Supporting Information A computational mechanistic study of CH hydroxylation with mononuclear copper-oxygen complexes

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S1 Transition structure search

Two approaches are employed to locate and verify transition structures (TSs). First, a TS guess is generated using the freezing-string method (FSM), in which a double-ended reaction path is constructed by sequential interpolation and optimization between an initial and final structure.^{1,2} The TS guess is refined using partitioned-rational function optimization.³ Once a TS is calculated, the intrinsic reaction coordinate (IRC) is calculated to verify the TS by creating a downhill path from the TS to find the corresponding reactant and product states.⁴

If the first approach fails to locate a TS, we construct TS guess structures by hand based on intuition or successfully determined TSs for other spin states. For example, as the first approach successfully finds a singlet TSoxo (TS for the OXO pathway) but fails in finding a triplet TSoxo for the oxyl complex, we adopt the optimized singlet TSoxo for the input of triplet TSoxo search, using the Hessian calculated at the singlet state to guide P-RFO. The remaining steps of TS search and verification are identical to the first approach.

The above calculations are conducted with unrestricted DFT, with two exceptions. Spin-restricted DFT is necessary to locate singlet TS2 for the oxyl complex 1 and restricted open-shell Kohn-Sham (ROKS) is necessary to find singlet TS3 for the superoxo complex 2. Two singlet TSs for complex 2, TS1_S and TS3_S, contain a second, very small imaginary frequency ($|\omega| < 100 \text{ cm}^{-1}$) in their vibrational spectrum in addition to the imaginary frequency corresponding to the reaction coordinate. In these two cases, the zero-point energy is calculated by replacing that imaginary mode with 100 cm⁻¹.

S2 Catalyst geometries: Dihedral angles

Dihedral angles for oxyl and superoxo complexes are shown in Table S1. The dihedral angle between two half-planes formed by atom O/O_1-Cu-N_3 and N_2-Cu-N_3 is denoted by α . The dihedral angles between two half-planes formed by atom O/O_1-Cu-N_1 and N_1-Cu-N_2 is denoted by β . α and β angles closer to 180° indicates planar geometries. Catalyst geometries are bent when α and β angles deviate strongly from 180°.

	α (°)	β (°)		
		DFT	176.3	176.3
	\mathbf{S}	ROKS	178.7	178.7
		CDFT	179.4	179.4
$[Cu(II)O(Im)_3]^+$	Т	Planar, DFT, (a)	177.0	177.0
		Nonplanar, DFT, (b)	147.0	146.9
		Planar, $CDFT$, (c)	177.4	177.4
		Nonplanar, CDFT, (d)	165.6	165.4
	S	DFT	162.5	162.6
		ROKS	164.3	164.9
$[Cu(II)OO(Im)_3]^+$		CDFT	165.5	165.8
	Т	CDFT (a)	167.7	167.2
		CDFT (b)	153.1	151.1

Table S1: Dihedral angles for singlet and triplet oxyl and superoxo bare catalysts.

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S3 PES scan: Complex 2

Unrestricted DFT optimization of the triplet superoxo $[CuOO(Im)_3]^+$ complex yields a structure in which O_2 is dissociated from the complex. To understand the reason why unrestricted DFT fails in reaching a energy minimum, a potential energy surface (PES) scan is carried out by systematically varying $Cu-O_1$ distance and relaxing the remaining geometry at every value. Figure S1 shows the energy profile for stable states when the $Cu-O_1$ distance is varied between 1.8 Å and 2.6 Å. Energy decreases monotonically with increasing $Cu-O_1$ separation. We believe this is a consequence of over-delocalization of electron density that favors greater $Cu-O_1$ separation. Therefore, unrestricted DFT is unable to find a minimum energy triplet superoxo complex.



Figure S1: PES scan with unrestricted DFT as a function of varying $Cu-O_1$ distance for the triplet superoxo $[CuOO(Im)_3]^+$ complex. The energy for a geometry with $r(Cu-O_1) = 1.80$ Å is selected as the reference.

S4 Electronic structure characterization

Table S2 and Table S3 list natural bond orbital (NBO) charges of key atoms for all states along reaction pathways with the $[Cu(II)O(Im)_3]^+$ and $[Cu(II)OO(Im)_3]^+$ complexes.

Table S2: NBO charges for all states along the reaction pathways of the $[Cu(II)O(Im)_3]^+$ complex. H₁ is the hydrogen atom participating CH activation and H₂₋₄ are other hydrogen atoms originally in the substrate.

State	Cu	0	\mathbf{C}	\mathbf{H}_1	\mathbf{H}_2	\mathbf{H}_3	\mathbf{H}_4	\mathbf{CH}_{3}	\mathbf{CH}_4
IS_S	1.577	-0.827	-0.864	0.246	0.212	0.211	0.211	-0.229	0.017
INT_S	1.275	-0.985	-0.684	0.452	0.200	0.202	0.211	-0.071	0.382
FS_S	0.786	-0.755	-0.213	0.470	0.179	0.168	0.167	0.301	0.771
TSoxo_S	1.290	-1.011	-0.568	0.332	0.199	0.195	0.200	0.027	0.359
$TS1_S$	1.373	-0.935	-0.652	0.292	0.193	0.190	0.206	-0.063	0.228
$TS2_S$	1.064	-1.061	-0.234	0.457	0.164	0.205	0.205	0.340	0.796
IS_T	1.548	-0.812	-0.772	0.122	0.202	0.210	0.228	-0.133	-0.010
INT_T	1.360	-1.164	-0.491	0.445	0.166	0.158	0.175	0.008	0.452
FS_T	0.884	-0.770	-0.200	0.480	0.172	0.171	0.181	0.325	0.805
$TS1_T$	1.343	-0.913	-0.643	0.297	0.192	0.190	0.205	-0.056	0.242
$TS2_T$	1.148	-1.000	-0.415	0.189	0.462	0.176	0.170	0.394	0.583

Table S3: Charges for all states along the reaction pathways of the $[Cu(II)OO(Im)_3]^+$ complex. O_1 is the oxygenatom associated with Cu and O_2 is the oxygen-atom associated with O_1 in the bare catalyst. H_1 is the hydrogen atom participating CH activation and H_{2-4} are other hydrogen atoms originally in the substrate.

State	Cu	\mathbf{O}_1	\mathbf{O}_2	С	\mathbf{H}_1	\mathbf{H}_2	\mathbf{H}_3	\mathbf{H}_4	\mathbf{CH}_{3}	\mathbf{CH}_4
IS_S	1.558	-0.511	-0.304	-0.857	0.244	0.211	0.208	0.208	-0.230	0.014
INT_S	1.295	-0.580	-0.475	-0.498	0.463	0.161	0.176	0.164	0.003	0.466
FS_S	1.399	-0.779	-0.793	-0.202	0.503	0.165	0.174	0.168	0.305	0.808
$FS2_S$	1.415	-1.086	-0.431	-0.244	0.451	0.210	0.164	0.192	0.323	0.774
TSoxo_S	0.953	-0.376	-0.267	-0.534	0.431	0.206	0.202	0.204	0.079	0.510
$TS1_S$	1.360	-0.321	-0.271	-1.115	0.386	0.204	0.239	0.206	-0.467	-0.081
$TS2_S$	1.378	-0.675	-0.605	-0.400	0.484	0.181	0.168	0.166	0.115	0.599
$TS3_S$	1.394	-0.643	-0.637	-0.353	0.466	0.175	0.177	0.162	0.161	0.627
$TS4_S$	1.409	-0.602	-0.868	-0.197	0.461	0.178	0.155	0.164	0.299	0.761
IS_T	1.638	-0.535	-0.285	-0.829	0.226	0.219	0.192	0.192	-0.226	0.000
INT_T	1.289	-0.574	-0.471	-0.502	0.462	0.161	0.177	0.168	0.004	0.466
FS_T	1.341	-0.708	-0.787	-0.203	0.501	0.168	0.175	0.169	0.307	0.809
$FS2_T$	1.409	-0.541	-0.917	-0.224	0.454	0.174	0.180	0.189	0.319	0.773
$TS1_T$	1.252	-0.511	-0.372	-0.592	0.372	0.183	0.202	0.192	-0.014	0.358
$TS2_T$	1.355	-0.651	-0.597	-0.404	0.482	0.181	0.167	0.166	0.111	0.593
$TS3_T$	1.359	-0.601	-0.594	-0.389	0.466	0.173	0.173	0.160	0.117	0.583
$TS4_T$	1.389	-0.535	-0.888	-0.196	0.456	0.177	0.151	0.159	0.291	0.747

S5 CDFT energy difference

Table S4 reports the difference between CDFT energies and single-point energies calculated using spin-unrestricted DFT at the CDFT geometry for both singlet and triplet CAT and IS.

Table S4: Difference between CDFT energies (E_{CDFT}) and single-point energies (E_{SP}) calculated using spinunrestricted DFT at the same geometry for CAT and IS. Note that energies are not spin-corrected.

Center	State	\mathbf{Spin}	Geometry	$\mathrm{E_{CDFT}}$ - $\mathrm{E_{SP}}~(\mathrm{kJ}{\cdot}\mathrm{mol}^{-1})$
$[Cu(II)O(Im)_3]^+$		S	-	96.7
	CAT	Т	Planar	88.4
			Nonplanar	89.2
		S	-	65.5
	IS	т	Planar	54.0
		T	Nonplanar	62.9
[Cu(II)OO(Im) ₃] ⁺		S	-	92.4
	CAT	т	(a)	100.6
		T	(b)	108.2
	IS	S	-	66.9
		т	(a)	74.6
		1	(b)	105.7

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