Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Revealing the halide effect on the aerobic oxidation kinetics of Cu(I) to Cu(II)

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Content

General Information 3

XANES and EXAFS Data Collection and Analysis 3

IR Data Collection 4

Catalytic oxidation 4

Condition screening for model reaction 5

Blank control experiment 7

Stoichiometric oxidation 8

"Step by step" Stoichiometric reaction 8

Inhibition experiment 9

Interference experiment with sodium halide: 10

Density Functional Theory Calculation 11

Discussion on the dissociation of $[Cu(TMEDA)X]_2$ dimer 11

Complete reference for Gaussian 09 12

B3LYP absolute calculation energies, enthalpies, and free energies 13

B3LYP geometries for all the optimized compounds and transition states 14

References 31

General Information

All manipulations were carried out either in a glovebox or using standard Schlenk techniques. All glassware was oven dried at 120 ^{o}C for more than 1 h prior to use. Super dry DMF, acetonitrile were from commercial source (J&K chemical) and used as received. THF, DME were dried and distilled from sodium/benzophenone ketyl in nitrogen atmosphere. Anhydrous CuCl, CuBr and CuI were from commercial source (Sigma-Aldrich) and used as received without further purification. Commercially available TMEDA were used as received. GC analysis was done on a Varian GC 3900 gas chromatography instrument with a FID detector. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T.

XANES and EXAFS Data Collection and Analysis

X-ray absorption measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The data were collected in transmission quick scan mode. Insertion device experiments utilized a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point. The ionization chambers were optimized for the maximum current with linear response (~10^{10} photons detected/sec) with 10% absorption (N_2) in the incident ion chamber and 70% absorption (60% N_2 and 40% Ar) in the transmission detector. A Cu foil spectrum (edge energy 8979 eV) was acquired simultaneously with each measurement for energy calibration. Multiple scans were taken to reduce the noise. The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. The pre-edge energy was determined from the maximum of the pre-edge peak. Background removal and normalization procedures were carried out using the Athena software package using standard methods.[1]

Each solid sample was mixed with boron nitride to a weight ratio of about 2% (Cu). The mixture was grinded well with mortar and pestle, and then 25 mg of the mixture

was pressed into a cylindrical sample holder consisting of six wells with a radius of 2.0 mm, forming a self-supporting wafer. The sample holder was placed in a quartz tube (1–in. OD, 10–in. length) sealed with Kapton windows by two Ultra-Torr fittings and then used for transmission mode measurement.

Air sensitive solution samples were prepared in a glove box and placed in a sample holder made of PEEK (polyether ether ketone) equipped with a screw top and O-ring fitting to prevent exposure to air and water.[2] The path length of the cell is 3.5 mm and the Cu concentration was adjusted to be about 0.05 M.

THF solution of CuX/TMEDA: In a glovebox, CuX (0.5 mmol) and TMEDA (116 mg, 1.0 mmol) were added in 10 mL of dry THF. Then the mixture was stirred at room temperature for 15 min in the glovebox. 3 mL of the solution was then transferred into the solution cell and sealed. XAS spectrum was then measured at room temperature.

The solution was then exposed to air and stirred at room temperature for 10 min. XAS spectrum was collected at room temperature, again.

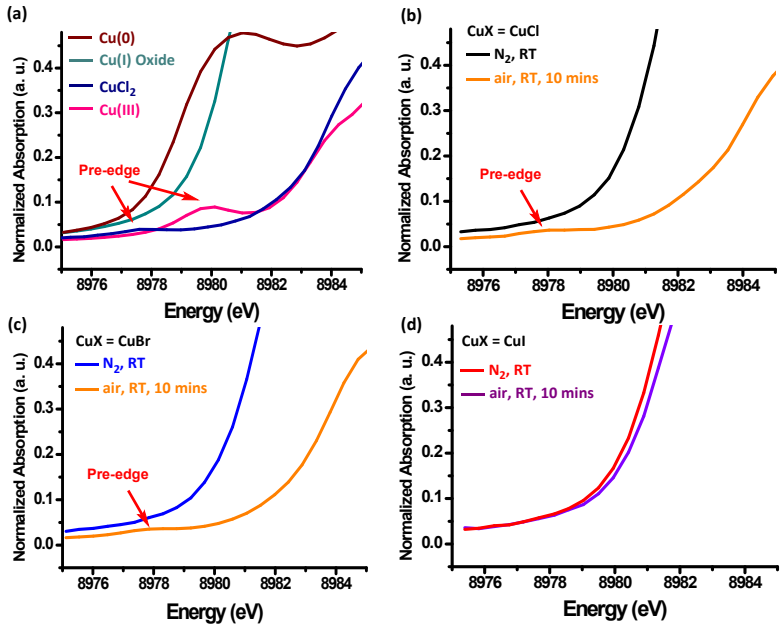

Figure S1. Expanded pre-edge region of various Cu species in Figure 1

IR Data Collection

All reactions and manipulations were conducted in a home-made three-neck micro reactor at room temperature.[3] IR spectra were recorded on a Mettler Toledo ReactIR™ 15 spectrometer using a diamond comb. For the catalytic oxidation of hydroquinone, the correlation/relationship between the yield of 1,4-benzoquinone and the intensity of characteristic absorption peak was calibrated by GC using naphthalene as the internal standard.

Catalytic oxidation

To an oven dried home-made three-neck reactor was added hydroquinone (110 mg, 1.0 mmol) as substrate, CuX (X=Cl, Br, I) (0.1 mmol) as pre-catalyst and a magnetic stirrer. The reactor was allowed to be vacuumed and purged with nitrogen several times. The ligand TMEDA (23.2 mg, 0.2 mmol) was weighted with a micro-syringe and injected in the reactor while 5 mL of dry THF was added via a syringe. The mixture was stirred at room temperature, and an initial spectrum was obtained by ReactIR spectrometer. After stirring for about 5 min, the reaction was started with purging the inert atmosphere with dry air. The formation of 1,4-benzoquinone could be monitored by the characteristic absorption peak at 1306 cm^{-1} (see the Figure S2) . After complete conversion of substrate, naphthalene (30 mg) was added as the internal standard and the yield of product was determined by GC analysis.

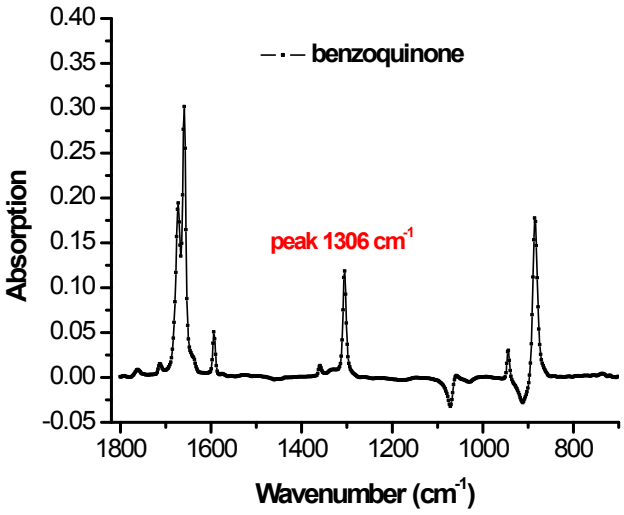

Figure S2. Characteristic absorption peak of 1,4-benzoquinone

Condition screening for model reaction

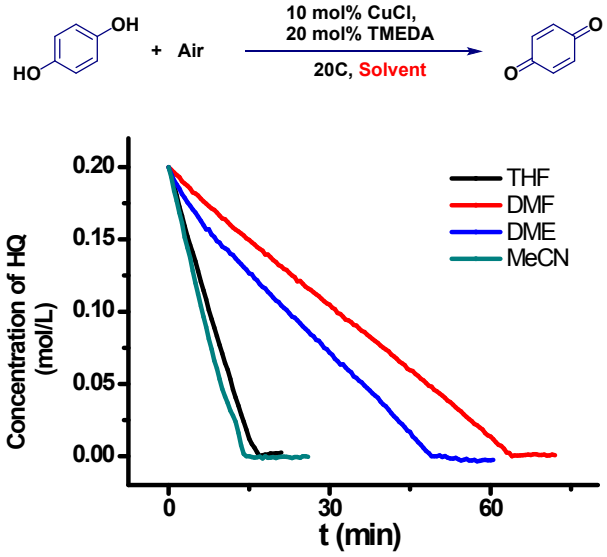

Figure S3. Screening of solvent for model reaction

For the screening of the solvent, we tried various solvents, such as toluene, acetonitrile, DMF and THF, etc. It turned out that THF gave the best results considering the high solubility and suitable reaction rate for in situ measurement.

As a bidentate nitrogen ligand, TMEDA has been extensively used in Cu oxidation chemistry. We believe revealing the Cu oxidation kinetics in the presence of TMEDA should be of general interest to a broader readership. In addition, TMEDA forms soluble Cu complexes and make it ideal for XAFS study. Both of Cu(I)-TMEDA and Cu(II)-TMEDA complexes have characteristic absorption peaks in the IR spectra at 797 cm^{-1} and 809cm^{-1}, respectively, which makes it also ideal for in situ IR study. For other reaction parameters, such as concentration and temperature, we also chose the best ones according to our initial experiment results

Additionally, we tested the equivalent of TMEDA in the model reaction as shown in Figure S4, which didn't affect the oxidation rate of model reaction. So at last we chose 20 mol% TMEDA to perform all of our reactions.

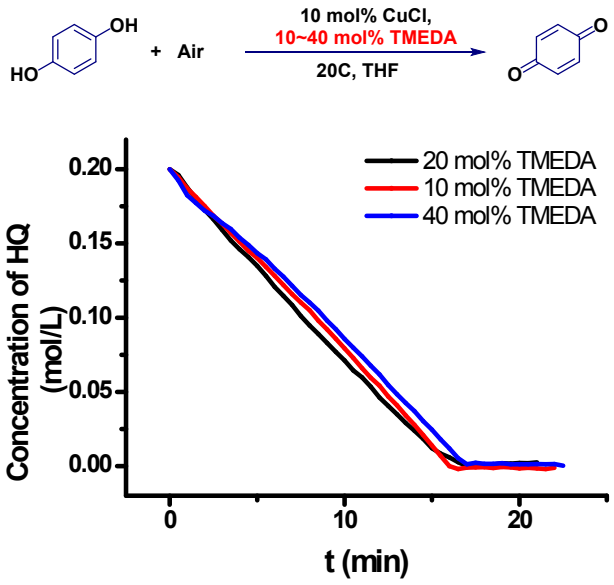

Figure S4. Screening of equivalent of TMEDA for model reaction

Effect of molecular sieve (MS): As shown in Figure S5, MS (30 equiv. weight compared to the amount of generated water) was added into the reaction, no acceleration of the reaction was observed since MS may absorb the copper catalyst hence lower its catalytical activity. In another hand, water (5 equiv. compared to the amount of generated water) was added into the reaction, very slight deceleration of the reaction was observed.

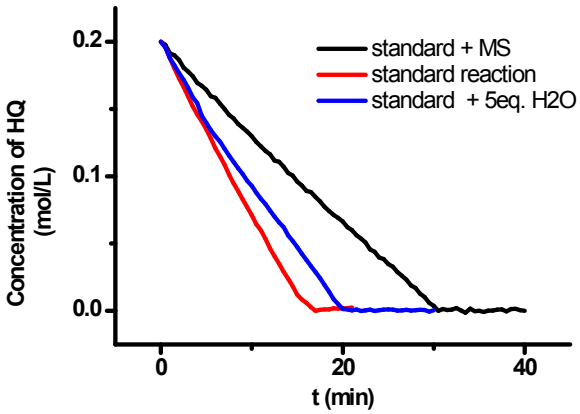

Figure S5. Effect of molecular sieves on standard reaction

Blank control experiment

The results of the control experiments in the absence of copper halide were shown below. No product benzoquinone was observed indicating that Cu catalyst plays an crucial role in the reaction. The control experiment using NaBr instead of copper halide is also shown below, as well as in the revised supporting information. No product benzoquinone was observed, either, excluding the possibility that Br· radical or hypobromite is mediating the oxidation.

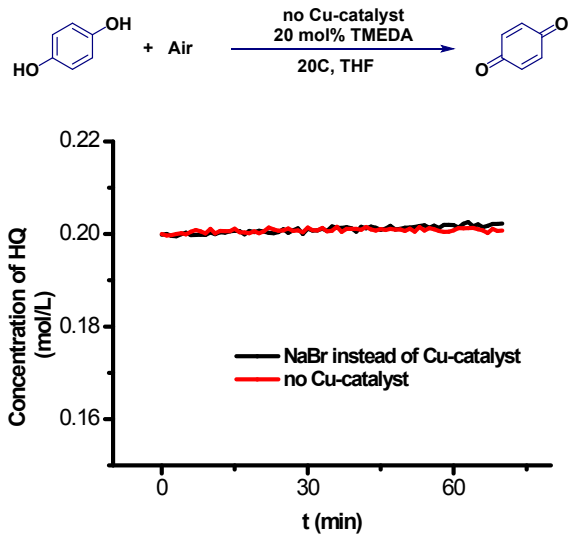

Figure S6. Blank control experiment without Cu-catalyst

Stoichiometric oxidation

To an oven dried home-made three-neck reactor was added CuX (X=Cl, Br, I) (0.25 mmol) as pre-catalyst and a magnetic stirrer. The reactor was vacuumed and purged with nitrogen several times. The ligand TMEDA (58.0 mg, 0.5 mmol) was weighted with a micro-syringe and injected into the reactor, while 5 mL of dry THF was added *via* syringe. The mixture was stirred at room temperature, and an initial spectrum was obtained by ReactIR 15 spectrometer. After stirring for about 5 min, the reaction was started with purging the inert atmosphere with dry air. The conversion of $Cu^{I}X$(TMEDA) complexes were monitored by the characteristic absorption peak at 796 cm^{-1} (see the Figure S7).

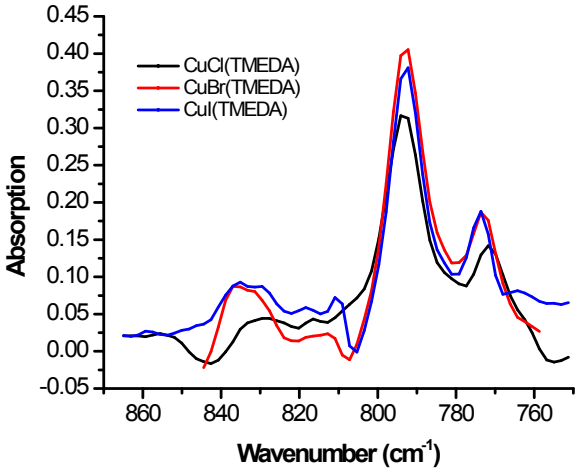

Figure S7. Characteristic absorption peak of CuCl(TMEDA)

"Step by step" Stoichiometric reaction

CuCl/TMEDA solution was oxidized by air first to generate the active Cu(II) intermediate, and was subsequently used for the oxidation of hydroquinone. As showed in Figure S8, the reaction could be completed within 30 seconds which is 4 times faster than using CuCl/TMEDA under standard reaction conditions. These results indicated that the rate of hydroquinone oxidation does mirror the rates of Cu(I) to Cu(II) oxidation.

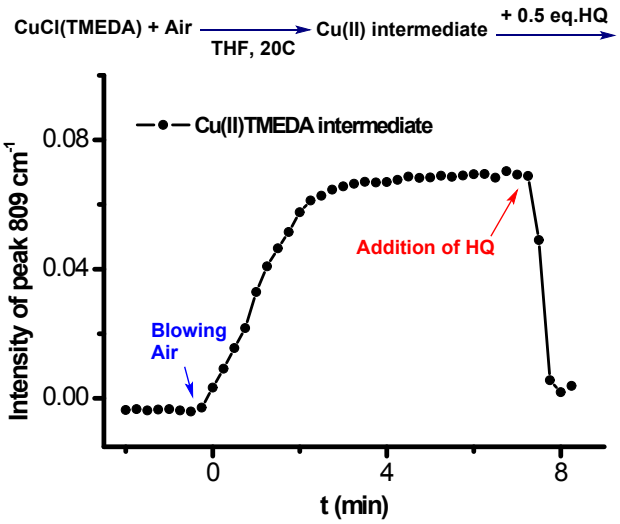

Figure S8. "step by step" Stoichiometric reaction

Inhibition experiment

To an oven dried home-made three-neck reactor was added hydroquinone (110 mg, 1.0 mmol) as substrate, CuCl (9.9 mg, 0.1 mmol) as pre-catalyst and a magnetic stirrer. The reactor was evacuated and purged with nitrogen several times. The ligand TMEDA (23.2 mg, 0.2 mmol) was weighted with a micro-syringe and injected in the reactor while 5 ml of dry THF was added *via* syringe. The mixture was stirred at room temperature, and an initial spectrum was obtained by ReactIR. After stirring for about 5 min, the reaction was started with purging the inert atmosphere with dry air. The consumption of hydroquinone was monitored by the characteristic absorption peak at 829 cm^{-1} (Figure S9). After partial substrate consumption, NaI (30 mg, 0.2 mmol) was added. When the reaction was finished, naphthalene (30 mg) as the internal standard was added and the yield of the product was determined by GC analysis.

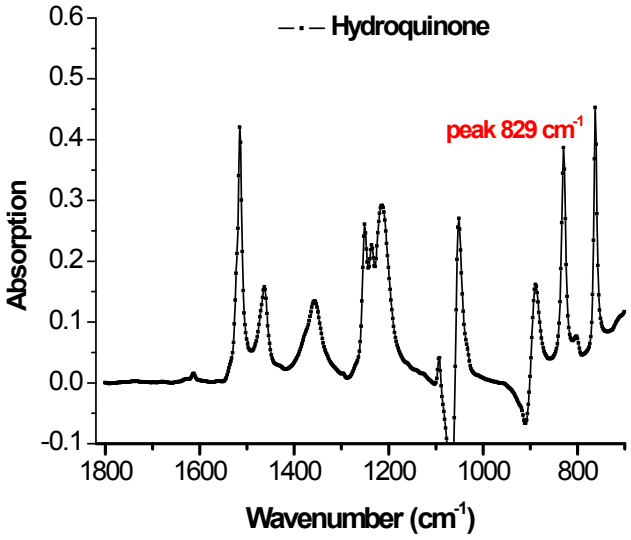

Figure S9. Characteristic absorption peak of hydroquinone

Interference experiment with sodium halide:

To further investigate the interaction of halide ions, we did the complementary experiments as showed in Figure S10. Various equivalents of NaI (0, 0.15, 0.2, 0.4 eq) were added into standard CuCl catalyzed reactions at the same conversion rate, resulting nearly the same effect to slow down the reaction rate (Figure S10a). In opposite to the above mentioned experiment, the addition of excess of NaCl slightly accelerated CuI-catalyzed oxidation reaction (Figure S10b). All of these experiments suggested that equivalent of NaI may be enough to inhibit the copper catalyst, in

opposite, excess of other halide such as NaCl will slightly interfere inhibition effect of iodide ions.

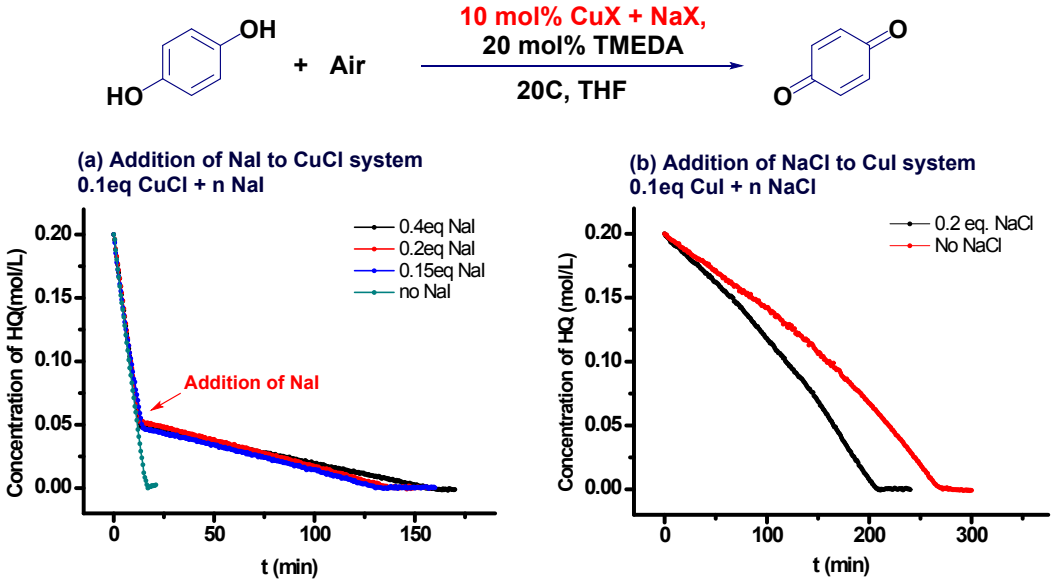

Figure S10. Interference of halide ions on catalytic oxidation reactions

Density Functional Theory Calculation

Discussion on the dissociation of $[Cu(TMEDA)X]_2$ dimer

As shown in Figure S11, the dissociation energy of CuCl/TMEDA and CuI/TMEDA dimer is 2.7 kcal/mol and 10.9 kcal/mol, respectively, which indicate that both CuCl/TMEDA and CuI/TMEDA prefer to exist in dinuclear form, especially the CuI/TMEDA.

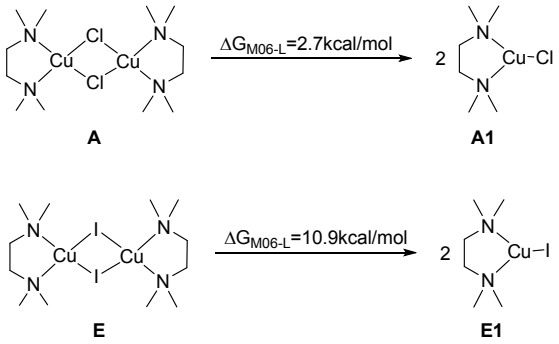

Figure S11. Free energy for the dissociation of CuCl/TMEDA dimer and CuI/TMEDA dimer

Relative energies and geometries for other peroxo $[(TMEDA)CuX]_2O_2$ complex

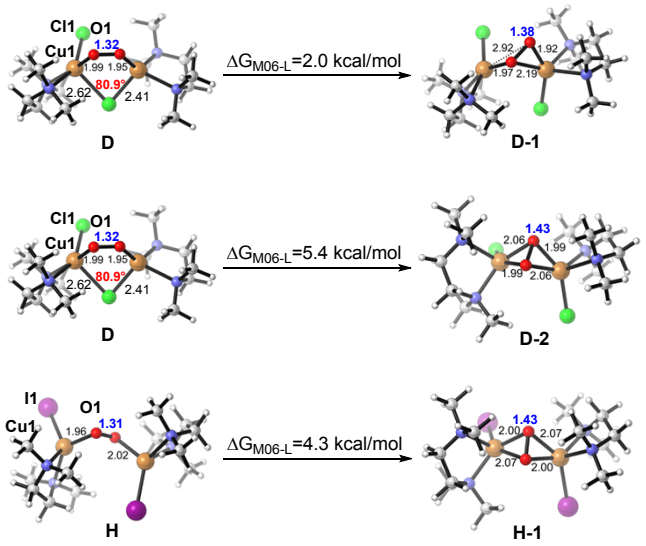

Figure S12. Relative free energies and geometries for other peroxo $[(TMEDA)CuX]_2O_2$ complex.

As shown in Figure S12, the end-on μ-peroxo Cu_2O_2 complex **D** is more stable than the side-on peroxo complex **D-1** and **D-2**. Similarly, comparing with complex **H-1,** complex **H** is more stable. Therefore, computational results indicate that both chloride system and iodide system prefer to form a side-on peroxo geometry.

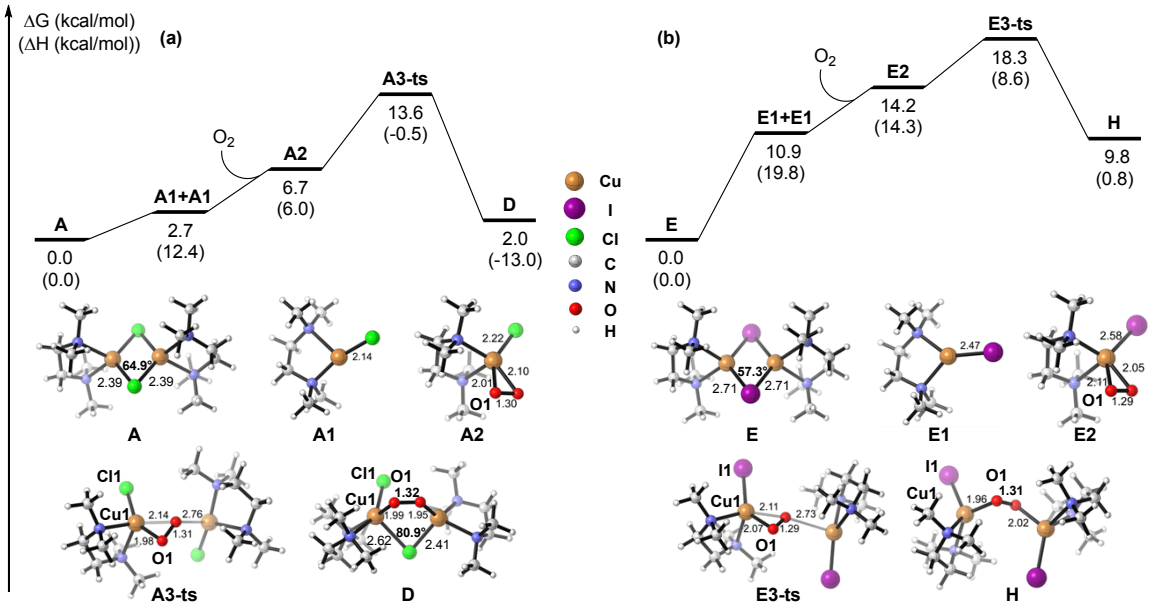

Figure S13. Free energy profile for the monomeric oxidation of CuCl/TMEDA and CuI/TMEDA. The values for bond lengths are given in angstrom.

The monomeric pathway was located and the free energy profile was shown in Fig. S13. The overall activation energy for **A3-ts** is 13.6 kcal/mol (Fig. S13a), which is 6.4 kcal/mol higher than that of **C-ts** (Fig. 5a). For the oxidation of CuI/TMEDA, the corresponding barrier of **E3-ts** (Fig.

S13b) is 4.8 kcal/mol higher than that of **G-ts** (Fig. 5a). Therefore, the monomeric pathway is unfavorable compared with the binuclear pathway.

Complete reference for Gaussian 09

Gaussian 09, Revision A.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

B3LYP absolute calculation energies, enthalpies, and free energies

All the Density functional theory (DFT) calculations were carried out with the GAUSSIAN 09 series of programs. The DFT method B3LYP[4] with a standard 6-31G(d) basis set (SDD basis set for Cu) was used for geometry optimizations. M06-L,[5] which is reported to be the more accurate functional for transition metals, is employed to calculate the single point energies with a 6-311+G(d,p) basis set (def2-TZVP for Cu and I). Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies. The solvent effects were considered by single point calculations on the gas-phase

stationary points with a SMD[6] continuum solvation model in THF solvent. Geometries are displayed with CYLview.[7]

Geometry	$E_{(elec)}$	E_{M06-L}	$H_{(gas\ phase)}$	$G_{(gas\ phase)}$	IF*
A	-2010.799841	-4897.209831	-2010.313156	-2010.409813	-
B	-2161.116399	-5047.576846	-2160.620772	-2160.723375	-
C-ts	-2161.114795	-5047.578458	-2160.619966	-2160.719577	-44.45
D	-2161.124825	-5047.591895	-2160.628514	-2160.724468	-
E	-1113.266076	-4572.563405	-1112.778994	-1112.875979	-
F	-1263.575356	-4722.919044	-1263.079859	-1263.187425	-
G-ts	-1263.571459	-4722.920712	-1263.076631	-1263.177440	-46.56
H	-1263.585880	-4722.922344	-1263.189393	-1263.089874	-
CuCl/TMEDA	-1005.389096	-2448.594462	-1005.146340	-1005.202379	-
CuI/TMEDA	-556.622139	-2286.264073	-556.380482	-556.436036	-

* IF: The imaginary frequencies for the transition states.

B3LYP geometries for all the optimized compounds and transition states

A

Cu	-1.27971700	-0.00046300	0.00033100
Cu	1.27971900	0.00011200	0.00016200
C	-4.12247200	0.69221500	-0.33152700
H	-5.06021800	1.21529700	-0.07028200
H	-4.11547100	0.57827000	-1.41989500
C	-4.12333300	-0.69035500	0.33046700
H	-5.06133500	-1.21262100	0.06852700
H	-4.11703800	-0.57640500	1.41883800

C	-3.07774100	-2.07447900	-1.38407900
H	-2.14840700	-2.58309900	-1.64962800
H	-3.91567500	-2.79335100	-1.43435600
H	-3.23913500	-1.28858100	-2.12433100
C	-2.70278500	2.56193300	-0.94465400
H	-3.55828000	3.25755700	-1.01677000
H	-1.81644200	3.12876800	-0.64787400
H	-2.50744200	2.12069800	-1.92492700
C	-2.70578900	-2.56131800	0.94476000
H	-2.51078000	-2.12018800	1.92514900
H	-3.56198900	-3.25612900	1.01630600
H	-1.81976300	-3.12901100	0.64867800
C	-3.07680300	2.07522500	1.38388100
H	-3.23967900	1.28941900	2.12391100
H	-2.14707700	2.58272600	1.65020200
H	-3.91395100	2.79505200	1.43362900
N	-2.94422000	-1.49477800	-0.03900800
N	-2.94292700	1.49554600	0.03884900
C	3.07730100	-2.07498500	1.38390200
H	2.14773500	-2.58286800	1.65004900
H	3.91472800	-2.79447900	1.43377000
H	3.23973200	-1.28913400	2.12398000
C	2.70479100	2.56150900	0.94463900
H	1.81864000	3.12891400	0.64837900
H	2.50974700	2.12035900	1.92501100
H	3.56076200	3.25659200	1.01629900
C	2.70378400	-2.56177500	-0.94469800
H	1.81756900	-3.12889200	-0.64807700
H	2.50847200	-2.12059000	-1.92500000

H	3.55951300	-3.25712500	-1.01667800
C	3.07724200	2.07467600	-1.38412300
H	3.23906600	1.28879600	-2.12430200
H	2.14775400	2.58292000	-1.64985500
H	3.91490700	2.79386800	-1.43430700
C	4.12276000	-0.69159200	-0.33132200
H	5.06063700	-1.21435400	-0.06991000
H	4.11590600	-0.57766200	-1.41969300
C	4.12304100	0.69098700	0.33065300
H	5.06091400	1.21356500	0.06886800
H	4.11659400	0.57705200	1.41902500
N	2.94342200	-1.49532300	0.03886000
N	2.94372200	1.49500200	-0.03904200
Cl	0.00006400	-0.00027000	2.01329900
Cl	-0.00006500	-0.00035100	-2.01294800

B

Cu	1.48504600	-0.10494800	0.15398700
Cu	-1.46131200	0.06312800	-0.30852000
C	4.39870100	-0.51908600	-0.72545900
H	5.47319500	-0.64621700	-0.50492900
H	4.25478600	-0.84141900	-1.76073300
C	4.04506600	0.96614100	-0.59438300
H	4.69921800	1.55487900	-1.25806800
H	4.23187500	1.30670900	0.42922100
C	2.32902700	1.07904200	-2.34689000
H	1.28151000	1.33463900	-2.52172600
H	2.97995200	1.73021700	-2.95208400
H	2.49130000	0.04089300	-2.64493300

C	3.38856900	-2.71785900	-0.39311500
H	4.33834200	-3.28114300	-0.41877200
H	2.67215500	-3.25795700	0.23137800
H	2.98028500	-2.67053400	-1.40672300
C	2.30390500	2.65833000	-0.52692300
H	2.49650800	2.80245300	0.53825000
H	2.92616300	3.35980200	-1.10432600
H	1.24805900	2.84396200	-0.73560500
C	4.06447300	-1.41756300	1.51592700
H	4.17779200	-0.41017200	1.92302700
H	3.34530700	-1.95189000	2.14262800
H	5.03993600	-1.93336300	1.57249500
N	2.62107400	1.25722000	-0.90059100
N	3.55959000	-1.36142100	0.13869200
C	-3.81874200	-0.41741900	-2.25190900
H	-3.07486600	-0.41819100	-3.05156700
H	-4.74708900	-0.89400400	-2.61685100
H	-4.02032500	0.62637600	-2.00653900
C	-2.85840500	2.04589000	1.62962500
H	-1.88216500	2.27574500	2.06413400
H	-2.94217300	2.58791100	0.68492600
H	-3.64525800	2.38631200	2.32711000
C	-2.92877500	-2.50380800	-1.45198900
H	-2.21497300	-2.48716300	-2.28038500
H	-2.45286600	-3.00351900	-0.60466800
H	-3.81593700	-3.08410200	-1.76473700
C	-2.68505700	-0.14044500	2.61785000
H	-2.71213700	-1.21684800	2.43613500
H	-1.68515700	0.10516800	2.98256200

H	-3.42658100	0.10870300	3.39905800
C	-4.20916700	-1.10561600	0.05354000
H	-5.23525600	-1.35740800	-0.27247500
H	-3.89717200	-1.88974400	0.75054900
C	-4.23850600	0.24328300	0.78020500
H	-5.03430900	0.21555900	1.54748400
H	-4.50770200	1.03489400	0.07437400
N	-3.27301900	-1.12457800	-1.08421800
N	-2.93944400	0.60001900	1.37536900
O	1.80874600	0.88485300	2.08967500
O	0.82627500	1.27810200	2.74543100
Cl	-0.05509100	-1.62174200	0.67379200
Cl	-1.09989800	1.87554100	-1.61151300

C-ts

Cu	-1.61328100	-0.16951700	0.05692800
Cu	1.68562600	0.34542700	-0.16521400
C	-4.56508900	-0.06572700	0.74082800
H	-5.61589500	-0.39829700	0.66515100
H	-4.47108900	0.45909500	1.69644000
C	-4.27184600	0.90210800	-0.41023400
H	-4.99866600	1.73065800	-0.38234900
H	-4.40629900	0.39056500	-1.36858700
C	-2.71111500	2.44400800	0.68501100
H	-1.67595800	2.79156400	0.66504500
H	-3.39440000	3.29513300	0.52963400
H	-2.91304400	2.00302400	1.66411500
C	-3.51151500	-1.80027300	2.09085600
H	-4.45756700	-2.25937800	2.42884800

H	-2.73008900	-2.56391400	2.07016300
H	-3.21121900	-1.03590800	2.81270200
C	-2.56585800	2.06352200	-1.68865100
H	-2.67124300	1.32461700	-2.48592200
H	-3.24315300	2.90968700	-1.88656200
H	-1.53183900	2.41317600	-1.66214100
C	-3.99083700	-2.22968000	-0.22840500
H	-4.04471500	-1.79980800	-1.23177300
H	-3.21845100	-3.00323900	-0.23746600
H	-4.96317200	-2.70021300	0.00502200
N	-2.88717600	1.43258200	-0.38602500
N	-3.63250200	-1.20143800	0.75640100
C	4.02890500	1.73021200	1.33564400
H	3.32025300	2.54681000	1.48965400
H	4.85483700	1.81282200	2.06554300
H	4.43839300	1.84306500	0.32927600
C	3.23218000	-0.63166900	-2.54337500
H	2.28337400	-0.76344900	-3.06577600
H	3.52071000	0.42020000	-2.61183600
H	4.00109700	-1.25175700	-3.03603100
C	2.76399700	0.32683500	2.81987900
H	2.09914400	1.17376400	3.00943000
H	2.17270400	-0.58803600	2.89364000
H	3.55652000	0.31835100	3.59029900
C	2.59241900	-2.40523400	-1.04598100
H	2.43706600	-2.69419100	-0.00592100
H	1.63151200	-2.48572100	-1.55647100
H	3.31785700	-3.09237800	-1.51499300
C	4.15833800	-0.70086800	1.11496700

H	5.15499200	-0.64088300	1.59052700
H	3.67143800	-1.59881700	1.50827100
C	4.34438400	-0.83605700	-0.39930200
H	5.02340700	-1.67971000	-0.61006200
H	4.82620600	0.06413000	-0.79190200
N	3.31736200	0.45187400	1.46581200
N	3.06323600	-1.00812800	-1.12529600
Cl	0.81315900	2.39834000	-0.39053400
Cl	0.03128200	-1.26965900	1.08359400
O	-1.28600900	-0.80904700	-1.96871700
O	-0.12229400	-0.65810400	-2.40770500

D

Cu	1.66328900	0.26587500	-0.25855300
Cu	-1.57033100	-0.15443600	-0.40800100
C	4.26680300	0.16746900	1.02723200
H	5.32078400	0.43497100	1.22349600
H	3.80558100	-0.05849500	1.99353500
C	4.22240300	-1.07539500	0.13307300
H	4.81640000	-1.87904800	0.59957100
H	4.69382300	-0.85505900	-0.82966100
C	2.31362200	-2.35050000	0.97532400
H	1.27948500	-2.61823700	0.75010900
H	2.91423300	-3.26772600	1.10153500
H	2.32156900	-1.78124900	1.90696000
C	3.22921700	2.31479400	1.47033300
H	4.15123600	2.72613100	1.91757000
H	2.66452900	3.13228400	1.01448500
H	2.60626200	1.87149200	2.24978100

C	2.76941700	-2.30402500	-1.38971900
H	3.12808600	-1.68962300	-2.22015800
H	3.38251400	-3.21955700	-1.32908400
H	1.72815800	-2.57157600	-1.58048500
C	4.25755200	1.92490900	-0.67186300
H	4.44491700	1.19576200	-1.46333100
H	3.64813000	2.72718600	-1.09561500
H	5.22420700	2.34673700	-0.34337500
N	2.83927300	-1.52695400	-0.13338200
N	3.52704700	1.30357400	0.44342800
C	-3.99797900	-1.86300800	0.22952900
H	-3.45792000	-2.69364200	-0.22596700
H	-4.77978700	-2.24568800	0.90576300
H	-4.47275200	-1.29547000	-0.57358000
C	-3.47112900	1.85414400	-1.72448000
H	-2.60878700	2.09177500	-2.34938500
H	-3.97119600	0.97679400	-2.14400300
H	-4.17321500	2.70358100	-1.72832100
C	-2.37463900	-1.85902800	1.99856400
H	-1.85502300	-2.67867200	1.49860900
H	-1.64083900	-1.25894400	2.53721500
H	-3.11955200	-2.26739800	2.70097200
C	-2.29060900	2.73190800	0.18695600
H	-1.93238600	2.52106000	1.19515500
H	-1.42114300	2.93929900	-0.43842800
H	-2.95629900	3.61044700	0.20065500
C	-3.67102700	0.15421200	1.58578300
H	-4.53586200	-0.14331200	2.20302300
H	-2.93060300	0.61430900	2.24672600

C	-4.12303300	1.15583400	0.52417700
H	-4.56767000	2.03695200	1.01096400
H	-4.90595300	0.71360100	-0.09782000
N	-3.02974900	-1.02561800	0.96849100
N	-2.99920200	1.55393100	-0.35719500
Cl	-0.94873900	-2.19693800	-1.26046200
Cl	0.06497900	0.53556900	1.52032800
O	0.68033200	1.02431600	-1.76457700
O	-0.63257700	0.93198700	-1.79085100

E

I	-0.00037200	2.37585000	-0.00044000
Cu	1.29715100	0.00024700	-0.00079600
Cu	-1.29658500	0.00006200	0.00042600
I	-0.00024300	-2.37560400	-0.00029400
C	4.15872500	-0.34730900	0.68387600
H	5.09986200	-0.10503400	1.20927200
H	4.14222700	-1.43279300	0.54691700
C	4.15974200	0.34548500	-0.68158300
H	5.10086900	0.10182100	-1.20631200
H	4.14472700	1.43098900	-0.54467300
C	3.14877400	-1.34869900	-2.10937600
H	2.23673600	-1.61086100	-2.64983900
H	4.00532300	-1.37077500	-2.80651100
H	3.29711600	-2.10706100	-1.33858500
C	2.77017400	-0.98020600	2.56566000
H	3.63806100	-1.04870400	3.24511200
H	1.89021500	-0.69769100	3.14933600
H	2.57831100	-1.95842400	2.11910100

C	2.77312800	0.98085900	-2.56401800
H	2.58201900	1.95909000	-2.11717300
H	3.64160800	1.04870100	-3.24276700
H	1.89329700	0.69960300	-3.14848100
C	3.14848600	1.34872700	2.11005500
H	3.29842700	2.10645700	1.33895700
H	2.23616000	1.61217500	2.64940800
H	4.00435300	1.37038900	2.80805500
N	2.98834500	-0.01674900	-1.50335500
N	2.98727400	0.01661500	1.50470100
C	-3.14856400	1.34844000	-2.10960700
H	-2.23646900	1.61156800	-2.64950200
H	-4.00479900	1.37013800	-2.80715500
H	-3.29790400	2.10636400	-1.33859200
C	-2.77221400	0.98076500	2.56492100
H	-1.89247000	0.69923600	3.14939700
H	-2.58086000	1.95901000	2.11819700
H	-3.64068800	1.04874900	3.24367000
C	-2.77101300	-0.98058700	-2.56506300
H	-1.89119800	-0.69841100	-3.14911700
H	-2.57930000	-1.95886000	-2.11856900
H	-3.63920500	-1.04881700	-3.24415200
C	-3.14815300	-1.34865100	2.10999400
H	-3.29698700	-2.10682100	1.33912000
H	-2.23598300	-1.61114700	2.65007000
H	-4.00445900	-1.37067700	2.80744300
C	-4.15862600	-0.34711800	-0.68279300
H	-5.09987000	-0.10460900	-1.20788900
H	-4.14240800	-1.43259200	-0.54575600

C	-4.15901300	0.34589000	0.68255600
H	-5.10015900	0.10278000	1.20752400
H	-4.14352400	1.43135700	0.54538200
N	-2.98734700	0.01638700	-1.50408400
N	-2.98763000	-0.01664600	1.50416900

F

Cu	2.17799200	-0.27683000	0.16337600
Cu	-1.81924700	-0.04337200	-0.09624600
C	4.90358100	0.39556300	-0.75363000
H	6.00494800	0.39234100	-0.69179100
H	4.64735000	0.47557900	-1.81402900
C	4.36284900	1.61363100	0.00116800
H	4.83772100	2.52559400	-0.39658300
H	4.63506700	1.54677900	1.05947800
C	2.44359400	2.20678800	-1.40261300
H	1.35347500	2.27823600	-1.40914600
H	2.87416100	3.19833100	-1.61647400
H	2.74978900	1.50951400	-2.18602700
C	4.41167400	-1.93338600	-1.26706700
H	5.45491000	-2.16025700	-1.54479400
H	3.94289600	-2.84060100	-0.87797900
H	3.86080900	-1.62757500	-2.15980900
C	2.38881400	2.65391300	0.96591400
H	2.66630300	2.28396900	1.95614100
H	2.81570900	3.65976800	0.82684000
H	1.30022200	2.71716400	0.89695400
C	5.02068200	-1.31742900	0.97962600
H	4.95634300	-0.55040400	1.75447900

H	4.53330400	-2.21951200	1.35811100
H	6.08435400	-1.54052700	0.78974200
N	2.88718700	1.72256800	-0.07222300
N	4.33778100	-0.87267200	-0.24704800
C	-4.55875900	0.17247300	-1.44076900
H	-4.06100400	0.75622800	-2.21761100
H	-5.52272000	-0.20584700	-1.82597300
H	-4.74578700	0.84706400	-0.60383000
C	-2.64360900	0.26341300	2.85727000
H	-1.59529400	0.41633400	3.12420100
H	-3.02915700	1.20423600	2.45828400
H	-3.20663500	-0.01300900	3.76652600
C	-3.40629400	-1.79897300	-2.18464600
H	-2.93305100	-1.20675600	-2.97196000
H	-2.71715900	-2.59721700	-1.89767400
H	-4.33066100	-2.24988200	-2.58764400
C	-2.11226000	-2.02096400	2.32883400
H	-2.12554200	-2.79868900	1.56266300
H	-1.06789200	-1.82300900	2.57923300
H	-2.63336300	-2.39448600	3.22876200
C	-4.26989300	-1.71101200	0.07916100
H	-5.33831100	-1.92048400	-0.10987700
H	-3.76000100	-2.67870600	0.11630700
C	-4.13629700	-1.00547700	1.43186200
H	-4.67235700	-1.59552800	2.19708800
H	-4.62300200	-0.02680900	1.38584100
N	-3.67898200	-0.93419900	-1.02721500
N	-2.73099500	-0.78478300	1.82567700
O	2.24644200	-0.48345700	2.24412900

O	1.28118800	-0.06779600	2.91181800
I	0.32896500	-1.75276900	-0.78220700
I	-1.55744700	2.53213500	-0.35494000

G-ts

Cu	2.05216800	-0.15404300	0.44811900
Cu	-1.60895100	-0.06494500	0.06535800
C	4.65168100	0.03004400	-0.68750000
H	5.74775600	-0.08410100	-0.69551600
H	4.28592700	-0.24274800	-1.68180000
C	4.28650900	1.48236100	-0.37749600
H	4.75874600	2.14379900	-1.12015200
H	4.68713700	1.76854100	0.59961900
C	2.27952400	1.91428600	-1.71120700
H	1.19435600	2.01986500	-1.65210900
H	2.71453300	2.82744900	-2.14721500
H	2.50488000	1.06035200	-2.35281200
C	4.09831600	-2.29553600	-0.23933500
H	5.14331500	-2.61502900	-0.37642400
H	3.60735400	-2.96785200	0.46774100
H	3.56464200	-2.35472700	-1.18911300
C	2.47010800	2.84785500	0.50898600
H	2.81412400	2.66581800	1.53114500
H	2.93858000	3.76940900	0.12955600
H	1.38521200	2.97246500	0.51837900
C	4.70154300	-0.85866000	1.59989300
H	4.63666100	0.14472600	2.02521300
H	4.19769500	-1.54711400	2.28147500
H	5.76252100	-1.14353400	1.51781700

N	2.81787200	1.68905900	-0.34770100
N	4.03506700	-0.91260100	0.28014400
C	-4.48793600	0.26388000	-1.09686900
H	-4.09260800	1.05387200	-1.73768800
H	-5.44360500	-0.10419500	-1.51098300
H	-4.66906300	0.70873800	-0.11722800
C	-2.40595300	-0.36314500	2.99236300
H	-1.37270700	-0.16420300	3.27866700
H	-2.88978300	0.59402400	2.78362100
H	-2.92362500	-0.86418700	3.82842700
C	-3.24599900	-1.36111000	-2.34868000
H	-2.86577100	-0.56177800	-2.98952600
H	-2.48784200	-2.14542600	-2.29920500
H	-4.16632400	-1.77197200	-2.80031600
C	-1.67175500	-2.44377400	2.02085500
H	-1.65622400	-3.06262000	1.12170300
H	-0.63871000	-2.19730200	2.27277300
H	-2.12104900	-3.01901200	2.84920900
C	-3.94715200	-1.88988400	-0.09081300
H	-4.99654100	-2.17147500	-0.29312100
H	-3.33554900	-2.77611800	-0.28755600
C	-3.81834000	-1.48646500	1.37872500
H	-4.24386100	-2.28287400	2.01329500
H	-4.40660800	-0.58362300	1.56521700
N	-3.49815800	-0.82278600	-1.00340300
N	-2.42169700	-1.19855400	1.77480100
O	1.31165700	-0.69767600	2.30755000
O	0.65171300	0.33229700	1.84454500
I	0.45580300	-1.53166800	-1.27748700

I	-1.59143900	2.54826400	-0.04819400

H

I	2.39794800	-1.63317400	-1.55013800
I	-2.41773700	1.79613300	-1.36259200
C	3.17662100	2.38243700	0.99597200
H	3.84087500	3.23462200	0.78267700
H	2.42023200	2.73214000	1.70445000
C	3.98525800	1.24250000	1.61844900
H	4.55442100	1.63597300	2.47895300
H	4.71868600	0.87047900	0.89678000
C	2.43361600	0.36489600	3.28381800
H	1.75004900	-0.46270800	3.48545600
H	3.14831800	0.45765200	4.12021900
H	1.83526600	1.27612000	3.22378800
C	1.38913500	2.94548000	-0.55458400
H	1.81035300	3.94994600	-0.71420800
H	0.85867100	2.62984100	-1.45441800
H	0.66981400	2.97487700	0.26489100
C	3.89137500	-1.13916500	2.09844500
H	4.33894400	-1.36696800	1.12862800
H	4.68163500	-1.08329000	2.86702700
H	3.21124900	-1.95637200	2.35266000
C	3.39965200	1.91324000	-1.39295600
H	4.19662400	1.19392500	-1.20345100
H	2.85854600	1.57758500	-2.27827600
H	3.83432900	2.90763800	-1.57848400
N	3.12525300	0.11313500	2.01092700
N	2.46586000	1.97174400	-0.24506300

C	-2.39146000	-0.73590200	3.23964700
H	-1.71898300	0.07780600	3.51971000
H	-3.09207700	-0.93149700	4.07017500
H	-1.77846300	-1.62378900	3.07325100
C	-1.37620600	-2.83124800	-0.92017800
H	-0.88656100	-2.40081900	-1.79499900
H	-0.62450000	-2.94100800	-0.13747000
H	-1.78576400	-3.81884600	-1.18263500
C	-3.89807600	0.85452600	2.23931000
H	-3.23244500	1.65439500	2.57428300
H	-4.36093800	1.17569300	1.30335200
H	-4.67901200	0.69924300	3.00383400
C	-3.42502900	-1.73961800	-1.56574500
H	-4.21788500	-1.05146500	-1.27190300
H	-2.91129800	-1.30083100	-2.42168200
H	-3.86177800	-2.70884300	-1.85212600
C	-3.94590500	-1.46515500	1.50862700
H	-4.47999900	-1.97350800	2.33043500
H	-4.70991800	-1.03645800	0.85335700
C	-3.12216900	-2.49898900	0.73824700
H	-3.76756500	-3.34084800	0.44147300
H	-2.33679500	-2.90349600	1.38278600
N	-3.10651900	-0.36362500	2.01000800
N	-2.45697200	-1.92373100	-0.46066300
Cu	1.58715000	0.10250800	0.22738300
Cu	-1.59172100	-0.11000900	0.22362700
O	0.08956200	-0.76371900	1.23640800
O	-0.08916900	0.65032000	1.31185400

A1 CuCl/TMEDA

C	-0.65270000	2.15709400	-1.31505000
H	-1.70893800	1.91690800	-1.46105500
H	-0.51116900	3.24758000	-1.42853400
H	-0.08665300	1.65197200	-2.10291200
C	2.07253300	-1.71198600	-0.93259600
H	1.74328800	-2.70052900	-0.60567700
H	1.68357000	-1.53154200	-1.93725500
H	3.17425400	-1.69095600	-0.96181600
C	-1.02978500	2.31967800	1.05733000
H	-2.08262200	2.06842800	0.90328100
H	-0.73147900	1.93103200	2.03562300
H	-0.92056600	3.41924700	1.06490800
C	2.04378200	-0.97892100	1.36172500
H	1.64531800	-0.25702500	2.07649500
H	1.70785600	-1.97404600	1.66090500
H	3.14530000	-0.94513500	1.39280400
C	1.20962800	1.80385300	0.22408900
H	1.61446100	2.76365500	-0.14614900
H	1.39378200	1.78699900	1.30318900
C	1.98213900	0.66372100	-0.45051100
H	3.06187200	0.78994300	-0.26755000
H	1.83131100	0.70685900	-1.53326900
N	-0.23260000	1.68322600	0.00607800
N	1.54409500	-0.68624400	-0.00243200
Cu	-0.49960900	-0.73183700	0.00955700
Cl	-2.55323400	-1.32115400	0.00202500

E1 CuI/TMEDA

C	-1.67908100	-2.10998700	-1.33491600
H	-0.71835200	-2.57687200	-1.56436000
H	-2.47386300	-2.87376000	-1.38881000
H	-1.87303900	-1.34913300	-2.09473900
C	-1.50192500	2.50496800	-1.00189300
H	-0.59953200	3.06524300	-0.74671000
H	-1.36036200	2.06137000	-1.99078500
H	-2.35799100	3.19965900	-1.03781100
C	-1.32271300	-2.53727000	1.00811900
H	-0.37319400	-3.01832800	0.76199900
H	-1.22601600	-2.07968500	1.99618400
H	-2.11577300	-3.30350900	1.04313700
C	-1.83154000	2.03936500	1.33849000
H	-1.96770300	1.26238500	2.09429100
H	-0.91299200	2.58156700	1.57435100
H	-2.68561600	2.73602600	1.38877700
C	-2.84627400	-0.75948600	0.33410200
H	-3.74608000	-1.33174200	0.05053800
H	-2.87820900	-0.63711900	1.42112700
C	-2.88949400	0.61551300	-0.34254700
H	-3.82578600	1.12892400	-0.06587500
H	-2.90405400	0.49219800	-1.42982600
N	-1.61124400	-1.49739900	0.00407800
N	-1.70826100	1.43834400	-0.00353100
Cu	-0.03947900	0.04769700	-0.00106500
I	2.43068200	0.02178000	0.00014000

A2

C	1.66071900	1.58666500	1.42978000
H	2.18684900	0.88379800	2.07972900
H	2.26901200	2.49846200	1.32183300
H	0.71448400	1.84208200	1.90876500
C	-2.70264300	0.86297100	0.44587300
H	-3.20985500	-0.10548400	0.45384700
H	-2.39094300	1.09191200	1.46839600
H	-3.41847200	1.63177800	0.10818100
C	2.72228900	0.55424300	-0.47785000
H	3.25068400	-0.10216900	0.21778500
H	2.54089300	-0.00090900	-1.39893900
H	3.34576000	1.43947400	-0.67853400
C	-1.93536800	0.39710900	-1.79112300
H	-1.06183200	0.27514200	-2.43293900
H	-2.44021300	-0.57062300	-1.75357700
H	-2.61676200	1.14629300	-2.23030000
C	0.70045700	1.85467900	-0.80999600
H	1.19949500	2.83709100	-0.84607800
H	0.77154200	1.41285300	-1.80757100
C	-0.77065600	2.04977100	-0.43026400
H	-1.21717500	2.78265100	-1.12435100
H	-0.84145900	2.48705900	0.57053400
N	1.42565400	0.94924500	0.11725500
N	-1.52432600	0.78273500	-0.43004100

Cu	0.12377000	-0.73991000	0.29796900
O	-0.89583100	-1.79846200	1.79096500
O	-0.40027100	-0.68538600	2.23933000
Cl	0.60820000	-2.01045400	-1.45584000

A3-ts

C	3.93562500	-0.20895000	2.35285000
H	3.34387600	-0.85047300	3.01048000
H	4.98374300	-0.22022600	2.69531900
H	3.54580600	0.80658100	2.44002800
C	1.96031600	2.73720300	-0.02530200
H	0.91797900	2.73169800	-0.35184000
H	1.98400100	2.69767800	1.06747800
H	2.43777400	3.67351000	-0.35893700
C	4.24060600	-2.11354000	0.90793200
H	3.63032800	-2.70180100	1.59876700
H	4.08100900	-2.49475000	-0.10155900
H	5.30068200	-2.22242200	1.19037300
C	2.54565400	1.56883900	-2.05531800
H	3.00900100	0.67368000	-2.47383000
H	1.48916500	1.56572200	-2.33211200
H	3.02658000	2.46823700	-2.47509900
C	4.61253700	0.10684900	0.01479700
H	5.66697600	0.15738700	0.33728000

H	4.58109300	-0.41552000	-0.94590300
C	4.06905500	1.52897800	-0.14534400
H	4.70895300	2.07409300	-0.85713600
H	4.14363400	2.06220300	0.80682500
N	3.81707000	-0.70055400	0.96855300
N	2.65498700	1.55668600	-0.58091000
Cu	1.78950800	-0.42174200	0.13511800
O	-0.14216100	-0.43526400	1.06670200
O	0.77248600	0.25175600	1.69735100
C	-3.00207500	0.64358800	2.51803600
H	-2.42735300	1.57336000	2.52866800
H	-3.67669900	0.63055400	3.39409800
H	-2.29182900	-0.18151400	2.60486800
C	-1.74853700	-2.50141900	-0.89043500
H	-1.22655100	-2.25113400	-1.81500000
H	-1.02535800	-2.44322600	-0.07713900
H	-2.14179100	-3.52897500	-0.95699700
C	-4.63682000	1.70741300	1.10526100
H	-4.03719900	2.62139700	1.09975400
H	-5.16090700	1.64717300	0.14699900
H	-5.38495800	1.77309400	1.91615300
C	-3.80615200	-1.62838100	-1.78356900
H	-4.60747100	-0.89551900	-1.67209100
H	-3.27872200	-1.41706300	-2.71608800

H	-4.24688100	-2.63749300	-1.84079200
C	-4.44907700	-0.72566800	1.11386900
H	-4.92332800	-1.04720100	2.05907900
H	-5.26025300	-0.58898800	0.39167200
C	-3.51417600	-1.84237200	0.63672300
H	-4.08152500	-2.78471700	0.55583700
H	-2.72166200	-2.00234900	1.37302300
N	-3.74625000	0.55339300	1.25779800
N	-2.84904100	-1.53498900	-0.65618100
Cu	-2.18671600	0.41223100	-0.58551500
Cl	1.83736000	-1.84132600	-1.58690400
Cl	-1.49976100	2.34214400	-1.27868000

E2

C	2.16268000	-2.12267400	0.88445400
H	1.64699100	-2.43261600	1.79609400
H	2.74149200	-2.97411900	0.49351500
H	2.84611800	-1.31323700	1.14338600
C	2.33563000	2.30633900	-0.15128300
H	1.62053100	3.06504000	0.17694400
H	2.86169300	1.93002200	0.72962100
H	3.06422400	2.77860700	-0.83135000
C	0.23223800	-2.78319000	-0.39795800
H	-0.24832900	-3.10166900	0.52967800

H	-0.54599700	-2.44130300	-1.08146700
H	0.77327300	-3.63619900	-0.83613500
C	0.84366200	1.73350400	-1.95237800
H	0.27259100	0.93639000	-2.43154000
H	0.12522800	2.47506300	-1.59666800
H	1.51176100	2.20091400	-2.69592300
C	1.81204800	-1.21599400	-1.36513400
H	2.53168900	-1.97467700	-1.71339600
H	1.02630600	-1.13978400	-2.12181400
C	2.52658300	0.12999900	-1.21777700
H	3.02568100	0.37041000	-2.17206800
H	3.31630300	0.05168900	-0.46415100
N	1.16225500	-1.66789600	-0.10761600
N	1.60711600	1.20771700	-0.80634700
Cu	0.15116500	0.06802000	0.61535400
I	-2.28308600	0.06127700	-0.22789100
O	0.18993100	1.32130100	2.23159600
O	1.20851400	0.54352100	2.38170800

E3-ts

C	3.17571800	1.86249600	2.55763200
H	2.80389600	1.12024900	3.26740600
H	3.96157900	2.46131000	3.04392600
H	2.34522400	2.51502200	2.28582000

C	0.87072900	2.50416000	-1.35540300
H	0.22876200	1.77956100	-1.85978200
H	0.38793200	2.76777900	-0.41254900
H	0.94995400	3.40461300	-1.98573800
C	4.80558800	0.26482900	1.78184500
H	4.42573800	-0.44740500	2.51755300
H	5.16535200	-0.29914100	0.92021600
H	5.63275300	0.83852000	2.22796100
C	2.79413200	1.46975400	-2.38054300
H	3.76145300	0.99261500	-2.21138200
H	2.14448900	0.72837600	-2.85019200
H	2.92328500	2.32372300	-3.06637900
C	4.20806800	2.13527800	0.35274900
H	4.86007200	2.88254000	0.83303500
H	4.82390900	1.57218900	-0.35418300
C	3.07617500	2.84788600	-0.39160400
H	3.51657000	3.58394000	-1.08534000
H	2.46068100	3.41351300	0.31456600
N	3.70930800	1.16741500	1.36425000
N	2.19552900	1.90127800	-1.10387600
Cu	2.13281000	0.14151700	0.35245200
I	2.97995200	-2.09858100	-0.62037800
O	0.04887300	-0.13574400	0.56986800
O	0.47251600	0.68952800	1.46748600

C	-2.03218900	-1.53512200	2.68188600
H	-1.79015400	-0.53902000	3.05962900
H	-2.30159700	-2.18663000	3.53153800
H	-1.13861900	-1.93605600	2.19997900
C	-1.25509600	-2.10557500	-1.95407500
H	-1.27119800	-1.30272100	-2.69563400
H	-0.35566200	-2.00109300	-1.34419400
H	-1.21380300	-3.07324000	-2.48127600
C	-4.33189900	-0.88844800	2.38302400
H	-4.09802400	0.10131300	2.78252500
H	-5.14182200	-0.77447700	1.65799100
H	-4.67345700	-1.53852600	3.20720500
C	-3.66130800	-2.11681100	-1.96427800
H	-4.57128000	-2.02232900	-1.36782800
H	-3.65621200	-1.30516700	-2.69520100
H	-3.68200900	-3.08321600	-2.49629200
C	-3.42239300	-2.73746000	1.08196300
H	-3.38692800	-3.55749200	1.81946000
H	-4.44573700	-2.70535800	0.69575100
C	-2.44668000	-3.04773600	-0.05803400
H	-2.68622400	-4.03767300	-0.48239400
H	-1.42558900	-3.10514400	0.33046300
N	-3.13798200	-1.43381800	1.71462800
N	-2.46244700	-2.00476300	-1.10905800

Cu	-2.61022500	-0.13850500	-0.03776400
I	-3.12514700	2.27936400	-0.42120700

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