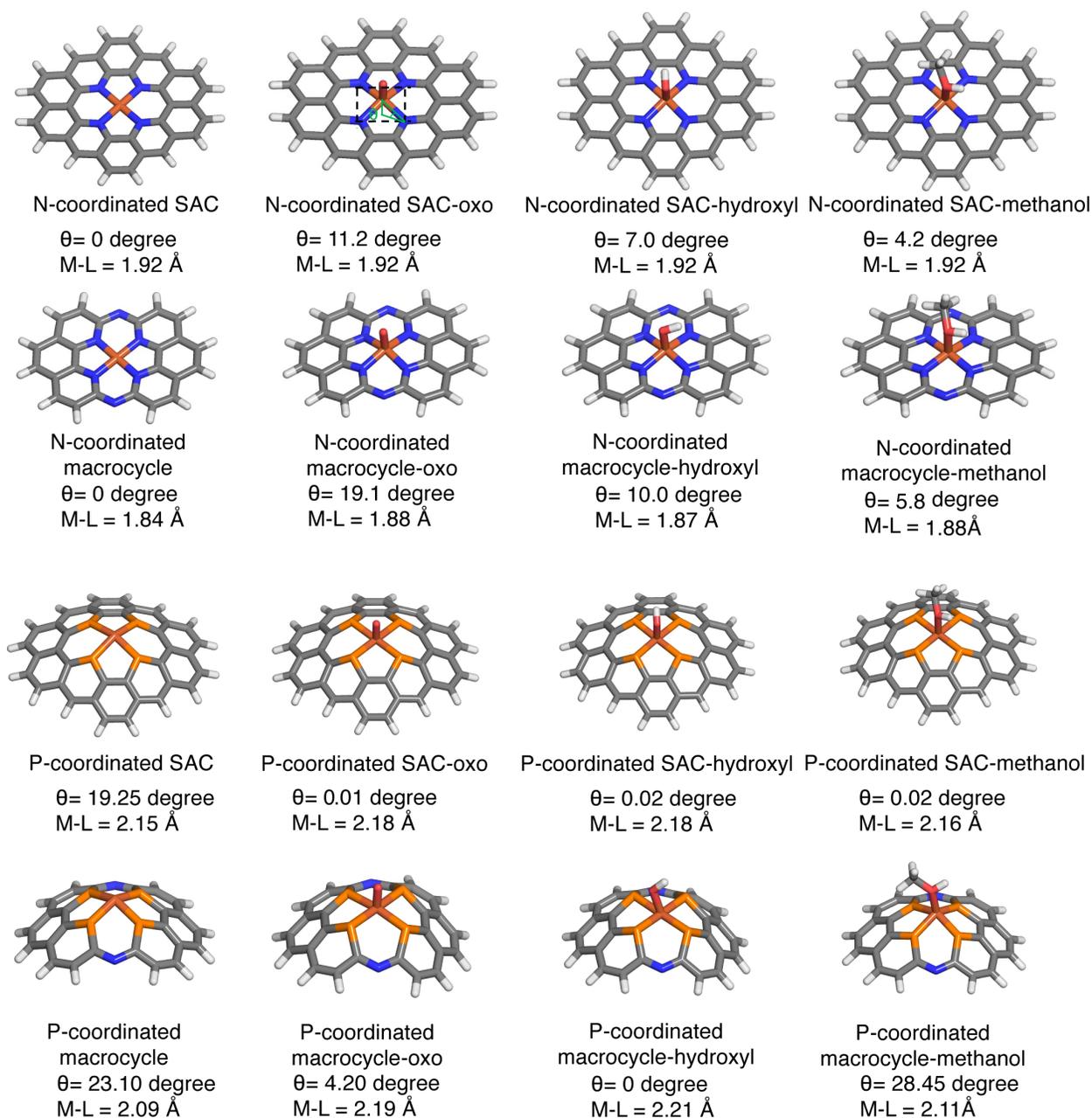
Figure S11. ΔE(oxo) vs ΔE(HAT) (top) and ΔE(oxo) vs ΔE(release) (bottom) reaction energies (in kcal/mol) of representative TMCs from prior work[2] compared to 5- (pentagon symbols) and 6-membered (hexagon symbols) ring SAC systems. The SACs are colored by the metal-coordinating atoms in the ligands, as indicated in inset legend. The TMCs are from the all LS Fe(II) in the tetragonal equilibrium (TE) set in Ref. 2. The TMCs KDEs are colored in gray and shown as contour lines with decreasing saturation in 7 evenly spaced levels. The SACs are distinguished by full geometry optimization (opaque) and constrained z-axis optimization (translucent).
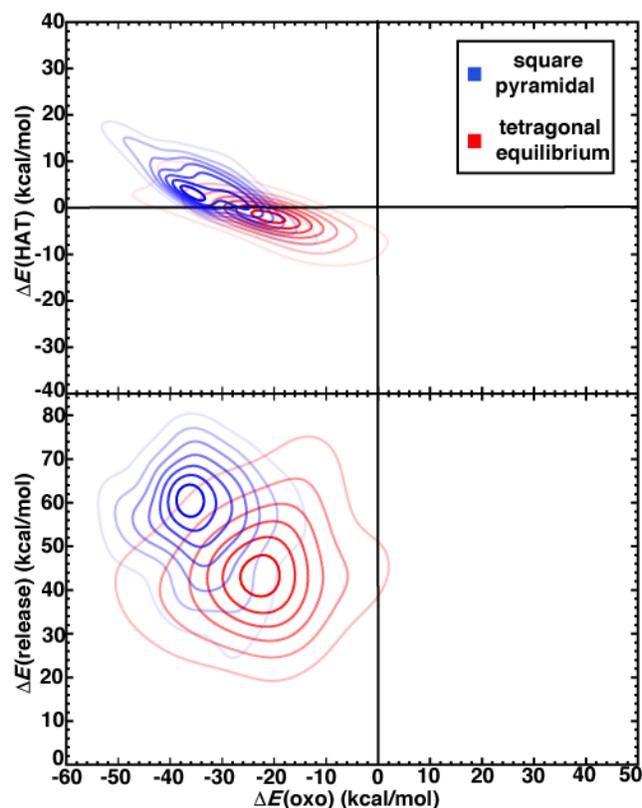
Figure S12. $\Delta E(oxo)$ vs $\Delta E(HAT)$ (top) and $\Delta E(oxo)$ vs $\Delta E(release)$ (bottom) reaction energies (in kcal/mol) for representative TMCs from prior work[2]. The TMCs are from the all LS Fe(II) in the tetragonal equilibrium (TE) and square pyramidal (SQ) set in Ref. 2. The TE and SQ TMC KDEs are colored in red and blue, respectively, and shown as contour lines with decreasing saturation in 7 evenly spaced levels.

Figure S13. ΔE(oxo) vs ΔE(HAT) (top) and ΔE(oxo) vs ΔE(release) (bottom) reaction energies (in kcal/mol) of representative TMCs from prior work[2]. The TMCs are from the all LS Fe(II) in the tetragonal equilibrium (TE) and square pyramidal (SQ) set in Ref. 2. The TE and SQ TMC scatters are colored in red and blue, respectively. To show structure in the data, the y-axis scale has been slightly truncated in a manner that excludes four points from LS Fe(II) complexes in the TE set (in red) with very high release values.

N-coordinated SAC
θ= 0 degree
M-L = 1.92 Å

N-coordinated SAC-oxo
θ= 11.2 degree
M-L = 1.92 Å

N-coordinated SAC-hydroxyl
θ= 7.0 degree
M-L = 1.92 Å

N-coordinated SAC-methanol
θ= 4.2 degree
M-L = 1.92 Å

N-coordinated
macrocycle
θ= 0 degree
M-L = 1.84 Å

N-coordinated
macrocycle-oxo
θ= 19.1 degree
M-L = 1.88 Å

N-coordinated
macrocycle-hydroxyl
θ= 10.0 degree
M-L = 1.87 Å

N-coordinated
macrocycle-methanol
θ= 5.8 degree
M-L = 1.88Å

P-coordinated SAC
θ= 19.25 degree
M-L = 2.15 Å

P-coordinated SAC-oxo
θ= 0.01 degree
M-L = 2.18 Å

P-coordinated SAC-hydroxyl
θ= 0.02 degree
M-L = 2.18 Å

P-coordinated SAC-methanol
θ= 0.02 degree
M-L = 2.16 Å

P-coordinated
macrocycle
θ= 23.10 degree
M-L = 2.09 Å

P-coordinated
macrocycle-oxo
θ= 4.20 degree
M-L = 2.19 Å

P-coordinated
macrocycle-hydroxyl
θ= 0 degree
M-L = 2.21 Å

P-coordinated
macrocycle-methanol
θ= 28.45 degree
M-L = 2.11Å

Figure S14. The metal dihedral angle, θ (labeled on the the N-coordinating SAC oxo intermediate structure), is the dihedral angle between the Fe metal and the plane formed by 3 coordinating atoms. We report this angle for each intermediate (resting state, oxo, hydroxo, methanol) in the radical rebound mechanism for methane-to-methanol conversion.
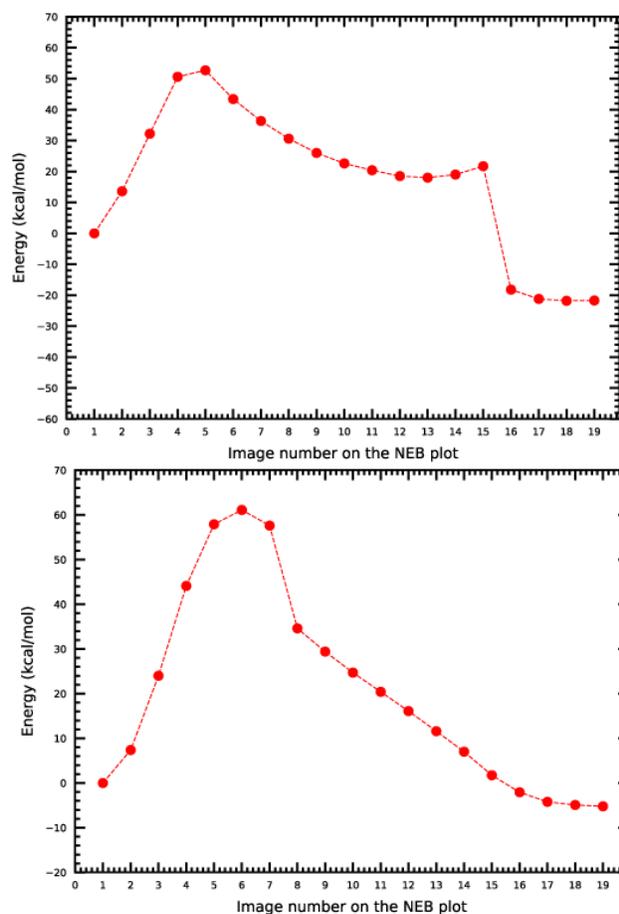
Figure S15. The last cycle of Nudged Elastic Band (NEB) in TeraChem (ωPBEh/LACVP*) for oxo formation putative transition states on N-doped 5- and 6-membered ring SACs (top and bottom respectively).
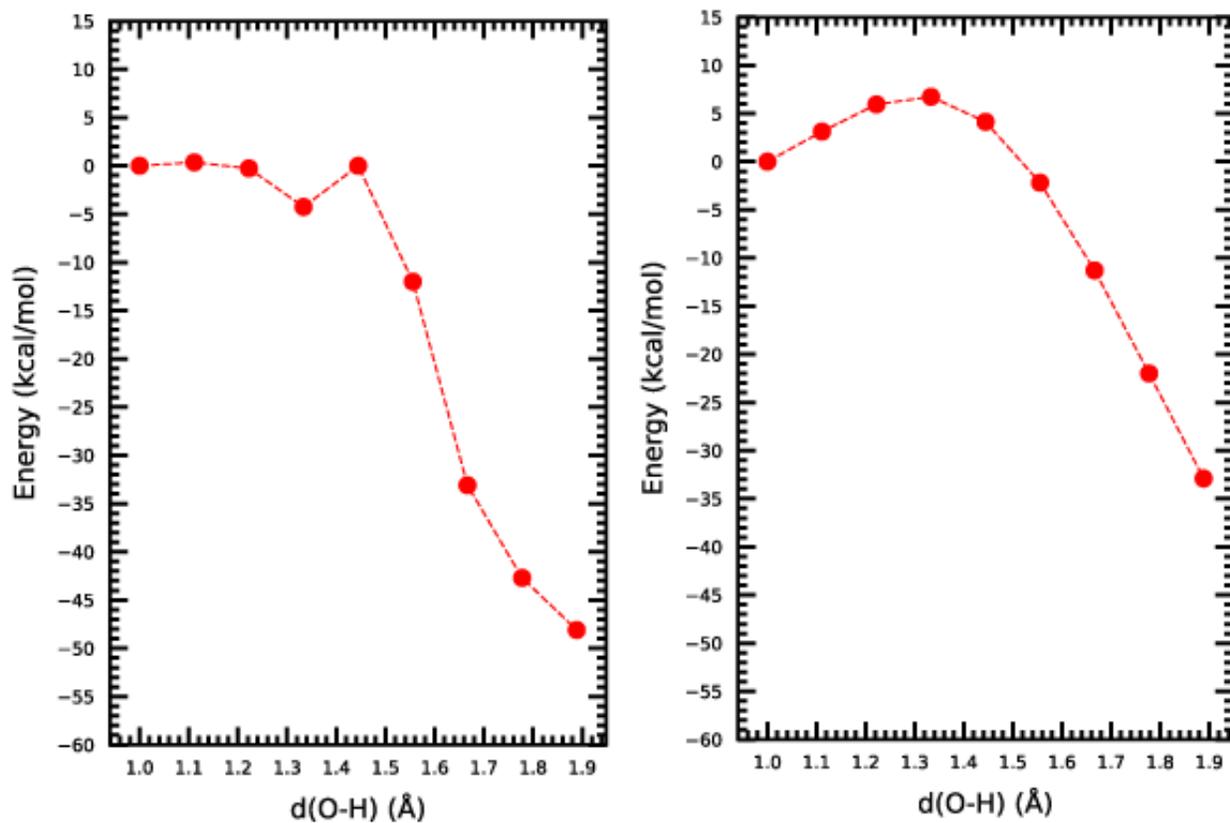
Figure S16. The bond length scan between O and H during hydrogen atom transfer (HAT) on N-doped 5- and 6-membered ring SACs (left and right respectively).

References

1.   B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans*., 2008, 2832-2838.
2.   A. Nandy and H. J. Kulik, *ACS Catal*., 2020, **10**, 15033-15047.