## Supplementary Information: Computational strategies to probe CH activation in dioxo-dicopper complexes

## 1 Isomerization energies

Table 1 shows a comparison of our DFT isomerization energies, calculated with varying basis sets and both 6-31G<sup>\*</sup> basis set and Stuttgart pseudopotentials for Cu, with single and multireference wavefunction methods in the literature.  $[Cu_2(NH_3)_4O_2]^{2+}$  isomerization energies with the large basis set show some agreement with one of the single reference CCSD(T) results. However, the wide range of reported single- and multireference isomerization energies precludes any meaningful recommendation of functional/basis set. On the other hand, the isomerization energy of  $[Cu_2(en)_2O_2]^{2+}$ with even the 6-31G<sup>\*</sup> basis set is in good agreement with the LPNO-CCSD reference in the absence of relativistic (ZORA) corrections, while the srsc energies exhibit significant deviations.

Table 1: Comparison of isomerization energies (**O-P**) (kJ/mol) of  $[Cu_2(NH_3)_4O_2]^{2+}$  and  $[Cu_2(en)_2O_2]^{2+}$  with computational literature. BS1 stands for the Stuttgart small core psuedopotential (srsc)<sup>1</sup> for Cu and atomic natural orbital (ANO)<sup>2</sup> basis set for the remaining atoms.

Source	Level of Theory	$[Cu_2(NH_3)_4O_2]^{2+}$	$[Cu_2(en)_2O_2]^{2+}$
Current work	$\omega$ B97X-D/6-31G*	36.9	9.8
	$\omega$ B97X-D/srsc(Cu),6-31G*	134.9	96.6
	$\omega$ B97X-D/srsc(Cu),6-31G**	120.5	134.6
	$\omega$ B97X-D/srsc(Cu),6-311G**	118.8	131.4
Cramer et al., $2006^3$	CCSD(T)/BS1	105.9	
Cramer et al., $2006^4$	CCSD(T)/BS1	-21.75	
Cramer et al., $2006^3$	CASPT2(14,13)	-4.2	
Cramer et al., $2006^4$	CASPT2(16,14)	-88.7	
Liakos and Neese, $2011^5$	LPNO-CCSD/CBS		22.7
Liakos and Neese, $2011^5$	LPNO-CCSD(ZORA)/CBS		-11.4

## 2 Solvation effects

The effect of 2-methyltetrahydrofuran (MeTHF)<sup>6-9</sup> on singlet barriers is examined using a conductorlike polarizable continuum model (C-PCM) for implicit solvation, <sup>10-12</sup> with a dielectric constant of 6.97.<sup>13</sup> Broken symmetry barriers for oxo-insertion increase from 144.2 kJ/mol in the gas phase to 172.2 kJ/mol in MeTHF, whereas the barrier to the radical pathway changes very little, from 229.6 kJ/mol to 235.6 kJ/mol. Therefore, the singlet oxo-insertion pathway remains favorable in spite of a higher barrier compared to the gas phase.

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