Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information to

Mechanism of Hydrogen Evolution in Cu(bztpen)-Catalysed Water Reduction: A DFT Study

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S1. Computational details.

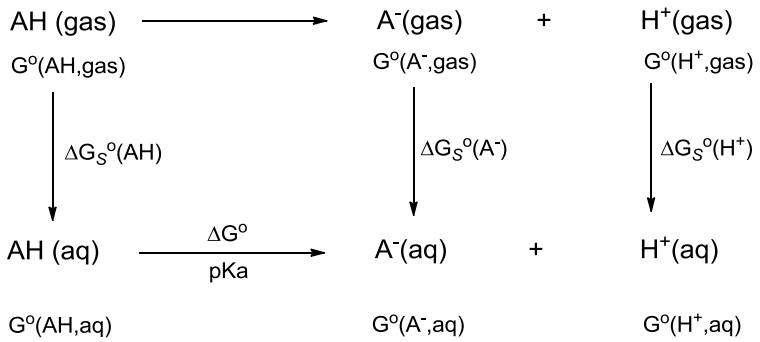
The calculations presented were done with the density functional B3LYP[S1] as implemented in the Gaussian 09 program. [S2] Geometries were optimized using the 6-31G(d,p) basis sets on all elements except for Cu, which were described by the SDD[S3] pseudopotential and its corresponding basis sets. The final and the solvation energies were calculated as single-point corrections on the optimized structures using the SMD[S4] continuum solvation model employing a larger basis set, where all elements, except Cu, were described by 6-311+G(*2df,2p*) at the B3LYP*[S5] (15% exact exchange) level. It has been shown that B3LYP* gives better results in describing relative energies in transition metal complexes.[5] D3 dispersion corrections proposed by Grimme[S6] were also added at single-points. Analytic frequency calculations were performed on all the optimized structures at the same level of theory, to identify all the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency) and to obtain Gibbs free energy corrections at 298.15 K. Reaction pathway for the H-H bond formation (**TS_C**) was subjected to intrinsic reaction coordinate (IRC) [S7] analysis, in order to trace its path and to confirm that the optimized TS structure connect reactant and product. Unless otherwise mentioned, we report the B3LYP*-D3 energies including Gibbs free energy corrections and D3 dispersion from B3LYP.

Calculation of Standard state Gibbs free energies. The standard Gibbs free energy of species *i in aqueous solution is expressed as:*

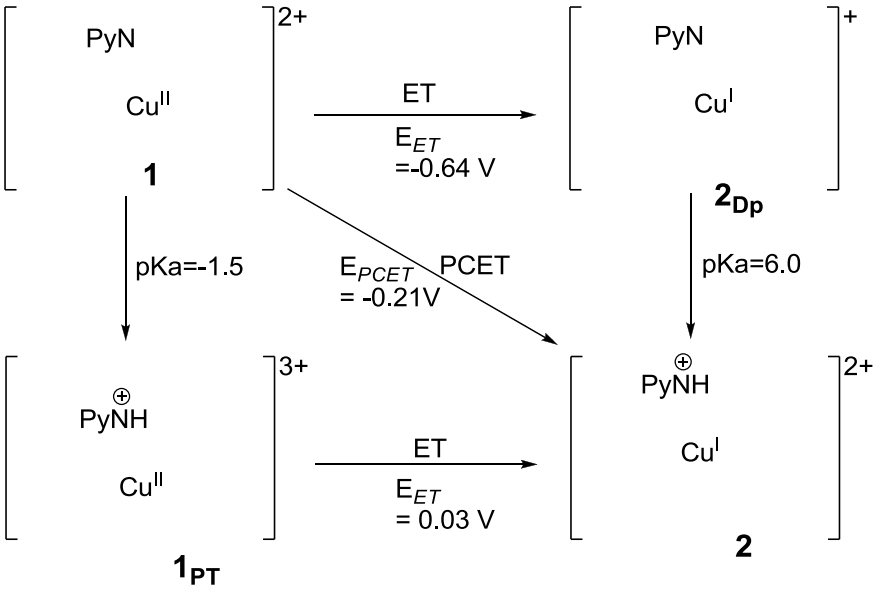
$$G^o(\text{i, aq}) = E_i(\text{i, gas}) + \Delta G_s^*(\text{i}) + \varepsilon_{ZPE}(\text{i, gas}) + G_{298K}^o(\text{i, gas}) + \text{Concentration correction} \quad (1)$$

in which E_i(i, gas) is the electronic energy in the gas phase, ΔG_s^*(i) is the solvation free energy of transferring the solute from the gas phase (1M) to a 1M aqueous solution at 298.15 K, ε_{ZPE}(i, gas) is the gas phase zero-point energy, G_{298K}^o(i, gas) is the thermal contribution to Gibbs free energy in the gas phase at 298.15 K, and the last term concentration correction is 1.9 kcal/mol for the free energy change of 1 mol of an ideal gas from 1 atm (24.5 L, 298.15 K) to 1 M aqueous solution.

Calculation of pKas. The pKa of various species were calculated using the following thermodynamic cycle. With AH as an example, the standard free energy of AH and A^- were calculated using the equation (1) as shown above. The standard free energy of proton in aqueous solution $G^o(H^+,aq)$ was estimated to be -270.3 kcal/mol (the experimental $\Delta G_s^o(H^+)$ is -264.0 kcal/mol, corresponding to 1 atm in the gas phase and 1 M in the solution phase).[S8] Therefore, the proton used is not modeled explicitly, either as H^+ or as H_3O^+.



Calculation of redox potentials. The following thermodynamic scheme is used to calculate one electron redox potential and proton-coupled electron transfer redox potential. The pKas were calculated using the protocol as shown before and were used to identify the protonation state of all species at the working pH=2.5. For the reduction of **1** to **2**, if the pKa of **2** is larger than 2.5, then **2** is the dominant species in solution, the reduction of **1** is a proton-coupled electron transfer process (see scheme below). If the pKa of **2** is smaller than 2.5, then $\mathbf{2_{Dp}}$ is the dominant species in solution, the reduction of **1** is a one electron transfer process. The absolute redox potential of H^+/H_2 (4.281 V) [S9] is used as the reference to calculate the redox potentials. The absolute redox potential of H^+/H_2 calculated using B3LYP*-D3 is 4.291 V, with an error of only 0.01 V (0.23 kcal/mol). For PCET reductions, the redox potential is increased by 1.364×(pKa – 2.5)/23.0605 V, in which the correction for the pH of the solution is considered. It should be pointed out that the experimental applied potential is not included explicitly in the calculations, and this potential is used as a reference to set up the thermodynamics for the whole energy diagram, similarly to our previous studies on photosystem II and other synthetic water oxidation catalysts.[S10-20]



To examine the sensitivity of the results to the choice of functional, single-point calculations have also been carried out using other functionals, including B3LYP-D3, M06-D3, [S21] and M06L-D3. [S22] For redox potentials (see **Table S1**), the typical error is in the range of 0.2 -0.3 V, except for M06, which underestimates the **3/2** potential by about 0.5 V. For total barriers, B3LYP*-D3, B3LYP-D3, and M06L-D3 gave very stable results, while M06-D3 overestimates the total barrier significantly due to the underestimation of the **3/2** potential.

References

S1. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
S2. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
S3. D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123-141.
S4. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.
S5. M. Reiher, O. Salomon, B. A. Hess, *Theor. Chem. Acc.*, 2001, **107**, 48-55.
S6. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
S7. C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154-2161.
S8. D. M. Camaioni, C. A. Schwerdtfeger, *J. Phys. Chem. A*, 2005, **109**, 10795-10797.
S9. A. A. Isse, A. Gennaro, *J. Phys. Chem. B*, 2010, **114**, 7894-7899.
S10. P. E. M. Siegbahn, *Chem. Eur. J.*, 2008, **14**, 8290-8302.
S11. P. E. M. Siegbahn, *Acc. Chem. Res.* 2009, **42**, 1871-1880.
S12. M. R. A. Blomberg, P. E. M. Siegbahn, *Biochim. Biophys. Acta* 2010, **1797**, 129-142.
S13. P. E. M. Siegbahn, M. R. A.Blomberg, *Chem. Rev.* 2010, **110**, 7040-7061.
S14. X. Li, G. Chen, S. Schinzel, P. E. M. Siegbahn, *Dalton. Trans.* 2011, **40**, 11296-11307.
S15. P. E. M. Siegbahn, *J. Photochem. Photobiol. B* 2011, **104**, 94-99.
S16. P. E. M. Siegbahn, *Phys. Chem. Chem. Phys.* 2012, **14**, 4849-4856.
S17. X. Li, P. E. M. Siegbahn, *J. Am. Chem. Soc.* 2013, **135**, 13804-13813.
S18. R.-Z. Liao, X. Li, P. E. M. Siegbahn, *Eur. J. Inorg. Chem.* 2014, 728-741.
S19. R.-Z. Liao, P. E. M. Siegbahn, *ACS Catal.* 2014, **4**, 3937-3949.
S20. R.-Z. Liao, M. D. Karkas, B.-L, Lee, B, Akermark, P. E. M. Siegbahn, *Inorg. Chem.* 2015, **54**, 342-351.
S21. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
S22. Y. Zhao, D. G. Truhlar, *J. Chem. Phys,*. 2006, **125**, 194101.

S2. Overlay of optimized structure of 1 and crystal structure.

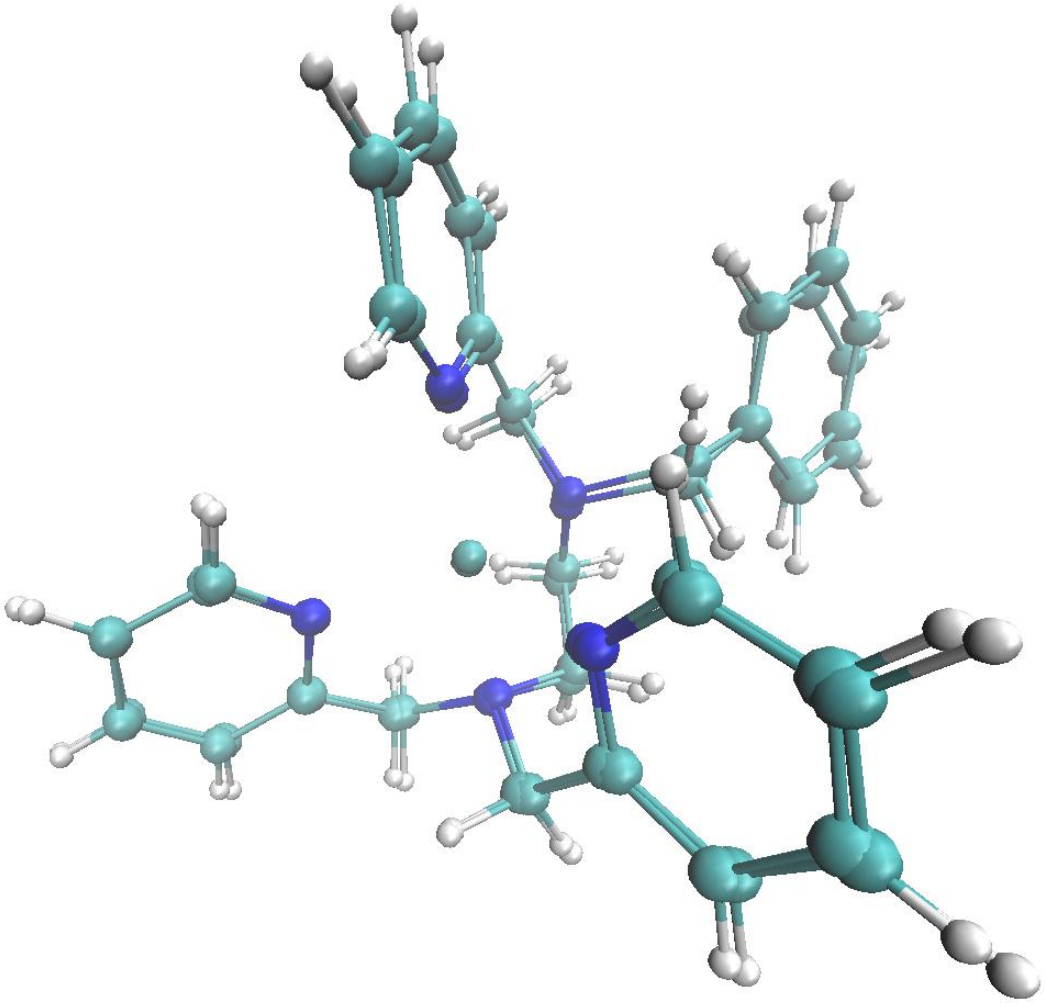


Figure S1. Overlay of the optimized structure of 1 and the crystal structure. The RMSD was calculated to be 0.161 Å.

S3. Structures of 1 in the protonated form.

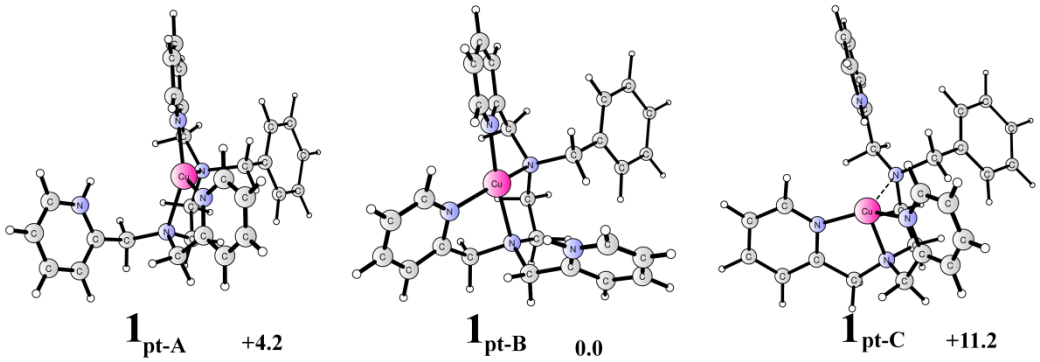


Figure S2. Optimized structure of 1 in the protonated form.

S4. Structures of 2 in the deprotonated form.

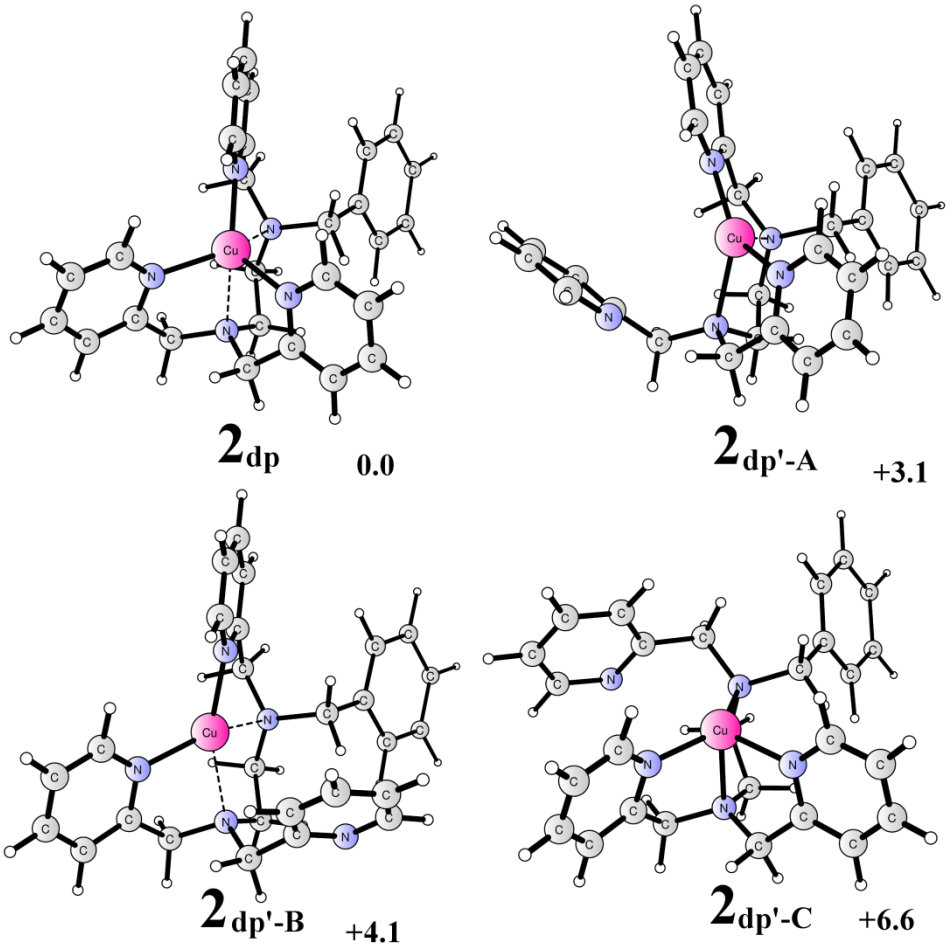


Figure S3. Optimized structure of 2 in the deprotonated form. Energies are given in kcal/mol relative to $\mathbf{2}_{\mathbf{dp}}$.

S5. Structures of transition states and intermediates for interconversion of 2_A, 2_B and 2_C.

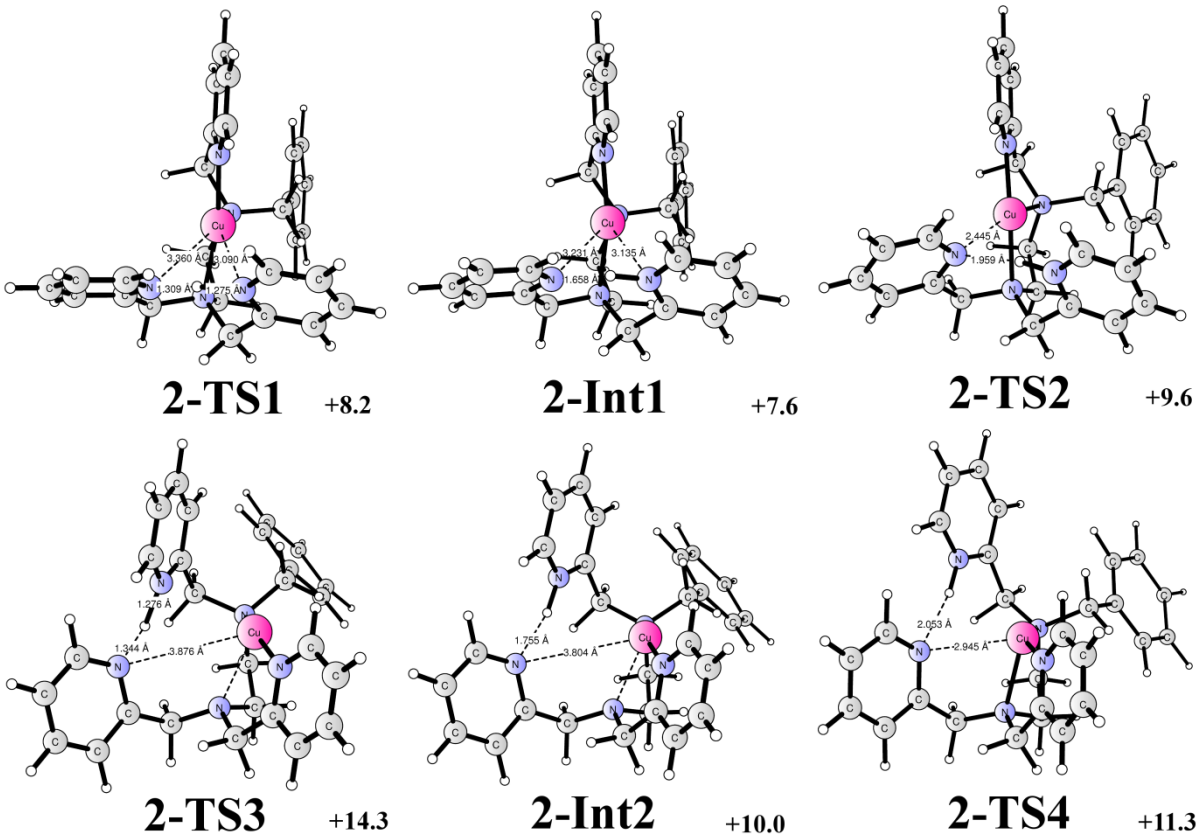


Figure S4. Optimized structures of transition states and intermediates for the interconversion of 2_A, 2_B, and 2_C. Energies are given in kcal/mol relative to 2_A.

S6. Structures of Cu^{III}-H.

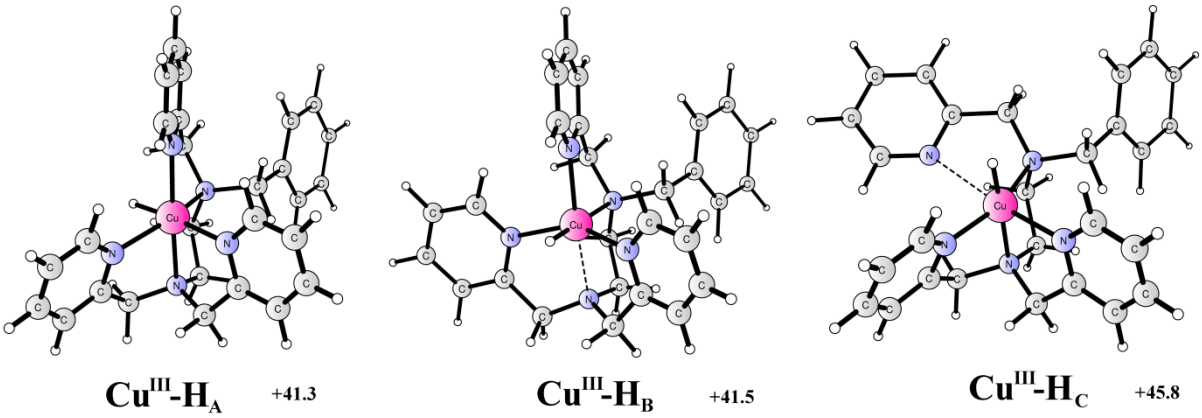


Figure S5. Optimized structures of hexa-coordinated Cu^{III}-H intermediates. Energies relative to $\mathbf{2_A}$ are given in kcal/mol.

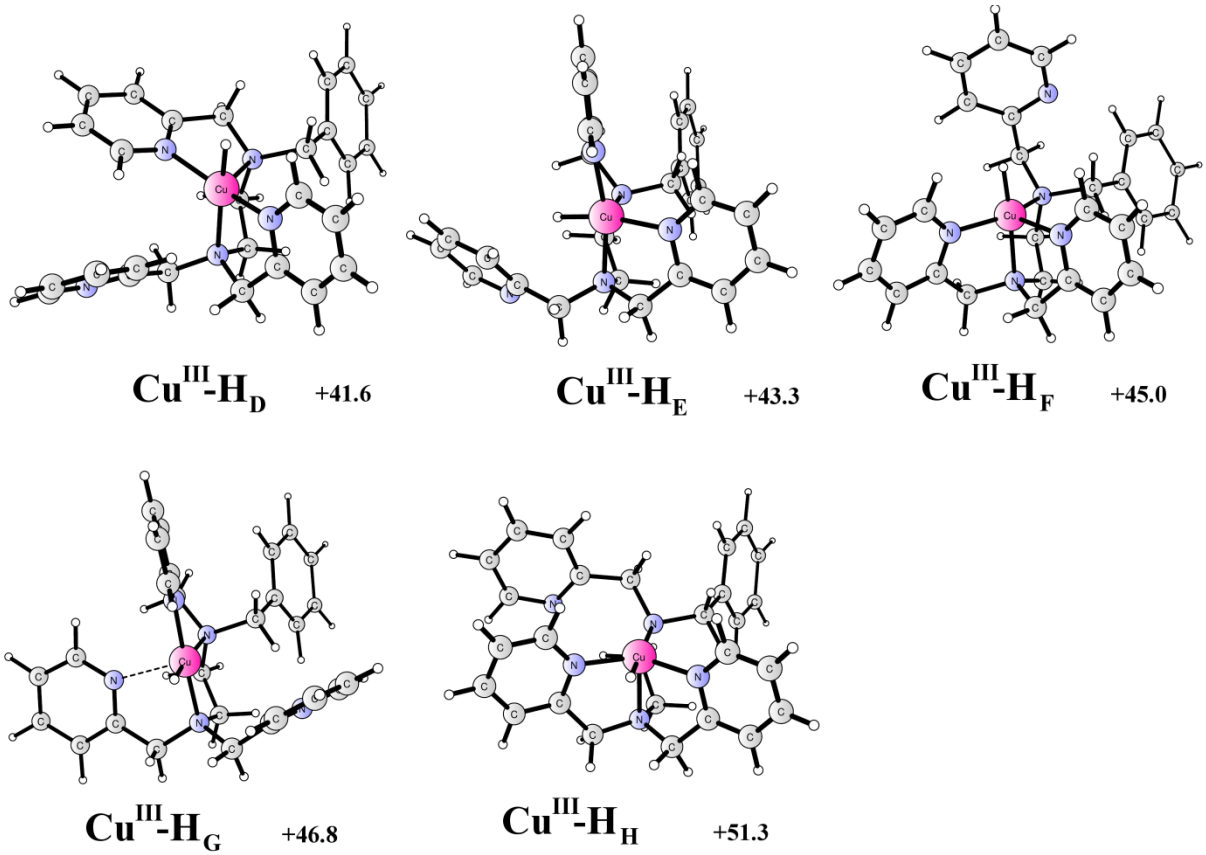


Figure S6. Optimized structures of penta-coordinated Cu^{III}-H intermediates. Energies relative to $\mathbf{2_A}$ are given in kcal/mol.

S7. Structures of 3 in the deprotonated form.

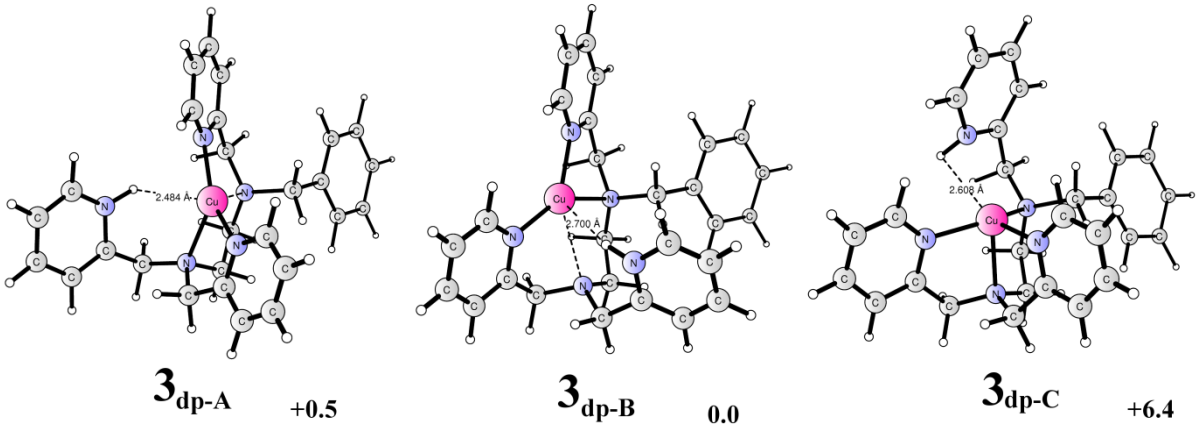


Figure S7. Optimized structures of **3** in the deprotonated form. Energies are given in kcal/mol relative to $\mathbf{3}_{\mathbf{dp\text{-}B}}$.

S8. Structures of Cu^0 di-pyridinium (3_{dipyH}).

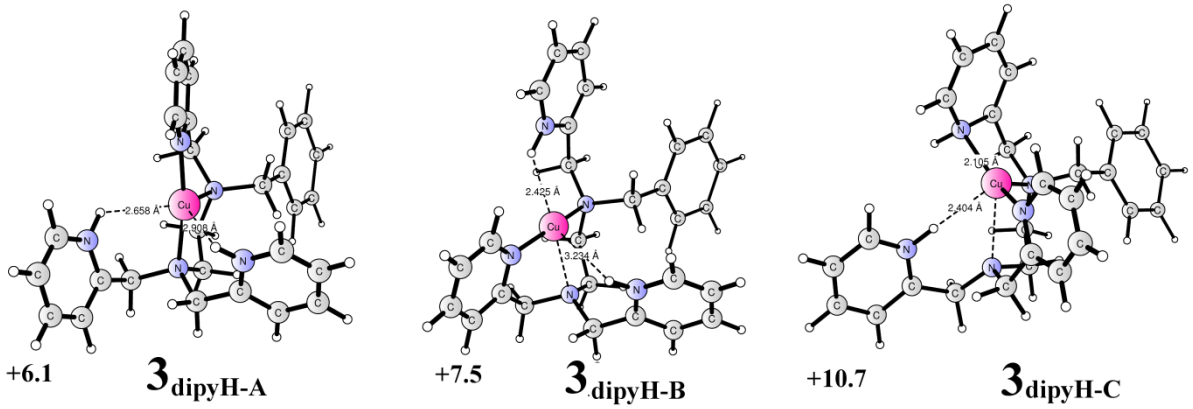


Figure S8. Optimized structures of Cu0 di-pyridinium. Energies are given in kcal/mol relative to $\mathbf{3_C}$.

S9. Structures of 2 in the protonated form.

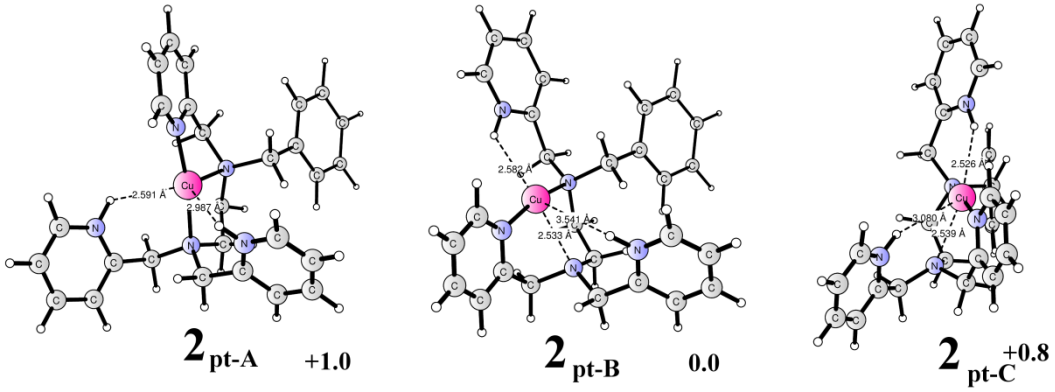


Figure S9. Optimized structures of **2** in the protonated form. Energies are given in kcal/mol relative to $\mathbf{2}_{\mathbf{pt\text{-}B}}$.

S10. IRC profile for TS_C.

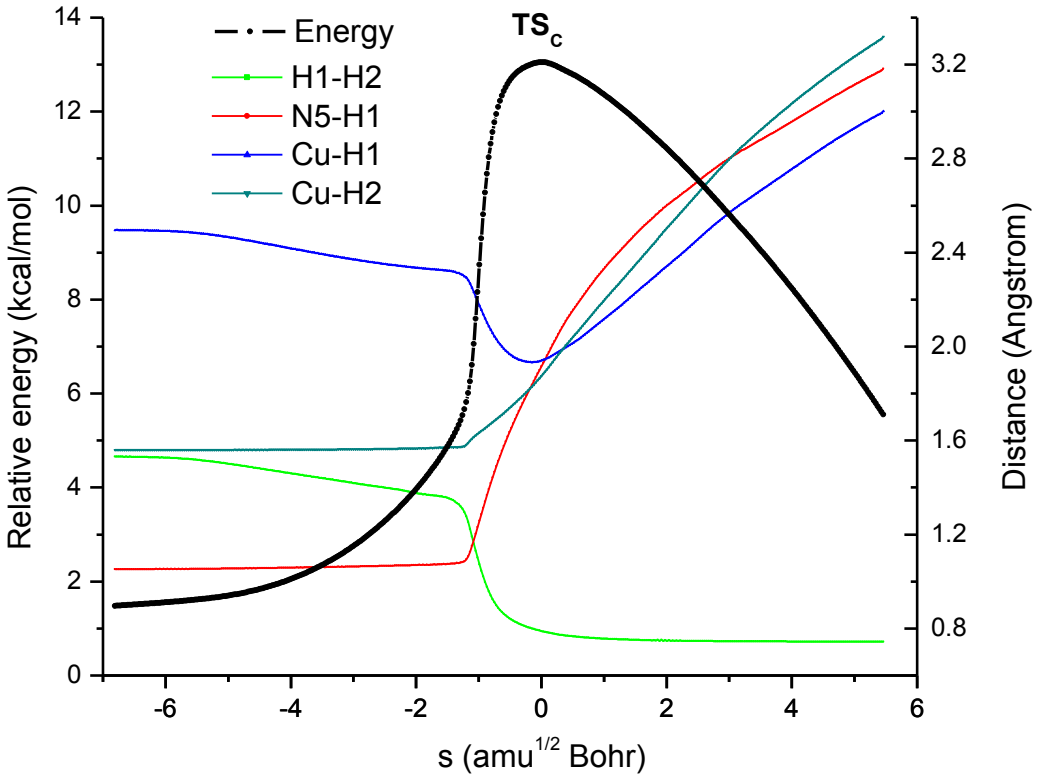


Figure S10. Energy profile and changes in selected bond lengths along the IRC path for $\mathbf{TS_C}$ with a stepsize of 0.05 $amu^{1/2}$ Bohr.

S11. Comparison of relative energies, total barriers, and redox potentials using different functionals.

Table S1. Comparison of relative energies, total barriers, and redox potentials using different functionals.

		2	3	TS[a]	Total Barrier[b]	2/1	3/2
Experiment						-0.03	-0.82
B3LYP*-D3	A	0.0	2.9	2.5	17.7	-0.21	-1.13
	B	0.4	5.3	0.8	18.7		
	C	5.0	0.0	1.9	14.2		
B3LYP-D3	A	0.0	3.0	2.4	16.0	-0.20	-1.06
	B	0.1	5.3	1.2	17.0		
	C	5.3	0.0	1.5	12.1		
M06L-D3	A	0.0	3.3	1.8	15.6	-0.37	-1.06
	B	1.1	6.4	-0.1	16.8		
	C	5.2	0.0	2.1	12.6		
M06-D3	A	0.0	3.4	3.3	26.0	-0.05	-1.44
	B	0.1	5.5	1.6	26.4		
	C	4.5	0.0	1.7	21.0		

a: Energy relative to corresponding isomer of 3.
b: Barrier relative to 2_A.

S12. Keywords for all calculations.

Keywords for optimization calculation:

#p b3lyp/gen pseudo=read opt

Cu
sdd
****
C N H
6-31g**
****

Cu
Sdd

Keywords for single-point calculation:

#p uBLYP/gen IOp(3/76=1000001500) IOp(3/77=0720008500) IOp(3/78=0810010000) pseudo=read scrf=(smd,solvent=water)

Cu
sdd
****
C N H
6-311+g(2df,2p)
****

Cu
Sdd

Keywords for dispersion correction calculation:

#p ub3lyp/sdd EmpiricalDispersion=GD3 scfcyc=1

Keywords for frequency calculation:

#p b3lyp/gen pseudo=read freq

Cu
sdd
****
C N H
6-31g**
****

Cu
Sdd

S13. Cartesian coordinates for optimized structures.

1 E(B3LYP/ SDD-6-31G(d,p))= -1517.049886 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.154740	-1.493612	-1.193060
2	6	0	-2.112106	-1.071121	-2.252004
3	1	0	-1.551286	-0.546151	-3.032379
4	1	0	-2.574817	-1.943836	-2.728819
5	6	0	-1.746266	-2.573130	-0.349603
6	1	0	-2.827493	-2.401568	-0.306308
7	1	0	-1.596449	-3.550523	-0.823743
8	6	0	0.182450	-1.873676	-1.750530
9	1	0	0.671644	-2.513489	-1.012537
10	1	0	0.063082	-2.467573	-2.665174
11	29	0	-0.832047	0.160098	0.014864
12	6	0	-3.159891	-0.136325	-1.687652
13	6	0	-4.436168	-0.031033	-2.234921
14	6	0	-3.621952	1.538506	-0.143477
15	6	0	-5.323427	0.908214	-1.707752
16	1	0	-4.728769	-0.670126	-3.061740
17	6	0	-4.908027	1.709521	-0.644026
18	1	0	-3.260602	2.139737	0.683146
19	1	0	-6.322514	1.009725	-2.119331
20	1	0	-5.565513	2.451012	-0.204309
21	6	0	-1.207268	-2.566040	1.066616
22	6	0	-1.139531	-3.731368	1.828600
23	6	0	-0.729694	-3.644840	3.159795
24	1	0	-1.409296	-4.687557	1.391685
25	6	0	-0.466511	-1.284467	2.852634
26	6	0	-0.389796	-2.397403	3.684101
27	1	0	-0.673873	-4.537218	3.775016
28	1	0	-0.195501	-0.297521	3.215253
29	1	0	-0.065173	-2.286206	4.712641
30	7	0	-2.762257	0.635278	-0.650861
31	7	0	-0.869969	-1.360595	1.571098
32	6	0	1.028994	-0.629704	-2.023734
33	1	0	2.016732	-0.920178	-2.397503
34	1	0	0.563487	-0.014951	-2.799276
35	7	0	1.133682	0.192016	-0.785639
36	6	0	1.339300	1.642139	-1.040359
37	1	0	2.389103	1.871751	-1.250701
38	1	0	0.761823	1.920550	-1.929621
39	6	0	2.158969	-0.351106	0.199240
40	1	0	2.056406	0.253715	1.103655
41	1	0	1.838507	-1.362467	0.457023
42	6	0	3.593006	-0.353799	-0.277683
43	6	0	4.430845	0.746060	-0.032031
44	6	0	4.125893	-1.471392	-0.940222
45	6	0	5.756749	0.742397	-0.466255
46	1	0	4.055964	1.597775	0.531470
47	6	0	5.451366	-1.476664	-1.375657
48	1	0	3.513801	-2.358197	-1.090894
49	6	0	6.266236	-0.366256	-1.145484
50	1	0	6.395646	1.595624	-0.261569
51	1	0	5.851683	-2.350586	-1.879624
52	1	0	7.299384	-0.372399	-1.477662
53	6	0	0.835921	2.443869	0.143400
54	6	0	1.388988	3.664670	0.523289

55	6	0	0.846371	4.350403	1.611096
56	1	0	2.232835	4.069438	-0.025731
57	6	0	-0.729131	2.565844	1.872274
58	6	0	-0.227636	3.788539	2.303342
59	1	0	1.263143	5.303691	1.920295
60	1	0	-1.556171	2.084169	2.385092
61	1	0	-0.667633	4.282017	3.162652
62	7	0	-0.217413	1.913695	0.809882

2_A E(B3LYP/ SDD-6-31G(d,p))= -1517.643008 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.457720	1.085852	-1.249538
2	6	0	2.181091	0.523161	-2.396683
3	1	0	1.469382	-0.013575	-3.034509
4	1	0	2.635934	1.298846	-3.033092
5	6	0	2.276449	2.131237	-0.606358
6	1	0	3.292843	1.734660	-0.481997
7	1	0	2.371813	3.014855	-1.256430
8	6	0	0.127088	1.610409	-1.668005
9	1	0	-0.199549	2.320530	-0.904660
10	1	0	0.215202	2.177843	-2.607396
11	29	0	0.409248	-0.017632	0.949790
12	6	0	3.259621	-0.465644	-2.008059
13	6	0	4.363691	-0.768580	-2.799994
14	6	0	3.968843	-2.085095	-0.401073
15	6	0	5.267319	-1.747050	-2.382694
16	1	0	4.508895	-0.239280	-3.735550
17	6	0	5.069777	-2.416296	-1.167511
18	1	0	3.738557	-2.539921	0.554804
19	1	0	6.128248	-1.985395	-2.999607
20	1	0	5.760629	-3.175541	-0.820056
21	6	0	1.791491	2.583679	0.758843
22	6	0	2.086760	3.878507	1.188241
23	6	0	1.735248	4.279035	2.475508
24	1	0	2.591314	4.564604	0.515531
25	6	0	0.809898	2.098990	2.811175
26	6	0	1.085446	3.366610	3.306015
27	1	0	1.962131	5.282474	2.821008
28	1	0	0.299825	1.364254	3.424482
29	1	0	0.790740	3.626940	4.316351
30	7	0	3.110881	-1.136112	-0.843146
31	7	0	1.149503	1.702927	1.560247
32	6	0	-0.929660	0.516017	-1.829864
33	1	0	-1.805045	0.940894	-2.334333
34	1	0	-0.556133	-0.264975	-2.498988
35	7	0	-1.301208	-0.107247	-0.537685
36	6	0	-1.552749	-1.557808	-0.652611
37	1	0	-2.579289	-1.778871	-0.967596
38	1	0	-0.897070	-1.955930	-1.436175
39	6	0	-2.436944	0.614100	0.155292
40	1	0	-2.525229	0.161654	1.148666
41	1	0	-2.103204	1.645449	0.305654
42	6	0	-3.782005	0.600815	-0.538902
43	6	0	-4.710224	-0.421101	-0.282324
44	6	0	-4.142338	1.625746	-1.428180
45	6	0	-5.949269	-0.438172	-0.923850

46	1	0	-4.476961	-1.191224	0.449885
47	6	0	-5.380674	1.610906	-2.071387
48	1	0	-3.465376	2.460537	-1.596356
49	6	0	-6.282863	0.574159	-1.825917
50	1	0	-6.659713	-1.230086	-0.708049
51	1	0	-5.647247	2.415035	-2.750075
52	1	0	-7.249327	0.565772	-2.319712
53	6	0	-1.233315	-2.310999	0.626504
54	6	0	-1.942568	-3.455048	0.990830
55	6	0	-1.570074	-4.161320	2.133839
56	1	0	-2.779402	-3.783726	0.383180
57	6	0	0.166086	-2.549706	2.474944
58	6	0	-0.492140	-3.700402	2.890723
59	1	0	-2.115475	-5.050984	2.432344
60	1	0	0.999456	-2.147443	3.041586
61	1	0	-0.171287	-4.212255	3.791087
62	7	0	-0.188682	-1.865219	1.364136
63	1	0	2.295724	-0.872119	-0.273021

2_B E(B3LYP/ SDD-6-31G(d,p))= -1517.642547 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.724488	0.855504	-1.272073
2	6	0	2.171709	-0.354741	-1.997370
3	1	0	1.287302	-0.872409	-2.372057
4	1	0	2.784600	-0.103813	-2.874942
5	6	0	2.819404	1.816992	-1.099852
6	1	0	3.773568	1.275761	-1.087526
7	1	0	2.886736	2.548176	-1.919421
8	6	0	0.544856	1.511798	-1.883390
9	1	0	0.318130	2.389775	-1.269662
10	1	0	0.787671	1.897658	-2.887556
11	29	0	0.278200	-1.786043	0.060583
12	6	0	2.928695	-1.305936	-1.097581
13	6	0	4.282132	-1.575458	-1.290821
14	6	0	2.872674	-2.758862	0.722508
15	6	0	4.943131	-2.466197	-0.441897
16	1	0	4.809785	-1.103044	-2.113146
17	6	0	4.224049	-3.062825	0.590051
18	1	0	2.276450	-3.220743	1.501598
19	1	0	5.994952	-2.689878	-0.588955
20	1	0	4.687596	-3.763595	1.275275
21	6	0	2.724765	2.556044	0.219453
22	6	0	3.340977	3.767300	0.517704
23	6	0	3.227320	4.294454	1.805179
24	1	0	3.902234	4.286792	-0.251473
25	6	0	1.887281	2.416959	2.451635
26	6	0	2.494236	3.612365	2.786691
27	1	0	3.705622	5.238779	2.046140
28	1	0	1.292445	1.827426	3.139032
29	1	0	2.391258	4.006342	3.790959
30	7	0	2.225542	-1.902856	-0.099827
31	7	0	2.025672	1.936683	1.194446
32	6	0	-0.710670	0.645937	-2.045720
33	1	0	-1.493523	1.310661	-2.440011
34	1	0	-0.540097	-0.104194	-2.823915
35	7	0	-1.174857	-0.075100	-0.840147

36	6	0	-2.274202	-0.992774	-1.217313
37	1	0	-3.200757	-0.452079	-1.446944
38	1	0	-1.972904	-1.510535	-2.136528
39	6	0	-1.589415	0.844898	0.275714
40	1	0	-1.765570	0.209433	1.148951
41	1	0	-0.719621	1.467573	0.506113
42	6	0	-2.803104	1.726439	0.041384
43	6	0	-4.069536	1.310978	0.481130
44	6	0	-2.693269	2.975023	-0.590549
45	6	0	-5.196627	2.107713	0.275711
46	1	0	-4.172502	0.364843	1.007169
47	6	0	-3.818212	3.773742	-0.799732
48	1	0	-1.719998	3.344431	-0.905392
49	6	0	-5.073694	3.338852	-0.370835
50	1	0	-6.167047	1.773704	0.629537
51	1	0	-3.714167	4.738230	-1.286994
52	1	0	-5.948464	3.961686	-0.528077
53	6	0	-2.550160	-2.044332	-0.162565
54	6	0	-3.837569	-2.531330	0.059861
55	6	0	-4.033769	-3.555224	0.985864
56	1	0	-4.672348	-2.112540	-0.492373
57	6	0	-1.678935	-3.525501	1.410194
58	6	0	-2.932511	-4.061169	1.676697
59	1	0	-5.028856	-3.949071	1.166663
60	1	0	-0.796191	-3.891968	1.922495
61	1	0	-3.036851	-4.855540	2.407024
62	7	0	-1.485306	-2.538859	0.507552
63	1	0	1.576625	1.064905	0.884559

2$_{C}$ E(B3LYP/ SDD-6-31G(d,p))= -1517.633024 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.627698	-1.389902	-1.220248
2	6	0	-2.528807	-0.714535	-2.168798
3	1	0	-1.927039	-0.312255	-2.991294
4	1	0	-3.237646	-1.414769	-2.631002
5	6	0	-2.293443	-2.427866	-0.414009
6	1	0	-3.349676	-2.147265	-0.323710
7	1	0	-2.272360	-3.410027	-0.907047
8	6	0	-0.323994	-1.796106	-1.779413
9	1	0	0.110869	-2.533460	-1.099712
10	1	0	-0.429755	-2.295327	-2.754325
11	29	0	-1.103229	0.132279	0.229938
12	6	0	-3.294493	0.443963	-1.538751
13	6	0	-4.539129	0.822936	-2.041640
14	6	0	-3.353631	2.180139	0.005997
15	6	0	-5.195795	1.926255	-1.499292
16	1	0	-4.987235	0.255130	-2.850913
17	6	0	-4.588523	2.620831	-0.453597
18	1	0	-2.861194	2.684952	0.830422
19	1	0	-6.164704	2.232183	-1.880544
20	1	0	-5.062688	3.480313	0.006850
21	6	0	-1.732172	-2.546218	0.997196
22	6	0	-1.812845	-3.754432	1.690152
23	6	0	-1.391916	-3.814760	3.017709
24	1	0	-2.209362	-4.634686	1.194200
25	6	0	-0.826821	-1.495043	2.859961

26	6	0	-0.893165	-2.658559	3.617596
27	1	0	-1.452283	-4.745810	3.572074
28	1	0	-0.438950	-0.577369	3.290370
29	1	0	-0.557736	-2.654651	4.648660
30	7	0	-2.706418	1.118398	-0.519416
31	7	0	-1.231522	-1.428257	1.575542
32	6	0	0.624908	-0.605221	-1.957224
33	1	0	1.548959	-0.949891	-2.436319
34	1	0	0.167527	0.118937	-2.637515
35	7	0	0.942470	0.129852	-0.683629
36	6	0	1.534166	1.435087	-1.062782
37	1	0	2.508524	1.306072	-1.550462
38	1	0	0.866686	1.907543	-1.793813
39	6	0	1.892157	-0.664183	0.203096
40	1	0	1.997767	-0.091348	1.129424
41	1	0	1.362420	-1.580473	0.467296
42	6	0	3.259414	-0.984849	-0.362996
43	6	0	4.352920	-0.140105	-0.114058
44	6	0	3.475230	-2.154630	-1.109347
45	6	0	5.618813	-0.437828	-0.620073
46	1	0	4.223632	0.740565	0.511616
47	6	0	4.739042	-2.454454	-1.618743
48	1	0	2.658535	-2.853786	-1.272400
49	6	0	5.811764	-1.592906	-1.380198
50	1	0	6.456457	0.219362	-0.408146
51	1	0	4.889852	-3.366256	-2.187859
52	1	0	6.796795	-1.830060	-1.769109
53	6	0	1.720147	2.424993	0.067497
54	6	0	2.765760	3.344669	0.103490
55	6	0	2.826216	4.293443	1.125865
56	1	0	3.524189	3.312219	-0.670832
57	6	0	0.823483	3.384978	2.065288
58	6	0	1.843863	4.315090	2.124110
59	1	0	3.639731	5.011937	1.148902
60	1	0	0.023676	3.321113	2.793901
61	1	0	1.871010	5.036570	2.932401
62	7	0	0.793759	2.489307	1.051001
63	1	0	0.024625	1.794511	1.005727

2_{dp} E(B3LYP/ SDD-6-31G(d,p))= -1517.347578 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.287596	-1.535435	-1.185542
2	6	0	-2.196595	-1.057200	-2.225240
3	1	0	-1.602515	-0.538961	-2.986144
4	1	0	-2.710109	-1.880870	-2.748371
5	6	0	-1.911237	-2.535357	-0.314573
6	1	0	-2.977864	-2.290979	-0.239217
7	1	0	-1.852902	-3.552604	-0.734081
8	6	0	0.037491	-1.931229	-1.685367
9	1	0	0.503566	-2.557370	-0.918862
10	1	0	-0.036369	-2.554478	-2.592168
11	29	0	-1.015850	0.316054	0.337687
12	6	0	-3.229582	-0.073515	-1.697262
13	6	0	-4.488885	0.025605	-2.293010
14	6	0	-3.733103	1.651882	-0.241883
15	6	0	-5.387457	0.988106	-1.837612

16	1	0	-4.755442	-0.644831	-3.104418
17	6	0	-5.000394	1.823222	-0.790061
18	1	0	-3.392566	2.278374	0.577248
19	1	0	-6.370202	1.081756	-2.288970
20	1	0	-5.663272	2.587570	-0.399548
21	6	0	-1.346499	-2.532379	1.095345
22	6	0	-1.203879	-3.718819	1.816840
23	6	0	-0.763457	-3.668768	3.138536
24	1	0	-1.439711	-4.667640	1.345070
25	6	0	-0.625872	-1.290546	2.911998
26	6	0	-0.471424	-2.427069	3.700646
27	1	0	-0.647960	-4.580919	3.715531
28	1	0	-0.399357	-0.304627	3.306658
29	1	0	-0.125020	-2.335020	4.724180
30	7	0	-2.860093	0.725606	-0.677276
31	7	0	-1.052939	-1.331345	1.637015
32	6	0	0.943943	-0.726503	-1.985910
33	1	0	1.876883	-1.094169	-2.437480
34	1	0	0.468404	-0.096828	-2.744169
35	7	0	1.181658	0.103307	-0.797972
36	6	0	1.400592	1.521560	-1.087015
37	1	0	2.424276	1.744759	-1.421687
38	1	0	0.731731	1.801973	-1.909845
39	6	0	2.185234	-0.459580	0.148330
40	1	0	2.131634	0.144693	1.059438
41	1	0	1.844774	-1.461838	0.423497
42	6	0	3.620394	-0.521461	-0.343319
43	6	0	4.500009	0.550058	-0.125552
44	6	0	4.103837	-1.652264	-1.019032
45	6	0	5.814663	0.505319	-0.591800
46	1	0	4.159022	1.417826	0.434529
47	6	0	5.417523	-1.701008	-1.487834
48	1	0	3.454847	-2.513483	-1.160559
49	6	0	6.274519	-0.618866	-1.280002
50	1	0	6.482628	1.341742	-0.408255
51	1	0	5.774762	-2.586934	-2.004341
52	1	0	7.298261	-0.657220	-1.639439
53	6	0	1.061097	2.407461	0.100768
54	6	0	1.805093	3.555838	0.378599
55	6	0	1.429971	4.380844	1.437460
56	1	0	2.667636	3.795583	-0.235332
57	6	0	-0.368639	2.862921	1.866816
58	6	0	0.318158	4.026251	2.199990
59	1	0	1.996684	5.278182	1.665180
60	1	0	-1.237606	2.549515	2.438516
61	1	0	-0.012265	4.630966	3.037435
62	7	0	-0.016075	2.065472	0.839993

Cu^{III}-H_A E(B3LYP/ SDD-6-31G(d,p))= -1517.572572 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.169474	-1.775877	-0.875524
2	6	0	-2.216239	-1.685081	-1.906345
3	1	0	-1.757762	-1.311889	-2.829214
4	1	0	-2.645983	-2.668457	-2.140717
5	6	0	-1.623903	-2.558383	0.299183
6	1	0	-2.719054	-2.526003	0.324684

7	1	0	-1.348654	-3.616247	0.203664
8	6	0	0.154351	-2.201004	-1.394403
9	1	0	0.675896	-2.715243	-0.583766
10	1	0	0.040667	-2.931127	-2.205882
11	29	0	-0.923923	0.297275	-0.062759
12	6	0	-3.325525	-0.730234	-1.488911
13	6	0	-4.637343	-0.893076	-1.933370
14	6	0	-3.907394	1.222758	-0.354246
15	6	0	-5.601061	0.049136	-1.574285
16	1	0	-4.894285	-1.743145	-2.557527
17	6	0	-5.230499	1.128187	-0.769795
18	1	0	-3.570518	2.043501	0.269540
19	1	0	-6.625395	-0.057515	-1.916805
20	1	0	-5.948428	1.881613	-0.465508
21	6	0	-1.122171	-2.001987	1.616526
22	6	0	-0.999625	-2.811317	2.745455
23	6	0	-0.631790	-2.239843	3.962995
24	1	0	-1.196784	-3.875777	2.669997
25	6	0	-0.506516	-0.122210	2.855059
26	6	0	-0.384773	-0.867364	4.020538
27	1	0	-0.536277	-2.856479	4.851063
28	1	0	-0.303170	0.943079	2.845103
29	1	0	-0.094689	-0.382082	4.945557
30	7	0	-2.984483	0.305705	-0.699265
31	7	0	-0.870381	-0.672406	1.678266
32	6	0	1.010751	-1.027036	-1.899688
33	1	0	1.968474	-1.423961	-2.256026
34	1	0	0.520429	-0.549896	-2.753804
35	7	0	1.204329	0.001184	-0.855064
36	6	0	1.537774	1.341972	-1.368070
37	1	0	2.612761	1.454520	-1.544794
38	1	0	1.038938	1.478623	-2.335206
39	6	0	2.155149	-0.419686	0.243704
40	1	0	2.098891	0.359126	1.009298
41	1	0	1.748478	-1.329800	0.688838
42	6	0	3.593200	-0.635886	-0.176394
43	6	0	4.528235	0.407327	-0.082698
44	6	0	4.027878	-1.889314	-0.636296
45	6	0	5.855654	0.211747	-0.465743
46	1	0	4.225473	1.370351	0.322781
47	6	0	5.354239	-2.086792	-1.020772
48	1	0	3.336577	-2.728717	-0.667634
49	6	0	6.268455	-1.033878	-0.942743
50	1	0	6.569487	1.024785	-0.378792
51	1	0	5.677280	-3.063459	-1.366959
52	1	0	7.301790	-1.188620	-1.236078
53	6	0	1.056526	2.436250	-0.424819
54	6	0	1.748639	3.640260	-0.291663
55	6	0	1.229282	4.642641	0.526905
56	1	0	2.679069	3.786937	-0.830773
57	6	0	-0.602769	3.187424	1.031976
58	6	0	0.029785	4.412957	1.203543
59	1	0	1.752270	5.587404	0.636294
60	1	0	-1.534515	2.962197	1.541720
61	1	0	-0.408670	5.163300	1.852004
62	7	0	-0.096126	2.221478	0.239673
63	1	0	-1.017431	0.865999	-1.341514

3_A E(B3LYP/ SDD-6-31G(d,p))= -1518.202367 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.507374	-1.143008	-0.827162
2	6	0	-2.438486	-0.831418	-1.935366
3	1	0	-1.908622	-0.192669	-2.651528
4	1	0	-2.706601	-1.748634	-2.480966
5	6	0	-2.132346	-2.071326	0.144292
6	1	0	-3.130276	-1.690780	0.388711
7	1	0	-2.277221	-3.066998	-0.300587
8	6	0	-0.261927	-1.748296	-1.398508
9	1	0	0.182403	-2.374370	-0.622860
10	1	0	-0.508275	-2.414450	-2.237479
11	29	0	-0.515896	0.572694	0.482805
12	6	0	-3.738071	-0.134452	-1.582024
13	6	0	-4.903467	-0.359922	-2.311268
14	6	0	-4.880822	1.493707	-0.275710
15	6	0	-6.061018	0.365372	-2.019713
16	1	0	-4.901351	-1.098153	-3.105769
17	6	0	-6.053449	1.308040	-0.987062
18	1	0	-4.780580	2.189300	0.549966
19	1	0	-6.966474	0.190207	-2.592278
20	1	0	-6.937650	1.881180	-0.733726
21	6	0	-1.350023	-2.199807	1.439338
22	6	0	-1.495966	-3.333128	2.240957
23	6	0	-0.836757	-3.385970	3.468179
24	1	0	-2.119624	-4.157856	1.910318
25	6	0	0.067065	-1.221988	2.989814
26	6	0	-0.041677	-2.306119	3.853907
27	1	0	-0.939955	-4.255316	4.109638
28	1	0	0.684098	-0.365877	3.245677
29	1	0	0.489540	-2.303370	4.799119
30	7	0	-3.775485	0.786031	-0.591901
31	7	0	-0.570255	-1.165799	1.804435
32	6	0	0.742405	-0.695841	-1.856590
33	1	0	1.587038	-1.184110	-2.355739
34	1	0	0.282519	-0.034288	-2.596599
35	7	0	1.204884	0.143582	-0.717461
36	6	0	1.670254	1.481972	-1.177000
37	1	0	2.689023	1.437929	-1.574679
38	1	0	1.018664	1.803960	-1.997521
39	6	0	2.273926	-0.543151	0.120620
40	1	0	2.442982	0.112114	0.979723
41	1	0	1.824459	-1.460231	0.504702
42	6	0	3.583563	-0.848155	-0.570923
43	6	0	4.644304	0.071260	-0.532622
44	6	0	3.780248	-2.073257	-1.228485
45	6	0	5.856531	-0.211386	-1.162965
46	1	0	4.533022	1.002001	0.019330
47	6	0	4.991299	-2.357615	-1.860495
48	1	0	2.994492	-2.825739	-1.222683
49	6	0	6.028694	-1.423472	-1.834577
50	1	0	6.670169	0.505644	-1.117400
51	1	0	5.130623	-3.311909	-2.358549
52	1	0	6.973564	-1.646805	-2.319567
53	6	0	1.558494	2.497963	-0.063510
54	6	0	2.411770	3.591348	0.064008
55	6	0	2.178850	4.515725	1.084030

56	1	0	3.240517	3.717509	-0.624959
57	6	0	0.291405	3.204376	1.762806
58	6	0	1.100798	4.320281	1.948472
59	1	0	2.830954	5.375239	1.202517
60	1	0	-0.563531	3.004454	2.400138
61	1	0	0.887995	5.015631	2.752639
62	7	0	0.520674	2.314726	0.779876
63	1	0	-2.907766	0.946178	0.001014
64	1	0	-1.873854	1.164918	0.975906

3_B E(B3LYP/ SDD-6-31G(d,p))= -1518.195967 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.349648	1.167776	-1.102161
2	6	0	2.214927	0.476413	-2.119204
3	1	0	1.556207	-0.015017	-2.838506
4	1	0	2.792365	1.217045	-2.685293
5	6	0	2.124142	2.342272	-0.603164
6	1	0	3.081736	1.955569	-0.237351
7	1	0	2.347394	3.018159	-1.438992
8	6	0	0.051022	1.566832	-1.726319
9	1	0	-0.432856	2.284991	-1.059377
10	1	0	0.219645	2.080144	-2.683324
11	29	0	0.789174	-0.402577	0.385492
12	6	0	3.120965	-0.579073	-1.529517
13	6	0	4.437035	-0.752051	-1.952967
14	6	0	3.248128	-2.422010	-0.140857
15	6	0	5.170318	-1.825325	-1.441147
16	1	0	4.877961	-0.071803	-2.674698
17	6	0	4.563829	-2.679814	-0.522190
18	1	0	2.742700	-3.053074	0.584040
19	1	0	6.196237	-1.988155	-1.755548
20	1	0	5.095904	-3.526310	-0.102532
21	6	0	1.500016	3.182982	0.491603
22	6	0	1.280528	4.550648	0.359299
23	6	0	0.811869	5.291007	1.450399
24	1	0	1.489253	5.037020	-0.587242
25	6	0	0.783007	3.289556	2.758685
26	6	0	0.560720	4.655710	2.668441
27	1	0	0.648021	6.359217	1.347872
28	1	0	0.614616	2.712257	3.661081
29	1	0	0.202376	5.203703	3.532174
30	7	0	2.536441	-1.397506	-0.635597
31	7	0	1.239671	2.608792	1.690404
32	6	0	-0.862463	0.355073	-1.945212
33	1	0	-1.813429	0.690187	-2.374028
34	1	0	-0.421746	-0.333869	-2.669644
35	7	0	-1.065737	-0.383429	-0.674880
36	6	0	-1.361615	-1.826550	-0.860719
37	1	0	-2.396792	-1.996435	-1.175830
38	1	0	-0.710027	-2.204050	-1.657252
39	6	0	-2.098957	0.287191	0.218387
40	1	0	-2.074471	-0.247206	1.170647
41	1	0	-1.733137	1.299479	0.412202
42	6	0	-3.512117	0.339991	-0.319024
43	6	0	-4.419560	-0.694679	-0.040480
44	6	0	-3.954967	1.436700	-1.075483

45	6	0	-5.724399	-0.649481	-0.532331
46	1	0	-4.113651	-1.527717	0.588255
47	6	0	-5.259311	1.483798	-1.568885
48	1	0	-3.287216	2.276066	-1.259007
49	6	0	-6.143699	0.436514	-1.303559
50	1	0	-6.417129	-1.452901	-0.302519
51	1	0	-5.588837	2.341079	-2.147348
52	1	0	-7.160298	0.474551	-1.681580
53	6	0	-1.058681	-2.581690	0.419720
54	6	0	-1.711372	-3.759845	0.775507
55	6	0	-1.343690	-4.410034	1.954852
56	1	0	-2.493517	-4.160176	0.138590
57	6	0	0.261011	-2.673285	2.343918
58	6	0	-0.342964	-3.857106	2.755294
59	1	0	-1.838653	-5.330170	2.248832
60	1	0	1.037160	-2.191135	2.928798
61	1	0	-0.037568	-4.326643	3.683617
62	7	0	-0.085642	-2.058470	1.198629
63	1	0	1.374264	1.551636	1.759868
64	1	0	1.534430	0.135698	1.669776

3_C E(B3LYP/ SDD-6-31G(d,p))= -1518.208244 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.700907	-1.103596	-1.153768
2	6	0	-2.516600	-0.381745	-2.168543
3	1	0	-1.837918	0.072625	-2.896687
4	1	0	-3.150913	-1.079072	-2.729352
5	6	0	-2.485679	-2.210773	-0.538651
6	1	0	-3.517455	-1.859366	-0.420732
7	1	0	-2.517090	-3.083750	-1.203288
8	6	0	-0.413789	-1.606748	-1.715156
9	1	0	-0.034486	-2.365725	-1.027683
10	1	0	-0.590471	-2.109422	-2.676034
11	29	0	-1.270461	0.206515	0.434305
12	6	0	-3.344739	0.718696	-1.538218
13	6	0	-4.531599	1.178384	-2.104965
14	6	0	-3.480868	2.298059	0.166701
15	6	0	-5.197322	2.247608	-1.503993
16	1	0	-4.926955	0.708618	-2.999903
17	6	0	-4.662374	2.819613	-0.349034
18	1	0	-3.031562	2.689376	1.073103
19	1	0	-6.123224	2.622899	-1.928070
20	1	0	-5.153726	3.646532	0.151219
21	6	0	-1.946485	-2.582891	0.826528
22	6	0	-2.111434	-3.852592	1.375954
23	6	0	-1.670749	-4.084979	2.679613
24	1	0	-2.583026	-4.641113	0.798336
25	6	0	-0.932923	-1.806998	2.771839
26	6	0	-1.074856	-3.043679	3.392605
27	1	0	-1.792406	-5.064290	3.131414
28	1	0	-0.478310	-0.963176	3.279873
29	1	0	-0.725060	-3.183690	4.409236
30	7	0	-2.832905	1.273934	-0.419282
31	7	0	-1.355398	-1.583515	1.514479
32	6	0	0.619244	-0.501213	-1.918548
33	1	0	1.491700	-0.932231	-2.427215

34	1	0	0.214302	0.258685	-2.593579
35	7	0	1.017135	0.187055	-0.659575
36	6	0	1.674302	1.458733	-1.035610
37	1	0	2.592238	1.278818	-1.611308
38	1	0	0.988345	2.005742	-1.694762
39	6	0	1.911888	-0.672797	0.206796
40	1	0	2.096355	-0.103123	1.122188
41	1	0	1.315344	-1.537472	0.504355
42	6	0	3.227271	-1.126760	-0.394846
43	6	0	4.396311	-0.369197	-0.222922
44	6	0	3.313702	-2.334361	-1.105987
45	6	0	5.609985	-0.790195	-0.767987
46	1	0	4.367385	0.540634	0.372122
47	6	0	4.525066	-2.758339	-1.653531
48	1	0	2.435498	-2.967634	-1.210427
49	6	0	5.674726	-1.983138	-1.490521
50	1	0	6.507156	-0.198362	-0.615234
51	1	0	4.574899	-3.698584	-2.193548
52	1	0	6.619297	-2.315648	-1.908862
53	6	0	2.035824	2.395989	0.096770
54	6	0	3.161581	3.216210	0.045189
55	6	0	3.404227	4.136685	1.066385
56	1	0	3.840896	3.130910	-0.795652
57	6	0	1.421612	3.392722	2.171387
58	6	0	2.523745	4.228200	2.149508
59	1	0	4.279804	4.776701	1.020260
60	1	0	0.686739	3.384790	2.968519
61	1	0	2.689332	4.928497	2.959766
62	7	0	1.210815	2.521466	1.160786
63	1	0	0.353739	1.909907	1.224285
64	1	0	-0.898643	1.184638	1.579750

$3_{dp\text{-}A}$ E(B3LYP/ SDD-6-31G(d,p))= -1517.89621hartree

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.257111	-1.064845	-1.207601
2	6	0	-1.981099	-0.343883	-2.309259
3	1	0	-1.257122	0.346783	-2.757564
4	1	0	-2.273699	-1.060920	-3.090752
5	6	0	-2.117807	-2.127832	-0.658712
6	1	0	-3.132706	-1.713262	-0.598467
7	1	0	-2.171696	-2.995546	-1.335041
8	6	0	0.030300	-1.622163	-1.696273
9	1	0	0.358835	-2.379825	-0.977968
10	1	0	-0.111676	-2.138407	-2.660002
11	29	0	-0.528750	0.032303	0.638086
12	6	0	-3.190790	0.409311	-1.864235
13	6	0	-4.469661	0.157859	-2.312275
14	6	0	-4.055290	2.293206	-0.586772
15	6	0	-5.564158	0.955917	-1.927340
16	1	0	-4.616427	-0.677211	-2.991956
17	6	0	-5.317350	2.036356	-1.031442
18	1	0	-3.809035	3.107856	0.083153
19	1	0	-6.562205	0.745602	-2.289516
20	1	0	-6.129323	2.671524	-0.693868
21	6	0	-1.710546	-2.588134	0.723745
22	6	0	-2.027425	-3.871473	1.175859

23	6	0	-1.714435	-4.234800	2.482751
24	1	0	-2.518005	-4.570538	0.506032
25	6	0	-0.782884	-2.051969	2.786268
26	6	0	-1.080264	-3.304527	3.308216
27	1	0	-1.958223	-5.226381	2.850850
28	1	0	-0.284079	-1.299374	3.388324
29	1	0	-0.816116	-3.541793	4.332649
30	7	0	-2.972431	1.531928	-1.040604
31	7	0	-1.088337	-1.693713	1.522053
32	6	0	1.130969	-0.564960	-1.855182
33	1	0	2.019735	-1.043327	-2.284150
34	1	0	0.816806	0.185193	-2.584235
35	7	0	1.439335	0.118153	-0.579796
36	6	0	1.642213	1.568708	-0.704256
37	1	0	2.687328	1.836766	-0.904878
38	1	0	1.064106	1.918468	-1.567333
39	6	0	2.499472	-0.557893	0.233597
40	1	0	2.495970	-0.073521	1.216093
41	1	0	2.167116	-1.588683	0.390536
42	6	0	3.904781	-0.550147	-0.336577
43	6	0	4.793747	0.494358	-0.038237
44	6	0	4.354055	-1.593292	-1.160943
45	6	0	6.081487	0.514898	-0.575538
46	1	0	4.484866	1.284882	0.642211
47	6	0	5.641109	-1.576254	-1.700180
48	1	0	3.702289	-2.440200	-1.362962
49	6	0	6.505008	-0.517653	-1.414238
50	1	0	6.757635	1.328132	-0.329362
51	1	0	5.973079	-2.394459	-2.332070
52	1	0	7.508277	-0.505942	-1.828777
53	6	0	1.141006	2.343866	0.504252
54	6	0	1.770935	3.515275	0.924426
55	6	0	1.225885	4.252761	1.974464
56	1	0	2.676930	3.843427	0.425044
57	6	0	-0.510381	2.611917	2.121789
58	6	0	0.058219	3.793597	2.583193
59	1	0	1.705027	5.166185	2.312311
60	1	0	-1.413743	2.212552	2.571412
61	1	0	-0.403764	4.331612	3.403430
62	7	0	0.013252	1.895740	1.104276
63	1	0	-2.111962	1.564501	-0.508536

$3_{dp\text{-}B}$ E(B3LYP/ SDD-6-31G(d,p))= -1517.890369 hartree

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.346689	-1.456482	-1.171611
2	6	0	-2.409704	-0.906436	-2.014060
3	1	0	-1.962293	-0.193691	-2.716186
4	1	0	-2.906760	-1.677320	-2.626052
5	6	0	-1.799071	-2.679026	-0.455553
6	1	0	-2.854629	-2.511952	-0.195051
7	1	0	-1.766022	-3.563144	-1.111453
8	6	0	-0.084575	-1.667742	-1.888851
9	1	0	0.507312	-2.361396	-1.287598
10	1	0	-0.242091	-2.162822	-2.863225
11	29	0	-1.052916	1.064058	-0.070649
12	6	0	-3.448332	-0.167447	-1.197078

13	6	0	-4.813939	-0.389577	-1.373996
14	6	0	-3.895322	1.462676	0.403695
15	6	0	-5.738989	0.344383	-0.634212
16	1	0	-5.141731	-1.136026	-2.090087
17	6	0	-5.267224	1.290859	0.276827
18	1	0	-3.489372	2.195266	1.093086
19	1	0	-6.803804	0.178909	-0.762559
20	1	0	-5.943941	1.887963	0.877621
21	6	0	-1.013829	-2.946223	0.785619
22	6	0	-0.270225	-4.079126	1.029841
23	6	0	0.405730	-4.272724	2.251702
24	1	0	-0.226549	-4.837693	0.253189
25	6	0	-0.427975	-2.126697	3.001074
26	6	0	0.308924	-3.250315	3.237255
27	1	0	0.985662	-5.168862	2.431663
28	1	0	-0.548334	-1.324836	3.719213
29	1	0	0.812604	-3.353086	4.192413
30	7	0	-2.992599	0.754198	-0.311255
31	7	0	-1.127416	-1.982077	1.801958
32	6	0	0.719104	-0.385346	-2.146999
33	1	0	1.668995	-0.671446	-2.621900
34	1	0	0.191463	0.249727	-2.866917
35	7	0	0.941716	0.432665	-0.935195
36	6	0	1.487478	1.759968	-1.271850
37	1	0	2.551698	1.724222	-1.539162
38	1	0	0.949092	2.130152	-2.153443
39	6	0	1.772453	-0.258814	0.112071
40	1	0	1.745059	0.380720	0.998626
41	1	0	1.251425	-1.179909	0.377679
42	6	0	3.215883	-0.551622	-0.255681
43	6	0	4.233101	0.357194	0.075007
44	6	0	3.574266	-1.740040	-0.910294
45	6	0	5.563569	0.100319	-0.259025
46	1	0	3.984206	1.265038	0.619991
47	6	0	4.903179	-2.000326	-1.247390
48	1	0	2.815023	-2.483864	-1.136291
49	6	0	5.900740	-1.077680	-0.927449
50	1	0	6.336827	0.812815	0.012533
51	1	0	5.160866	-2.928524	-1.748511
52	1	0	6.935505	-1.282181	-1.184462
53	6	0	1.275487	2.745772	-0.137155
54	6	0	2.178454	3.776719	0.122888
55	6	0	1.909027	4.677769	1.151973
56	1	0	3.079377	3.865026	-0.475722
57	6	0	-0.106757	3.462791	1.585224
58	6	0	0.744061	4.516103	1.901965
59	1	0	2.599080	5.487020	1.368969
60	1	0	-1.022562	3.298903	2.144318
61	1	0	0.496525	5.187133	2.716894
62	7	0	0.145754	2.595887	0.586179
63	1	0	-1.466505	-1.065660	1.537420

$3_{dp\text{-}C}$ E(B3LYP/ SDD-6-31G(d,p))= -1517.886275 hartree

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.220796	-1.693494	-1.130235
2	6	0	-2.208306	-1.285254	-2.129733

3	1	0	-1.677460	-0.785004	-2.947240
4	1	0	-2.730297	-2.142467	-2.583115
5	6	0	-1.713980	-2.699978	-0.187243
6	1	0	-2.804267	-2.593525	-0.130249
7	1	0	-1.521014	-3.727585	-0.532596
8	6	0	0.133786	-1.939917	-1.648198
9	1	0	0.670924	-2.514126	-0.888598
10	1	0	0.121377	-2.561132	-2.558476
11	29	0	-0.940534	0.161180	0.173786
12	6	0	-3.235363	-0.307055	-1.572820
13	6	0	-4.552727	-0.314396	-2.032169
14	6	0	-3.691943	1.486010	-0.176590
15	6	0	-5.457463	0.627546	-1.544119
16	1	0	-4.861831	-1.053206	-2.765082
17	6	0	-5.017501	1.548116	-0.594458
18	1	0	-3.314438	2.173403	0.574446
19	1	0	-6.485421	0.636145	-1.892246
20	1	0	-5.683397	2.295350	-0.177104
21	6	0	-1.172384	-2.532309	1.228417
22	6	0	-1.011769	-3.640340	2.061655
23	6	0	-0.610183	-3.452640	3.383451
24	1	0	-1.204763	-4.636721	1.676274
25	6	0	-0.539037	-1.101344	2.941930
26	6	0	-0.373791	-2.155182	3.835433
27	1	0	-0.482188	-4.303217	4.045490
28	1	0	-0.354419	-0.075937	3.246957
29	1	0	-0.060306	-1.957625	4.854551
30	7	0	-2.808844	0.587110	-0.652029
31	7	0	-0.927681	-1.276777	1.664676
32	6	0	0.895019	-0.640869	-1.955631
33	1	0	1.869668	-0.901222	-2.388633
34	1	0	0.354196	-0.078576	-2.723325
35	7	0	1.041348	0.252126	-0.777632
36	6	0	1.355747	1.658218	-1.207657
37	1	0	2.394481	1.742624	-1.548654
38	1	0	0.714511	1.858735	-2.077686
39	6	0	2.059076	-0.258153	0.211582
40	1	0	2.088794	0.482864	1.014420
41	1	0	1.652386	-1.176185	0.641750
42	6	0	3.463254	-0.522725	-0.304745
43	6	0	4.456713	0.466069	-0.244384
44	6	0	3.814596	-1.781888	-0.817315
45	6	0	5.748695	0.217765	-0.710250
46	1	0	4.225847	1.429571	0.199201
47	6	0	5.104274	-2.035362	-1.285281
48	1	0	3.079107	-2.583050	-0.832147
49	6	0	6.073817	-1.031934	-1.239395
50	1	0	6.503165	0.996309	-0.648988
51	1	0	5.354848	-3.017737	-1.674344
52	1	0	7.079204	-1.227807	-1.599161
53	6	0	1.090136	2.671428	-0.140102
54	6	0	2.045964	3.424972	0.496924
55	6	0	1.718551	4.352379	1.509120
56	1	0	3.080493	3.299170	0.192923
57	6	0	-0.612715	3.783537	1.202569
58	6	0	0.346861	4.509927	1.842799
59	1	0	2.484763	4.945788	1.991229
60	1	0	-1.672650	3.895373	1.396564
61	1	0	0.040407	5.224275	2.599879
62	7	0	-0.269750	2.805696	0.246241

63	1	0	-0.942130	2.678936	-0.505733

TS_A E(B3LYP/ SDD-6-31G(d,p))= -1518.191228 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.410747	-1.048872	-0.858367
2	6	0	-2.321359	-0.603594	-1.968354
3	1	0	-1.769862	0.129100	-2.565843
4	1	0	-2.512030	-1.464983	-2.621249
5	6	0	-2.107055	-2.007457	0.045147
6	1	0	-3.092514	-1.590668	0.273835
7	1	0	-2.275176	-2.962844	-0.469316
8	6	0	-0.199117	-1.698323	-1.468759
9	1	0	0.237394	-2.356493	-0.714423
10	1	0	-0.494092	-2.331040	-2.315187
11	29	0	-0.492786	0.446445	0.376689
12	6	0	-3.663127	-0.003866	-1.585372
13	6	0	-4.804277	-0.338608	-2.316939
14	6	0	-4.869010	1.513634	-0.307357
15	6	0	-6.010117	0.303796	-2.026809
16	1	0	-4.752194	-1.081841	-3.106205
17	6	0	-6.046061	1.250956	-1.005027
18	1	0	-4.846279	2.229418	0.510196
19	1	0	-6.906568	0.061718	-2.588688
20	1	0	-6.961823	1.770503	-0.745956
21	6	0	-1.364231	-2.234946	1.348776
22	6	0	-1.535632	-3.412742	2.076048
23	6	0	-0.906664	-3.540997	3.314361
24	1	0	-2.155377	-4.212227	1.682570
25	6	0	0.018747	-1.356859	2.991571
26	6	0	-0.116074	-2.491281	3.784436
27	1	0	-1.029683	-4.446234	3.900340
28	1	0	0.633548	-0.521679	3.313821
29	1	0	0.390770	-2.549438	4.741161
30	7	0	-3.708721	0.907956	-0.599253
31	7	0	-0.590838	-1.225940	1.797491
32	6	0	0.823991	-0.660838	-1.917761
33	1	0	1.691372	-1.151978	-2.370183
34	1	0	0.398449	-0.001909	-2.678411
35	7	0	1.235410	0.175286	-0.753740
36	6	0	1.639247	1.558048	-1.132072
37	1	0	2.669506	1.581939	-1.500361
38	1	0	0.992495	1.890938	-1.951801
39	6	0	2.298420	-0.498754	0.111650
40	1	0	2.422297	0.144420	0.986331
41	1	0	1.861115	-1.435479	0.460555
42	6	0	3.629197	-0.746015	-0.559030
43	6	0	4.651892	0.214508	-0.494447
44	6	0	3.882087	-1.957323	-1.223281
45	6	0	5.883535	-0.015503	-1.107906
46	1	0	4.498018	1.133852	0.066325
47	6	0	5.113236	-2.188302	-1.837588
48	1	0	3.126518	-2.740020	-1.235599
49	6	0	6.112370	-1.213999	-1.787386
50	1	0	6.668385	0.731337	-1.042753
51	1	0	5.297877	-3.131958	-2.340898
52	1	0	7.072459	-1.395831	-2.259563

53	6	0	1.449813	2.488128	0.045089
54	6	0	2.212164	3.635195	0.246152
55	6	0	1.919108	4.462666	1.331925
56	1	0	3.018251	3.877210	-0.438617
57	6	0	0.155750	2.956073	1.934275
58	6	0	0.874887	4.117438	2.191284
59	1	0	2.500128	5.362853	1.505461
60	1	0	-0.667719	2.646780	2.569590
61	1	0	0.618310	4.733244	3.045875
62	7	0	0.438740	2.161222	0.883720
63	1	0	-2.472639	1.057977	0.469170
64	1	0	-1.947369	1.102646	1.111122

TS_B E(B3LYP/ SDD-6-31G(d,p))= -1518.190656 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.239066	1.220473	-1.068230
2	6	0	2.176133	0.631190	-2.080770
3	1	0	1.588338	0.019813	-2.771348
4	1	0	2.636517	1.426756	-2.678834
5	6	0	1.914123	2.428284	-0.484341
6	1	0	2.858711	2.081220	-0.053100
7	1	0	2.164878	3.116423	-1.300952
8	6	0	-0.071799	1.562517	-1.706406
9	1	0	-0.597344	2.241727	-1.032089
10	1	0	0.087509	2.103036	-2.648954
11	29	0	0.841567	-0.424073	0.255316
12	6	0	3.225728	-0.249229	-1.443931
13	6	0	4.532637	-0.326698	-1.918273
14	6	0	3.634063	-1.889588	0.144295
15	6	0	5.409337	-1.239372	-1.327922
16	1	0	4.857784	0.307746	-2.736355
17	6	0	4.951656	-2.037623	-0.280144
18	1	0	3.238555	-2.485000	0.960307
19	1	0	6.432575	-1.322399	-1.679979
20	1	0	5.599770	-2.758504	0.205449
21	6	0	1.150645	3.216632	0.562460
22	6	0	0.911182	4.581916	0.414683
23	6	0	0.303594	5.288966	1.457503
24	1	0	1.208366	5.091299	-0.496087
25	6	0	0.195634	3.249927	2.704160
26	6	0	-0.059389	4.616225	2.623611
27	1	0	0.120594	6.354104	1.357267
28	1	0	-0.061480	2.661879	3.580475
29	1	0	-0.526952	5.132895	3.454179
30	7	0	2.786051	-1.016639	-0.425792
31	7	0	0.785681	2.589246	1.698199
32	6	0	-0.913837	0.309880	-1.957294
33	1	0	-1.891363	0.598596	-2.359056
34	1	0	-0.443277	-0.328548	-2.709130
35	7	0	-1.052006	-0.480077	-0.705547
36	6	0	-1.270682	-1.932172	-0.941625
37	1	0	-2.312496	-2.147607	-1.201431
38	1	0	-0.652886	-2.235951	-1.794559
39	6	0	-2.097230	0.097476	0.239868
40	1	0	-2.020341	-0.479491	1.164406
41	1	0	-1.774446	1.114984	0.473522

42	6	0	-3.520459	0.099036	-0.269517
43	6	0	-4.371555	-0.987965	-0.012677
44	6	0	-4.030220	1.200603	-0.975555
45	6	0	-5.687155	-0.987686	-0.477203
46	1	0	-4.014431	-1.826758	0.580639
47	6	0	-5.345273	1.202473	-1.441628
48	1	0	-3.407878	2.078253	-1.138073
49	6	0	-6.173218	0.104535	-1.198895
50	1	0	-6.336428	-1.830890	-0.263787
51	1	0	-5.727525	2.063811	-1.980181
52	1	0	-7.198315	0.107756	-1.555210
53	6	0	-0.844245	-2.717335	0.281345
54	6	0	-1.417724	-3.933113	0.646055
55	6	0	-0.943566	-4.595246	1.779776
56	1	0	-2.223517	-4.351527	0.051840
57	6	0	0.600423	-2.794262	2.115799
58	6	0	0.078254	-4.013861	2.532200
59	1	0	-1.376142	-5.544562	2.079266
60	1	0	1.378469	-2.285563	2.675657
61	1	0	0.459618	-4.487518	3.429783
62	7	0	0.158605	-2.172451	1.006981
63	1	0	0.968362	1.282103	1.751254
64	1	0	1.115202	0.303140	1.778186

TS_C E(B3LYP/ SDD-6-31G(d,p))= -1518.187446 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.987123	-1.271424	-1.056388
2	6	0	-3.004469	-0.522319	-1.847681
3	1	0	-2.845864	-0.683073	-2.920214
4	1	0	-3.995377	-0.927311	-1.618137
5	6	0	-2.515604	-2.519037	-0.436244
6	1	0	-3.562280	-2.348338	-0.162830
7	1	0	-2.498694	-3.352567	-1.148979
8	6	0	-0.719094	-1.528687	-1.816080
9	1	0	-0.206314	-2.354319	-1.318633
10	1	0	-0.964889	-1.863771	-2.831185
11	29	0	-1.363748	-0.070074	0.529615
12	6	0	-3.016395	0.962672	-1.539948
13	6	0	-3.730404	1.860635	-2.331883
14	6	0	-2.380204	2.680893	-0.089226
15	6	0	-3.769040	3.205905	-1.969290
16	1	0	-4.253883	1.507508	-3.214759
17	6	0	-3.082861	3.623626	-0.826277
18	1	0	-1.814060	2.955179	0.794049
19	1	0	-4.325360	3.918305	-2.570139
20	1	0	-3.087717	4.660836	-0.510871
21	6	0	-1.745908	-2.865480	0.820708
22	6	0	-1.671134	-4.163111	1.319210
23	6	0	-1.020432	-4.387828	2.533446
24	1	0	-2.121790	-4.982928	0.769330
25	6	0	-0.549134	-2.041699	2.651453
26	6	0	-0.451892	-3.308723	3.212603
27	1	0	-0.956957	-5.391442	2.941764
28	1	0	-0.114958	-1.173512	3.135495
29	1	0	0.061411	-3.442019	4.158160
30	7	0	-2.351533	1.375829	-0.437898

31	7	0	-1.184265	-1.825157	1.481687
32	6	0	0.193014	-0.302886	-1.886123
33	1	0	1.048873	-0.543161	-2.527871
34	1	0	-0.338409	0.524182	-2.365846
35	7	0	0.638694	0.153959	-0.541051
36	6	0	1.125922	1.560088	-0.659366
37	1	0	1.980807	1.601710	-1.344805
38	1	0	0.319054	2.138541	-1.123255
39	6	0	1.709165	-0.752580	0.042840
40	1	0	1.949240	-0.334171	1.022920
41	1	0	1.238665	-1.722506	0.219675
42	6	0	2.971735	-0.945730	-0.772647
43	6	0	4.088491	-0.118057	-0.580507
44	6	0	3.067041	-1.990852	-1.706179
45	6	0	5.255213	-0.309845	-1.321822
46	1	0	4.056743	0.663426	0.173362
47	6	0	4.230832	-2.183656	-2.451034
48	1	0	2.236733	-2.682725	-1.834754
49	6	0	5.325716	-1.337611	-2.264074
50	1	0	6.113734	0.333000	-1.154280
51	1	0	4.289089	-3.000606	-3.163388
52	1	0	6.234870	-1.490025	-2.836848
53	6	0	1.511911	2.240875	0.642711
54	6	0	2.651226	3.049732	0.690735
55	6	0	2.951797	3.741360	1.865137
56	1	0	3.290825	3.139759	-0.181335
57	6	0	0.996034	2.770223	2.836577
58	6	0	2.109748	3.596921	2.966073
59	1	0	3.830118	4.376890	1.918021
60	1	0	0.311025	2.632992	3.670836
61	1	0	2.305065	4.109607	3.901435
62	7	0	0.694074	2.112623	1.704767
63	1	0	-0.904155	1.102130	2.006304
64	1	0	-1.583446	0.750758	2.201471
