Electronic Supplementary Information for

Nitrite reduction by copper through ligand-mediated proton and electron transfer

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General Considerations

All commercially-available reagents were used as received without further purification with the exception of Ph_3SiCl, which was purified by sublimation (100 °C, 0.1 torr) prior to use. H_3thpa,[1] $CuF(H_3thpa)$,[2] $CuF(H_3thpa)BF_4$[2] and $CuF(PPh_3)_3$[3] were synthesized as previously described. All manipulations were carried out under a purified atmosphere of nitrogen using standard Schlenk techniques or in an MBraun Lab Master 130 or Innovative Technologies Pure LabHE GP-1 glovebox, unless otherwise stated. NMR spectra were recorded on either a Varian MR400 or a Varian vnmrs 500 spectrometer and are referenced to residual solvent peaks. Reported ^{19}F NMR chemical shifts are relative to $CFCl_3$ and ^{15}N NMR chemical shifts are relative to $MeNO_2$. Solid-state IR spectra were collected using a Nicolet iS10 spectrometer using a diamond attenuated total reflectance (ATR) accessory. Gas-phase IR spectra were collected using a Perkin-Elmer Spectrum BX spectrometer using a custom gas cell with an 11 cm path length and BaF_2 windows (see Figure S11). EPR spectra were collected on a Bruker EMX EPR spectrometer. Electronic absorption spectra were collected on a Varian Cary-50 spectrophotometer. Elemental analyses were performed by Midwest Microlabs, LLC, Indianapolis, IN.

Reaction of **1** with **Ph_3SiCl**:

In a small vial, **1** (5.2 mg; 0.012 mmol) was dissolved in CD_2Cl_2 (700 μL). To this yellow solution, **Ph_3SiCl** (4.0 mg; 0.014 mmol, dissolved in 700 μL CD_2Cl_2) was added dropwise *via* syringe. An aliquot (*ca.* 0.6 mL) was immediately transferred to an NMR tube and the reaction mixture analyzed by ^1H and ^{19}F NMR, which showed quantitative conversion to $CuCl(H_3thpa)$ along with Ph_3SiF and excess, unreacted Ph_3SiCl.

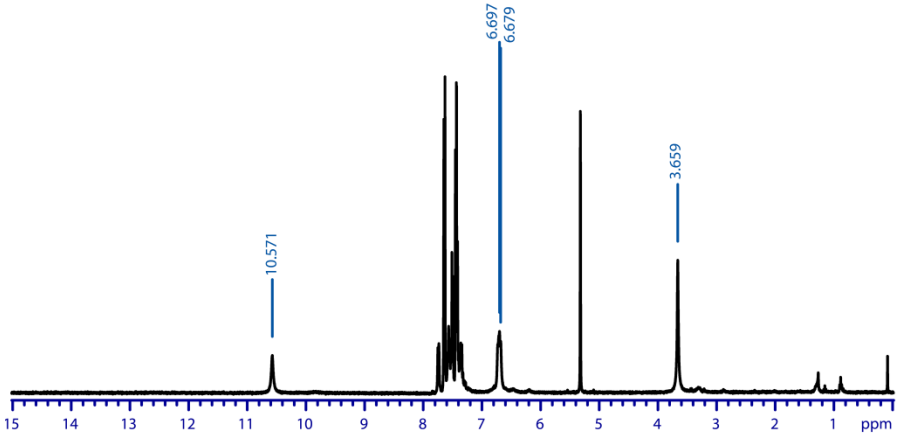


Figure S1. 400 MHz ^1H NMR spectrum of the reaction of **1** with **Ph_3SiCl** (CD_2Cl_2) showing the clean formation of $CuCl(H_3thpa)$. Note that the number and chemical shift of –OH resonances provides the number and identity of H_3thpa-containing products. The single –OH resonance at 10.57 ppm is characteristic of the product.[1]

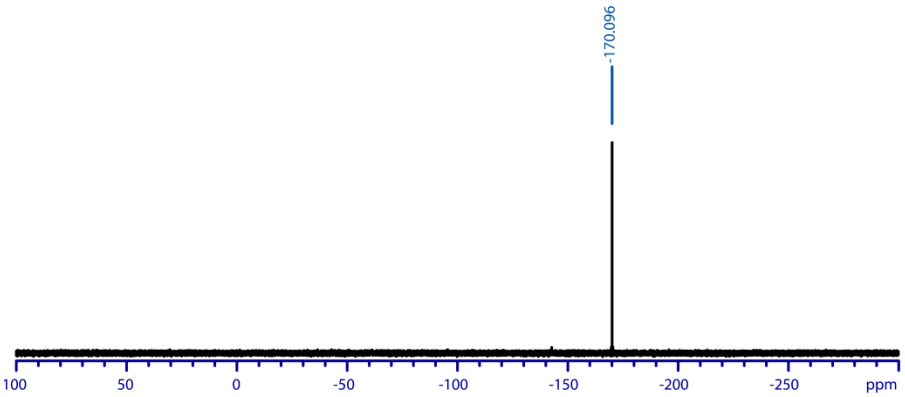


Figure S2. 377 MHz ^{19}F NMR spectrum of the reaction of **1** with **Ph_3SiCl** (CD_2Cl_2) showing the formation of Ph_3SiF.

$Ph_3Si(ONO)$

Benzene (*ca.* 10 mL) was added to a mixture of $AgNO_2$ (80.0 mg; 0.520 mmol) and Ph_3SiCl (139.0 mg; 0.471 mmol). The mixture was stirred protected from light for 24 h then filtered and concentrated to a white solid. The solid was redissolved in a minimal amount of pentane, filtered and concentrated to *ca.* 2 mL and placed in a –35 °C freezer overnight. The deposited colorless crystals (70.4 mg; 49%) were collected and dried briefly (*ca.* 10 min) under vacuum and used without further purification. This material slowly decomposes at room temperature over the course of *ca.* 2 days and was therefore stored at –35 °C. We have found samples stored at this temperature have remained unchanged for *ca.* 1 month. Note that we have been unable to obtain satisfactory combustion analyses for this material to date, presumably due to decomposition prior to analysis.

Characterization data for **$Ph_3Si(ONO)$**: ^{1}H NMR (400 MHz, CD_2Cl_2): 7.64-7.66 (m, 6H), 7.51-7.55 (m, 3H), 7.43-7.47 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): 136.1, 132.4, 131.5, 128.8. IR (ATR, cm^{-1}): 3069, 3016, 1631 (N=O)[4], 1589, 1428, 1119, 997, 908.

The ^{15}N isotopologue, **$Ph_3Si(O^{15}NO)$**, was prepared in an identical manner using $Na^{15}NO_2$ and dimethoxyethane solvent. Note that material obtained in this manner contained small amounts (*ca.* 5%) of unreacted Ph_3SiCl.

Characterization data for **$Ph_3Si(O^{15}NO)$**: ^{15}N NMR (51 MHz, CD_2Cl_2): 188.0. IR (ATR, cm^{-1}): 3068, 3016, 1603 (N=O), 1589, 1428, 1118, 997, 899.

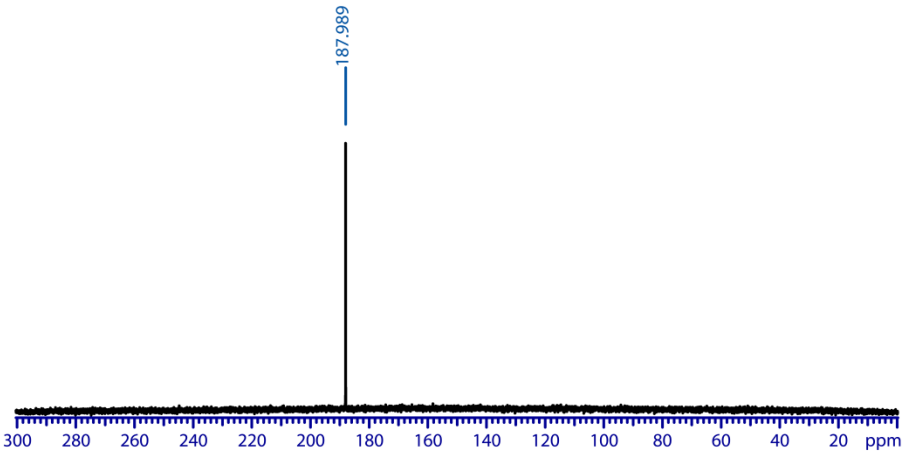


Figure S3. 51 MHz ^{15}N NMR spectrum of **$Ph_3Si(O^{15}NO)$** in CD_2Cl_2.

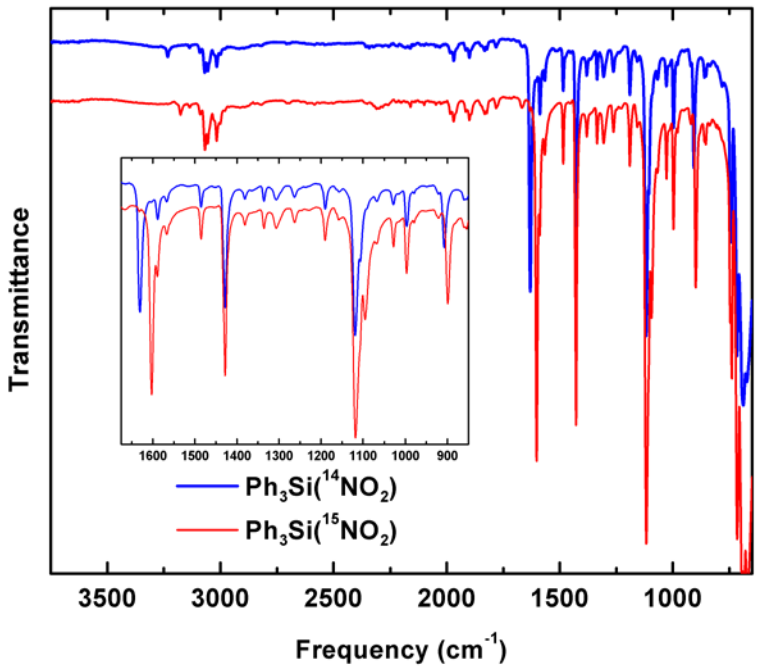


Figure S4. ATR-IR spectra of **$Ph_3Si(ONO)$** isotopologues (^{14}N blue, ^{15}N red).

$Cu(OH_2)$Hthpa (2)

Method A: In a scintillation vial, **1** (21.3 mg; 0.051 mmol) was dissolved in dichloromethane (*ca.* 10 mL) to give a yellow solution. With stirring, **$Ph_3Si(ONO)$** (16.2 mg; 0.053 mmol, dissolved in *ca.* 1 mL dichloromethane) was added dropwise immediately producing a color change to green. The reaction was stirred for 15 min, then pentane (*ca.* 10 mL) was added to produce a precipitate. The supernatant was decanted and the solid was triturated with pentane, then dried to an olive green powder (12.7 mg; 60%).

Method B: In the open air, a mixture of dichloromethane and ethanol (*ca.* 20 mL, 1:1) was added to solid H_3thpa (100.8 mg; 0.298 mmol) and $Cu(OH)_2$ (28.9 mg; 0.296 mmol). The suspension was stirred for 24 h and then filtered. The green filtrate was concentrated to a green residue and diethyl ether (*ca.* 10 mL) was added. The resulting green powder was collected on a sintered glass frit, washed with copious amounts of diethyl ether and dried to afford a mint green powder (83.4 mg; 67%).

Crystals of **2** suitable for X-ray diffraction were grown from vapor diffusion of diethyl ether into a 1:1 dichloromethane/ethanol solution of **2** at 5 °C.

Characterization data for **2**: IR (ATR, cm^{-1}): 1658 (C=O), 1614, 1488, 1437, 1155, 998, 796. EPR (1:1 CH_2Cl_2:EtOH, 77 K): $g_x = g_y = 2.177$, $g_z = 1.955$, $A_x = A_y = 103$ G, $A_z = 50$ G. UV-vis (CH_2Cl_2): 438 nm (50 $cm^{-1}M^{-1}$), 680 (35), 905 (160). Anal. calc'd ($C_{18}H_{18}CuN_4O_4$): 51.73 C, 4.34 H, 13.41 N%. Found: 51.58 C, 4.19 H, 13.20 N%.

Low temperature reaction of **1** with **Ph_3(ONO)**:

In a screw cap NMR tube, **1** (2.1 mg; 5.0 μmol) was dissolved in CD_2Cl_2 (700 μL). The tube was placed in a cold well (liquid N_2) and frozen. To the frozen solution, **Ph_3Si(ONO)** (200 μL of a 27 mM solution in CD_2Cl_2; 5.4 μmol) was layered onto the frozen solution using a syringe and sealed. The frozen tube was transferred directly into a pre-cooled NMR spectrometer and spectra were recorded immediately. The recorded spectra showed no reaction at -75 °C, upon warming to -50 °C immediate conversion of **1** to paramagnetic **2** (broad resonance at *ca.* 9.2 ppm, Figure S5) was observed without the appearance of a diamagnetic intermediate. Note any diamagnetic intermediates would be distinguishable by (1) a new –*CH_2* resonance between 3.5 and 4.5 ppm and/or (2) a new –*OH* resonance >8 ppm.

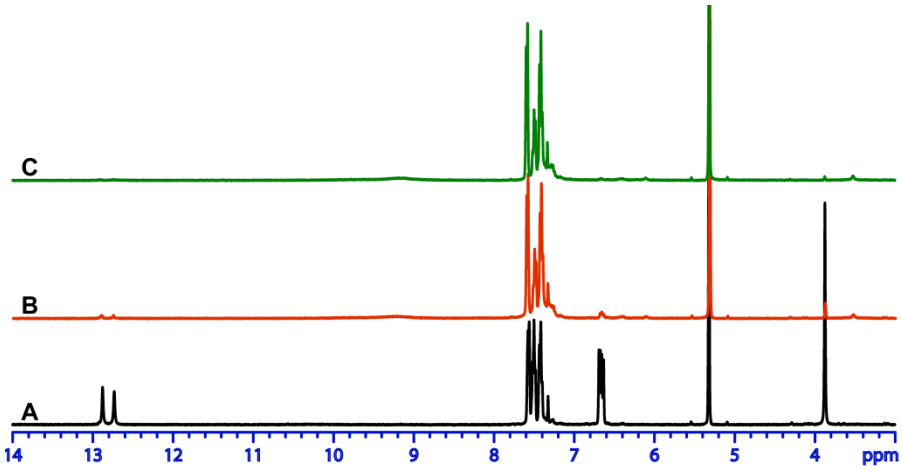


Figure S5. 400 MHz ^{1}H NMR spectra of the reaction of **1** with **Ph_3Si(ONO)** showing no reaction at -75 °C (A, black), nearly complete consumption of starting materials upon immediately warming to -50 °C (B, red) and complete consumption of **1** 15 min later at -50 °C (C, green).

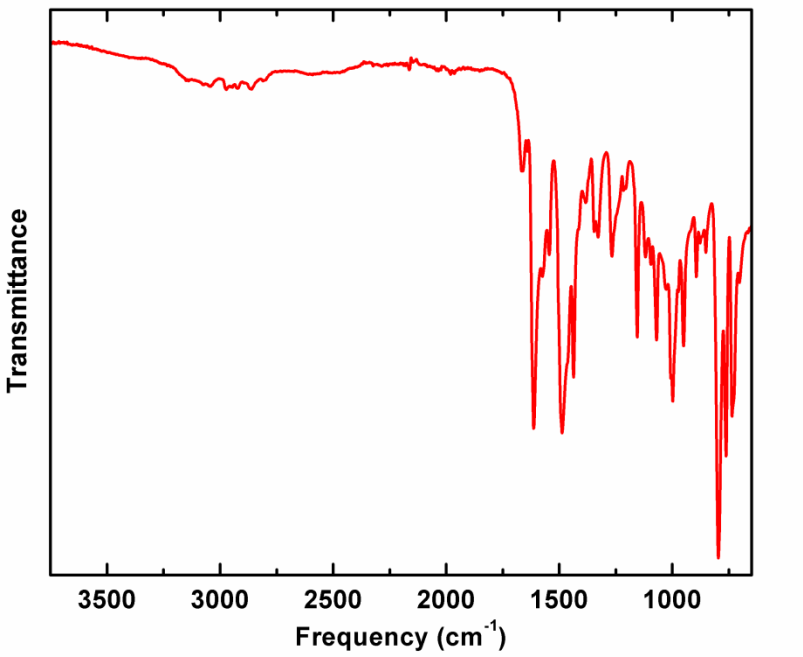


Figure S6. ATR-IR spectrum of solid **2**.

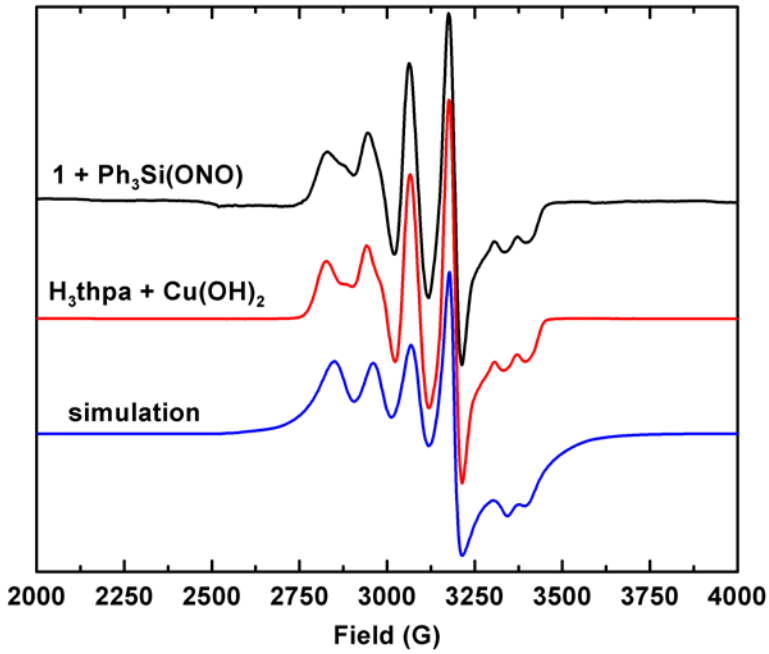


Figure S7. X-band EPR spectra (77 K, 1:1 CH_2Cl_2:EtOH) of samples of **2** and simulated spectrum.

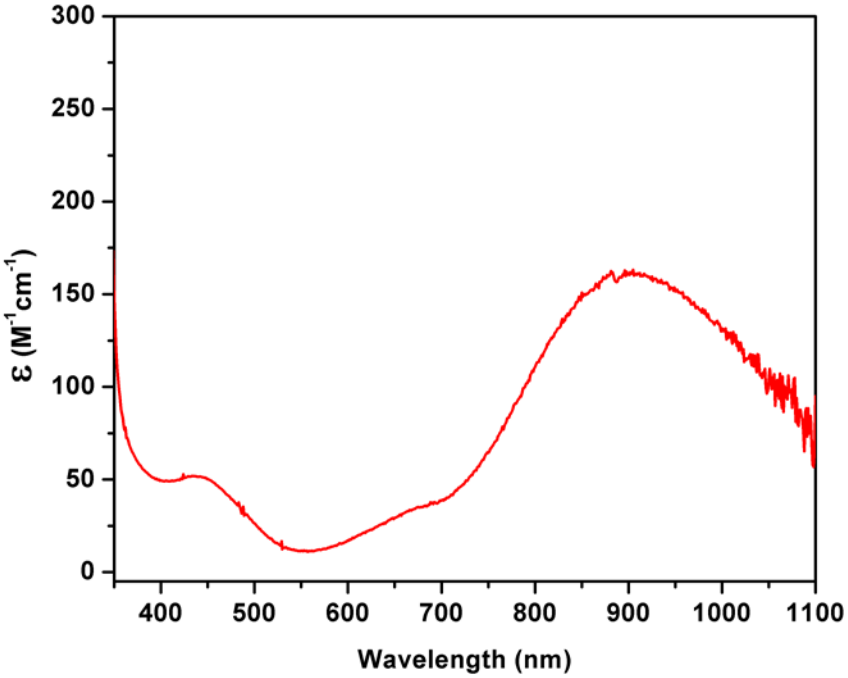


Figure S8. UV-vis spectrum (CH_2Cl_2) of pure **2** isolated from the reaction of H_3thpa and $Cu(OH_2)$.

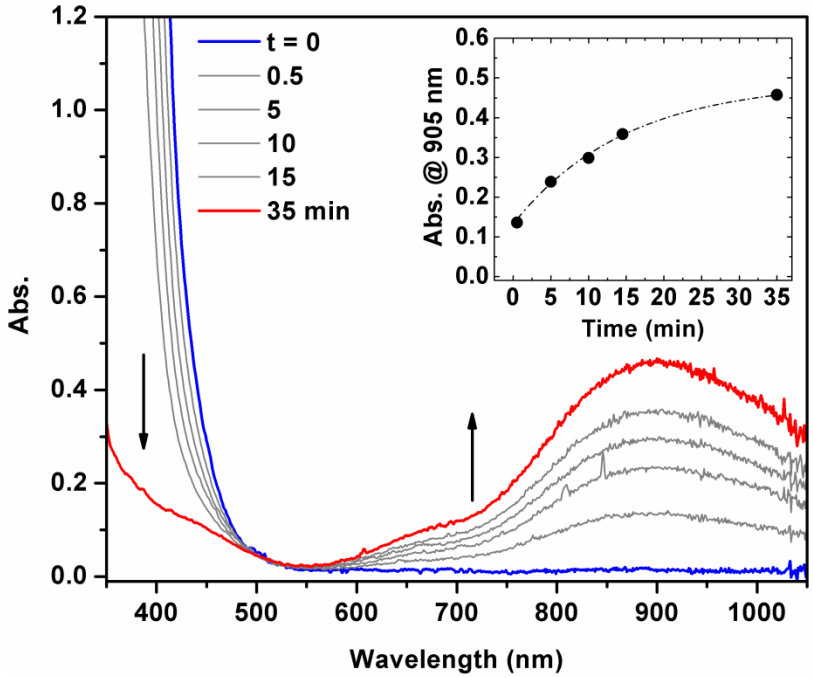


Figure S9. UV-vis spectra (CH_2Cl_2, 0 °C) recorded during the reaction of **1** with **$Ph_3Si(ONO)$** showing the formation of **2** with an isosbestic point at 510 nm.

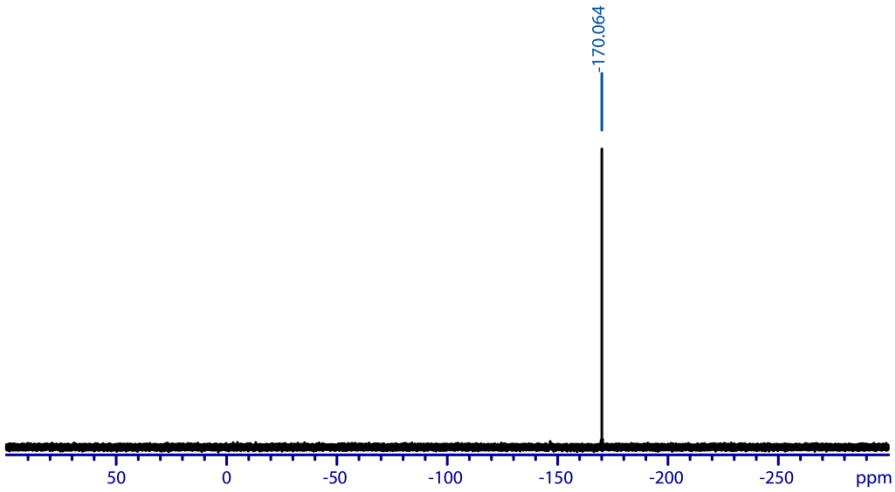


Figure S10. 377 MHz ^{19}F NMR spectrum of the reaction of **1** and **$Ph_3Si(ONO)$** showing the formation of Ph_3SiF.

Headspace measurements

IR spectroscopy: In a 20 mL scintillation vial with a Teflon stirbar in a glovebox, the copper fluoride (either **1**, **3** or **4** *ca.* 0.035 mmol) was dissolved in dichloromethane (5 mL) and then sealed using a septum and electrical tape. To the stirring solution, the nitrite (either $Ph_3Si(ONO)$ or $Ph_3Si(O^{15}NO)$, *ca.* 1.05 equivalents dissolved in 1.0 mL dichloromethane) was added *via* syringe through the septum. The solution was allowed to stir for 30 min and the headspace was then evacuated by attaching the IR cell (*ca.* 105 mL) under vacuum (0.25 torr) *via* a needle (Figure S11). IR spectra were recorded directly on the collected headspace samples in the IR cell.

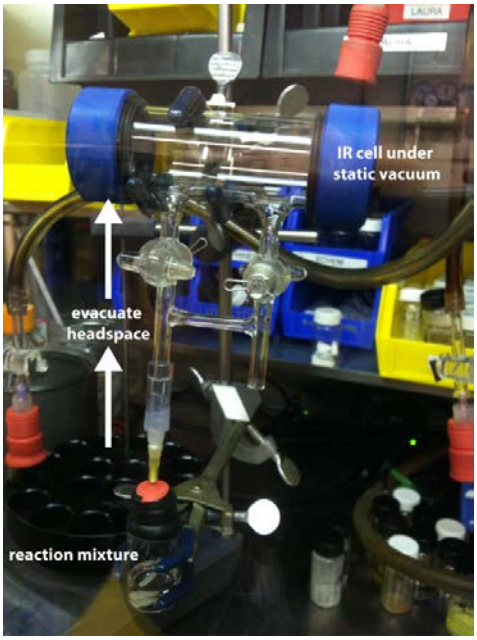


Figure S11. Experimental setup used to collect IR spectra of headspace samples.

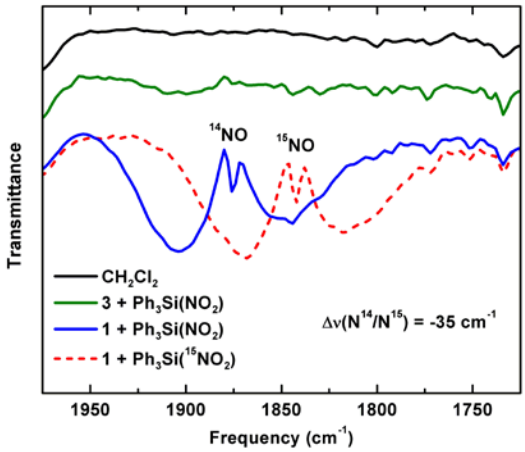


Figure S12. Gas-phase IR spectra of headspace samples.

UV-vis:[5] In a small Schlenk tube with a Teflon stirbar in a glovebox, the copper fluoride (either **1**, **3** or **4** *ca.* 5.0 μmol) was dissolved in dichloromethane (2 mL). Separately, CoTPP (5.0 μmol dissolved in 3 mL dichloromethane) was added to a small vial with a stir bar, and placed inside the Schlenk tube such that the two solutions could not mix, and the tube was sealed using a septum. To the stirring copper solution, the nitrite (**$Ph_3Si(ONO)$** *ca.* 1.05 equivalents dissolved in 1.0 mL dichloromethane) was added *via* syringe through the septum. The solution was allowed to stir for 60 min to assure complete diffusion of NO. After this time, 0.25 mL of the CoTPP solution was removed, diluted with dichloromethane (final volume 3.0 mL) and then a UV-vis spectrum was recorded. The yield of NO was determined by fitting the position of the Q-band of the resultant UV-vis spectrum (Figure S13). The position of the Q-band in authentic UV-vis spectra of CoTPP (528 nm) and CoTPP-NO (538 nm) were used for the fitting procedure.

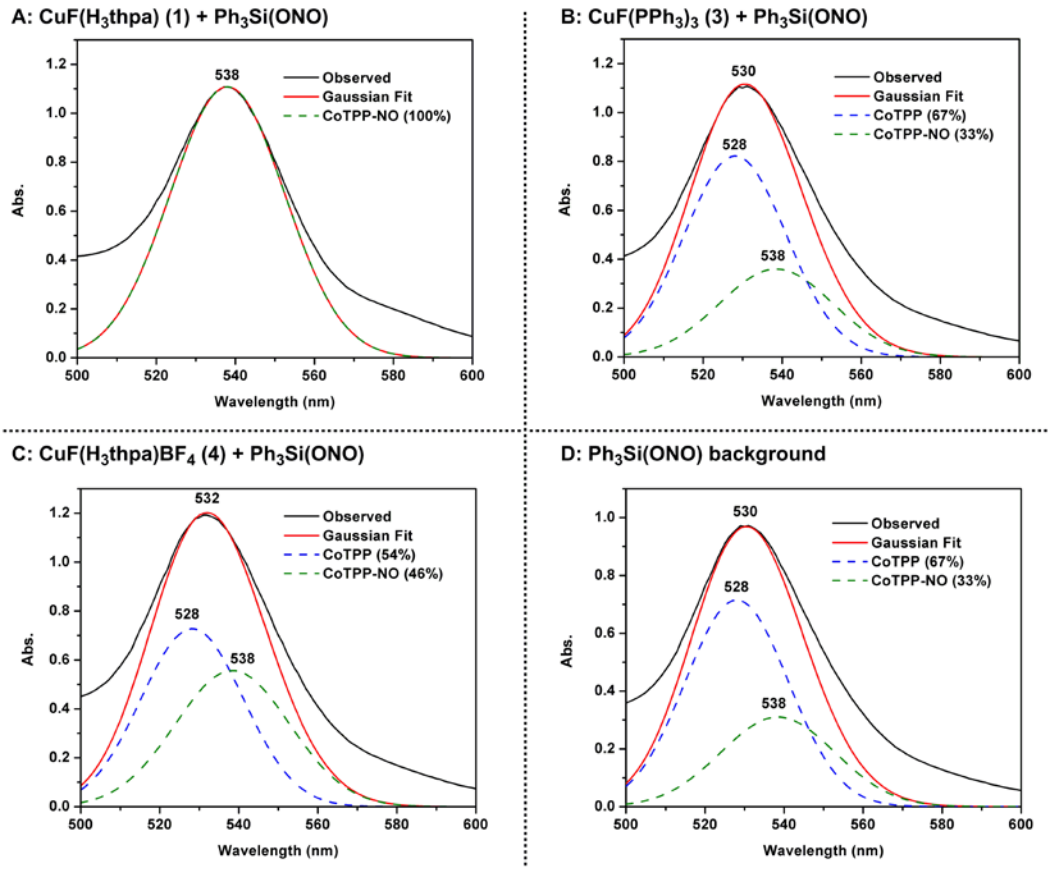


Figure S13. UV-vis spectra and Gaussian fits of CoTPP solutions after exposure to reactions of **1** (A), **3** (B) and **4** (C) with **$Ph_3Si(ONO)$**, as well as background decomposition of **$Ph_3Si(ONO)$** (D).

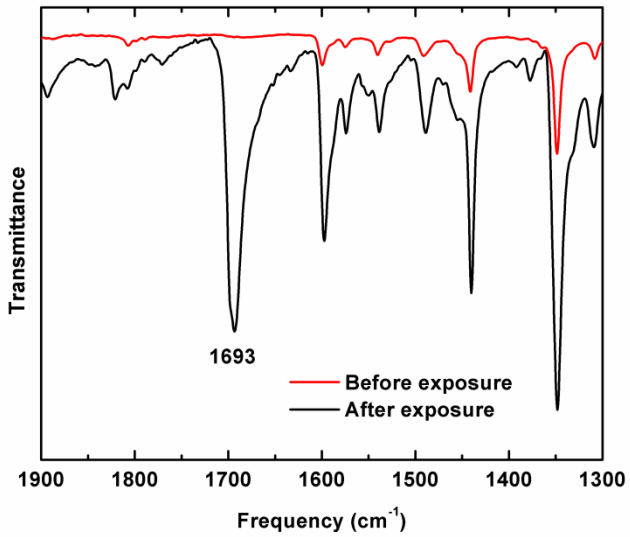


Figure S14. ATR-IR spectra of the CoTPP-containing material before (red) and after (black) exposure to reaction mixtures evolving NO, demonstrating that observed UV-vis changes are due to NO coordination.

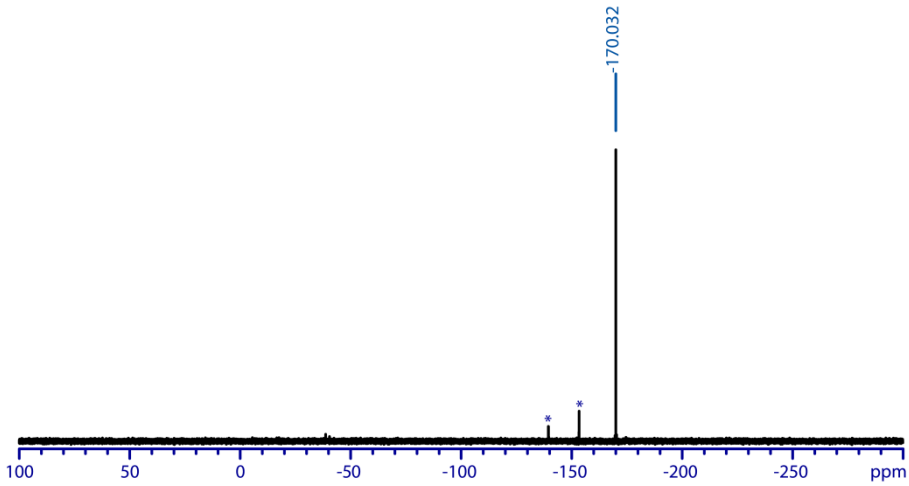
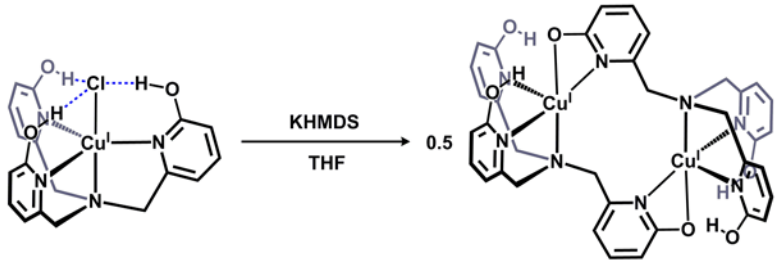


Figure S15. 377 MHz ^{19}F NMR spectrum of the reaction of **3** and $Ph_3Si(ONO)$ in CH_2Cl_2 showing the formation of Ph_3SiF (-170.0 ppm) as the major product with unknown minor side-products (-139.5 and -153.4) denoted with *.



Scheme S1. Deprotonation of $CuCl(H_3thpa)$ gives the dimer $[Cu(H_2thpa)]_2$.

$[Cu(H_2thpa)]_2$

In a scintillation vial, **$CuCl(H_3thpa)$** (105.0 mg; 0.240 mmol) was dissolved in tetrahydrofuran (*ca.* 20 mL) to give a yellow solution. With stirring, potassium hexamethyldisilylazide (KHMDS, 49.6 mg; 0.249 mmol) was slowly added immediately producing a precipitate. The reaction was stirred for 15 min, then diethyl ether (*ca.* 10 mL) was added. The precipitate was collected and washed with diethyl ether. The solid was redissolved in a minimal amount of dichloromethane, filtered, then concentrated to give the title compound as a pale yellow powder (94.4 mg; 98%). Note that the deprotonation can be achieved using a weak base such as sodium acetate (p*K*a = 4.8).

Crystals of **$[Cu(H_2thpa)]_2$** suitable for X-ray diffraction were grown by vapor diffusion of diethyl ether into a dichloromethane solution of **$[Cu(H_2thpa)]_2$**.

Characterization data for **$[Cu(H_2thpa)]_2$**: ^1H NMR (400 MHz, CD_2Cl_2): 12.92 (s, 4H), 7.59 (t, J = 6.8, 2H), 7.41 (t, J = 7.2, 4H), 6.79 (d, J = 7.6, 4H), 6.61 (d, J = 8, 4H), 6.42 (d, J = 6.8, 4H), 4.38 (s, 4H), 4.20 (d, J = 15.6, 4H), 3.21 (d, J = 14.8, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): 171.0, 164.2, 153.4, 139.9, 138.7, 129.7, 115.3, 114.2, 112.9, 111.2, 62.2, 57.4. IR (ATR, cm^{-1}): 1657, 1611, 1567, 1470, 1425, 1274, 1201, 1150, 1013, 788.

Computational details

All calculations were performed using Gaussian 09[6] and visualized using ChemCraft.[7] Becke's three-parameter hybrid function[8] using Lee, Yang and Parr's correlation function[9] (B3LYP) was used for all calculations using the triple-zeta basis set TZVP.[10] Structures were freely optimized in C_1 symmetry and were confirmed to be minima based on the absence of imaginary frequencies in the calculated vibrational spectra. Transition states were confirmed based on the presence of one imaginary frequency in the calculated vibrational spectra. All reported energies are enthalpies in kcal/mol. Spin densities were calculated using Mulliken population analyses.[11] Appropriate spin polarization of the ground state wavefunction was ensured by examining closed-shell and open-shell wave functions when calculating intermediates along the N-O bond cleavage pathways. For the formation of **II**, the intermediates along the N-O cleavage pathway from **I** are best described as open-shell singlet (broken symmetry) states until NO dissociation.[12] Compound **III** is best described as a Cu(II)-NO· species with an open-shell (broken symmetry) ground state wavefunction (Figure S17).

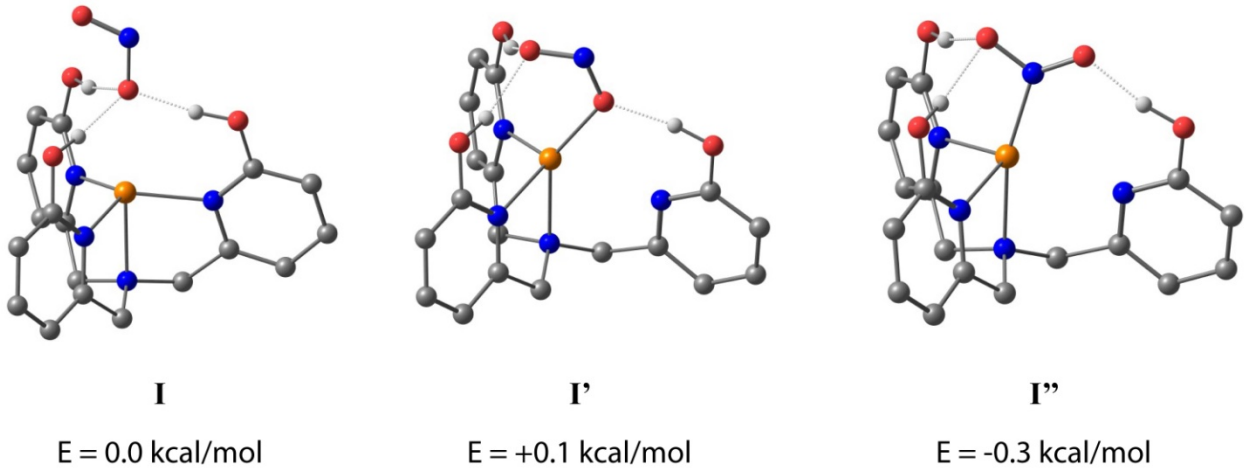
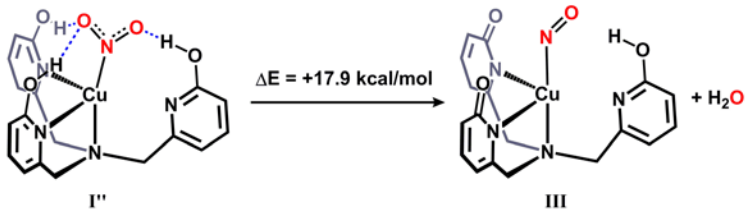
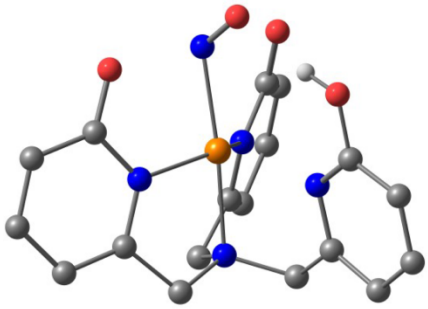


Figure S16. Optimized geometries and relative energies of Cu(H_3thpa)-nitrite adducts.



Scheme S2. Water elimination from **I''** to form a Cu(II)-nitrosyl is endothermic by 17.9 kcal/mol.



Closed-shell singlet: E = 0.0 kcal/mol

Open-shell triplet: E = +3.9 kcal/mol

Open-shell singlet (broken symmetry): E = -4.6 kcal/mol

Figure S17. Optimized geometry of **III** as a broken symmetry state and comparison of energies of alternative electronic configurations.

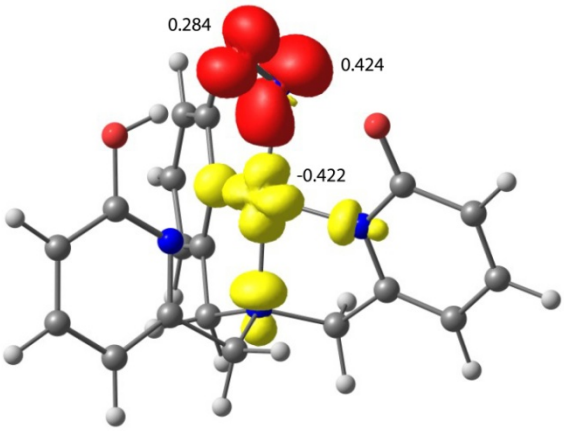


Figure S18. Mulliken spin density plot of **III**.

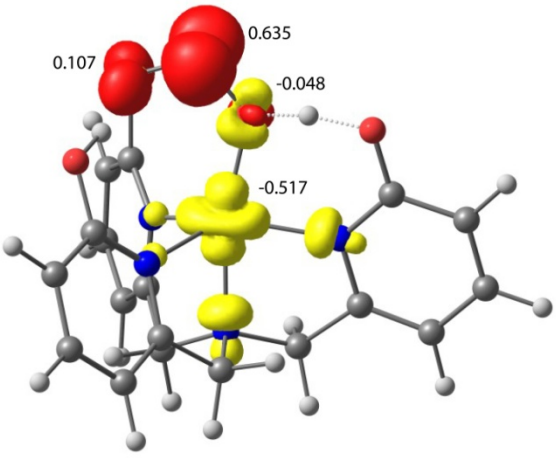


Figure S19. Mulliken spin density plot of the optimized transition state (**TS**^{I}) for O-NO bond cleavage.

Crystallographic Details

Crystals were mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(2) K with the detector placed at a distance 42.00 mm from the crystal. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0[13] and corrected for absorption. The structures were solved and refined with the Bruker SHELXTL (version 2008/4) software package.[14] All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a mix of idealized and refined positions. Please see the accompanying .cif file for more information regarding the determination of the space group for **2**.

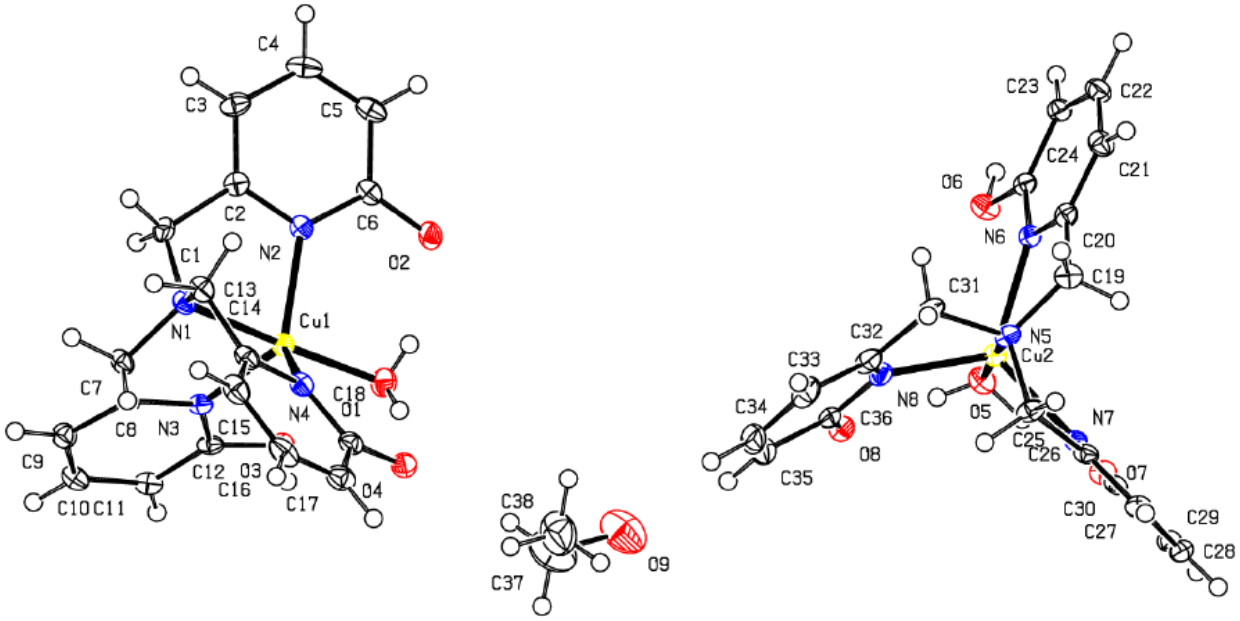


Figure S20. Solid state structure of **2** showing both independent molecules and ethanol solvate (50% probability ellipsoids).

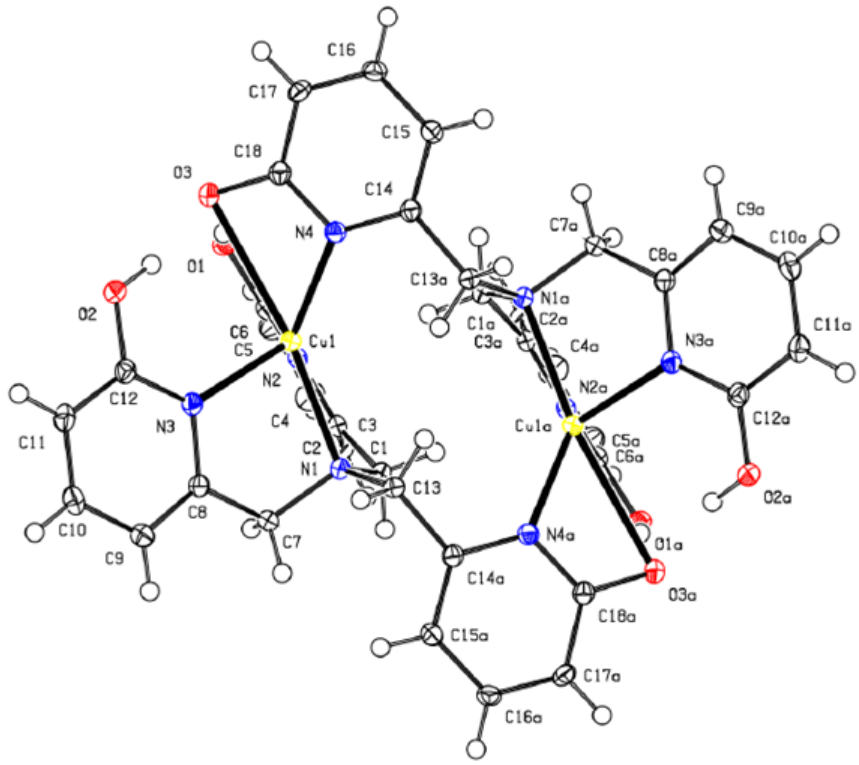


Figure S21. Solid state structure of **[Cu(H_2thpa)]$_2$** (50% probability ellipsoids).

Compound	**$[Cu(OH_2)Hthpa]_2 \cdot EtOH$**	**$[Cu(H_2thpa)]_2$**
Empirical Formula	$C_{38}H_{42}Cu_2N_8O_9$	$C_{36}H_{34}Cu_2N_8O_6$
Formula Weight	881.88	801.79
Temperature	85(2) K	85(2) K
Wavelength	1.54178 Å	1.54178 Å
Crystal system	Monoclinic	Orthorhombic
Space group	P21/c	Pbcn
Unit cell dimensions	a = 12.1843(2) Å α= 90° b = 13.6819(3) Å β= 99.683(7)° c = 22.5624(16) Å γ = 90°	a = 14.1161(3) Å α= 90° b = 15.8051(11) Å β= 90° c = 15.5380(3) Å γ = 90°
Volume	3707.7(3) $Å^3$	3243.5(2) $Å^3$
Z	4	4
Density (calc.)	1.580 g/cm^3	1.642 g/cm^3
Absorption coefficient	1.996 mm^{-1}	2.147 mm^{-1}
F(000)	1824.0	1648.0
Crystal size	0.12 x 0.02 x 0.02 mm^3	0.20 x 0.18 x 0.16 mm^3
Theta range for data	3.70 to 68.30°	4.20 to 68.24°
Index ranges	-14<=h<=14 -16<=k<=16 -27<=l<=26	-17<=h<=17 -19<=k<=18 -17<=l<=17
Reflections collected	102604	85886
Independent reflections	6790	2965
Completeness	100.0 %	100.0%
Absorption correction	Semi-empirical from equivalents	none
Max. and min. transmission	0.962 and 0.821	0.709 and 0.683
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints /parameters	6790 / 0 / 538	2965 / 0 / 244
Goodness-of-fit on F^2	1.162	1.152
Final R indices [I>2sigma(I)]	R1 = 0.0472 wR2 = 0.1457	R1 = 0.0327 wR2 = 0.0833
R indices (all data)	R1 = 0.0518 wR2 = 0.1499	R1 = 0.0328 wR2 = 0.0834
Largest diff. peak and hole	1.662 and -0.720 $e.Å^{-3}$	0.353 and -0.379 $e.Å^{-3}$

Table S1. Atomic coordinates for optimized structures calculated using the TZVP basis set.

I			
atom	x	y	z
Cu	2.914544	1.910031	1.959381
N	1.473995	3.392154	1.839217
N	4.487122	2.303374	3.243576
O	0.108148	2.557271	3.499715
O	3.958442	0.682929	4.796899
O	1.789458	-1.029427	1.010124
N	3.201255	0.667361	0.332136
N	4.040483	3.357802	0.654611
C	5.348555	3.236894	2.776009
C	2.659503	-1.125107	-1.167426
H	2.119891	-2.047952	-1.326701
C	2.555698	-0.476653	0.073748
C	6.023413	1.787906	5.010524
H	6.239781	1.192764	5.886261
C	-0.381986	4.686582	2.630236
H	-1.22844	4.753245	3.298833
C	3.975167	1.222172	-0.631338
C	2.968029	4.144434	0.044668
H	2.589562	3.574212	-0.808035
H	3.323374	5.103734	-0.351691
C	0.418893	3.536825	2.643992
C	4.813039	1.599787	4.330589
C	1.799161	4.391848	0.986441
C	-0.044481	5.703968	1.763136
H	-0.636085	6.610246	1.734425
C	4.110838	0.647974	-1.880863
H	4.726156	1.121439	-2.633769
C	4.759307	2.47169	-0.260063
H	5.670514	2.147644	0.249999
H	5.077234	2.984693	-1.176233
C	1.067043	5.562904	0.927051
H	1.355753	6.351495	0.245587
C	6.905378	2.72753	4.520105
H	7.854428	2.890402	5.015037
C	4.885125	4.085667	1.600831
H	4.290663	4.90786	2.008085
H	5.757896	4.541501	1.117409
C	6.56884	3.467966	3.383394
H	7.245267	4.20994	2.981274
C	3.439616	-0.549766	-2.145987
H	3.530069	-1.022312	-3.116011
H	0.726013	1.78885	3.430296
H	1.771115	-0.518727	1.876815
H	3.128424	0.639809	4.262491
O	1.575309	0.15217	3.383725
N	0.907231	-0.72424	4.118447
O	0.680885	-0.36443	5.252718

I’			
atom	x	y	z
Cu	2.703991	1.777797	2.418871
N	1.397415	3.440554	2.127227
N	4.415506	2.335076	3.5698
O	0.115949	3.048305	4.011476
O	3.987147	0.967276	5.37892
O	1.803719	-1.443146	0.429962
N	3.210542	0.345584	0.123405
N	3.866693	3.033142	0.866253
C	5.259991	3.164413	2.915467
C	2.715351	-1.109275	-1.721412
H	2.190143	-1.984218	-2.078705
C	2.586841	-0.714798	-0.380632
C	6.127218	1.919968	5.199769
H	6.414414	1.411061	6.108907
C	-0.352183	4.964298	2.740593
H	-1.149011	5.206633	3.42927
C	3.9855	1.084652	-0.68471
C	2.812576	3.766578	0.158048
H	2.379176	3.086026	-0.578939
H	3.209401	4.626881	-0.396928
C	0.407686	3.805624	2.944883
C	4.832054	1.748005	4.692152
C	1.703876	4.2346	1.077802
C	-0.036897	5.766439	1.664099
H	-0.597329	6.6746	1.4816
C	4.162097	0.783294	-2.02667
H	4.786152	1.406541	-2.652974
C	4.711552	2.244907	-0.041795
H	5.536364	1.844762	0.553889
H	5.155307	2.877855	-0.82238
C	1.015268	5.406311	0.819626
H	1.293402	6.02718	-0.021124
C	6.991733	2.741771	4.509217
H	8.001707	2.892187	4.869004
C	4.679489	3.902388	1.729326
H	4.029833	4.689236	2.119642
H	5.481216	4.399374	1.169983
C	6.553325	3.386867	3.348858
H	7.207031	4.047756	2.796142
C	3.513532	-0.34129	-2.5444
H	3.632124	-0.60728	-3.58752
H	0.700012	2.261099	4.081872
H	1.779731	-1.02216	1.32645
H	3.084365	0.98091	4.989838
O	1.779843	-0.05197	2.74301
N	1.192259	-0.33135	3.829821
O	1.27351	0.562005	4.702675

I’’

atom	x	y	z
Cu	2.662757	1.732544	2.328143
N	1.41424	3.451198	2.137307
N	4.403751	2.300568	3.67632
O	0.099869	3.042084	3.997417
O	3.944611	0.955931	5.496519
O	1.563443	-1.3434	0.146773
N	3.097084	0.371006	0.048046
N	3.881948	2.989921	0.951469
C	5.271037	3.096471	3.015978
C	2.610266	-0.92856	-1.91491
H	2.047331	-1.74164	-2.35181
C	2.43398	-0.6125	-0.55715
C	6.10423	1.858342	5.311373
H	6.378051	1.351946	6.226193
C	-0.31201	4.993785	2.757324
H	-1.1142	5.239751	3.438398
C	3.963447	1.100859	-0.67636
C	2.880147	3.779806	0.215946
H	2.451526	3.135215	-0.55466
H	3.331742	4.637065	-0.29827
C	0.421997	3.817391	2.949907
C	4.80379	1.711963	4.803141
C	1.757992	4.260434	1.112618
C	0.037578	5.810931	1.702218
H	-0.50275	6.733063	1.529721
C	4.193195	0.869308	-2.02311
H	4.890228	1.485796	-2.57448
C	4.726588	2.18019	0.056735
H	5.49092	1.70824	0.679532
H	5.249209	2.813326	-0.67184
C	1.09769	5.450497	0.867268
H	1.402243	6.085176	0.04623
C	6.990601	2.649243	4.613352
H	8.003914	2.777219	4.972769
C	4.708903	3.841562	1.82676
H	4.069678	4.638767	2.212436
H	5.518703	4.323023	1.266669
C	6.571271	3.290906	3.443657
H	7.242804	3.927054	2.883218
C	3.500777	-0.17256	-2.64617
H	3.658652	-0.38244	-3.6968
H	0.684231	2.261576	4.076392
H	1.512861	-1.04397	1.094794
H	3.04825	0.923963	5.079412
O	1.165147	-0.7758	2.723794
N	1.729218	0.208913	3.223807
O	1.462678	0.452288	4.443585

III – BS

atom	x	y	z
Cu	2.879046	2.095034	2.261967
N	1.412551	3.349556	1.800259
N	4.586217	2.068729	3.278135
O	-0.037888	2.447078	3.311418
O	4.081598	0.246154	4.548526
O	1.509953	-0.994535	0.69002
N	3.078415	0.669206	0.332358
N	4.005094	3.276645	0.94921
C	5.424349	3.077057	2.941717
C	2.503538	-0.867698	-1.425567
H	1.907603	-1.716496	-1.729015
C	2.381864	-0.370426	-0.122007
C	6.161649	1.33842	4.931649
H	6.420293	0.637425	5.71417
C	-0.626858	4.511574	2.299366
H	-1.560095	4.540489	2.845063
C	3.949819	1.267674	-0.510691
C	3.056463	4.141966	0.205854
H	2.814853	3.630767	-0.728331
H	3.521965	5.094576	-0.059976
C	0.235312	3.385021	2.513464
C	4.893881	1.158933	4.271288
C	1.768643	4.355892	0.967672
C	-0.255443	5.518261	1.448556
H	-0.908171	6.371689	1.305257
C	4.125778	0.850759	-1.817311
H	4.823237	1.364508	-2.464405
C	4.781781	2.392916	0.055805
H	5.593659	1.962677	0.644899
H	5.236005	2.970031	-0.754784
C	0.974005	5.459516	0.764385
H	1.286806	6.249333	0.095797
C	7.006089	2.351345	4.56693
H	7.960217	2.465282	5.069094
C	4.887391	4.016908	1.884856
H	4.280011	4.78943	2.362456
H	5.700188	4.517124	1.349842
C	6.646866	3.2535	3.543399
H	7.301873	4.059191	3.242677
C	3.385808	-0.240777	-2.277434
H	3.503127	-0.591564	-3.294686
H	1.536102	-0.615828	1.581641
O	1.341709	0.047981	3.484921
N	1.779167	1.083307	3.711842

TS^{I}

atom	x	y	z
Cu	-0.147595	-0.129811	0.361005
N	0.774791	1.921307	-0.127007
N	1.482383	-1.484257	-0.214345
O	2.176776	2.387056	1.668272
O	2.236375	-2.210254	1.849673
O	-2.716882	0.039084	2.458528
N	-2.227821	-0.390289	0.257127
N	-0.385645	-0.039127	-1.695002
C	1.490183	-1.640188	-1.561035
C	-4.518356	-0.328164	0.97371
H	-5.220999	-0.183333	1.782928
C	-3.128727	-0.21357	1.271941
C	2.792176	-3.488373	-0.028255
H	3.302783	-4.181029	0.625547
C	2.015625	3.977693	-0.021755
H	2.702494	4.592759	0.541975
C	-2.652493	-0.679233	-0.993689
C	-0.668279	1.377333	-2.014869
H	-1.678058	1.597506	-1.66338
H	-0.65754	1.536521	-3.097098
C	1.635977	2.729719	0.505998
C	2.153407	-2.369021	0.537228
C	0.305573	2.309717	-1.336684
C	1.517896	4.362481	-1.243978
H	1.803691	5.31361	-1.674996
C	-3.982855	-0.791958	-1.325364
H	-4.281822	-1.010541	-2.340986
C	-1.549725	-0.906514	-1.997332
H	-1.209935	-1.942754	-1.930309
H	-1.902387	-0.738541	-3.019146
C	0.652506	3.506445	-1.930696
H	0.260843	3.766513	-2.904412
C	2.753598	-3.656717	-1.391974
H	3.235946	-4.511286	-1.849299
C	0.849416	-0.526171	-2.348886
H	1.551509	0.308196	-2.393989
H	0.646105	-0.839958	-3.376012
C	2.101677	-2.706258	-2.185735
H	2.072722	-2.799594	-3.262425
C	-4.930209	-0.608849	-0.303048
H	-5.987411	-0.690991	-0.525841
H	1.94883	1.472191	2.006003
H	-1.387475	-0.110687	2.520903
H	1.992778	-1.283379	2.162347
O	-0.34264	-0.30934	2.313477
N	0.546229	0.151316	3.349999
O	1.738156	0.126761	2.872572

II

atom	x	y	z
Cu	2.723138	2.021351	1.940977
N	1.402718	3.564071	1.85356
N	4.374876	2.280557	3.314788
O	-0.0355	2.757181	3.438333
O	3.780557	0.653341	4.8281
O	1.510973	-0.85501	1.202565
N	3.044295	0.671976	0.453203
N	3.890831	3.255577	0.782695
C	5.258167	3.18996	2.856864
C	2.479806	-1.19088	-0.94022
H	1.914229	-2.10291	-1.07683
C	2.306586	-0.47325	0.286884
C	5.887414	1.693564	5.068379
H	6.090423	1.082981	5.936616
C	-0.43859	4.924739	2.547244
H	-1.3075	5.049773	3.179478
C	3.870969	1.131507	-0.51046
C	2.922628	4.133609	0.070549
H	2.529458	3.55761	-0.77
H	3.425554	5.013735	-0.33877
C	0.296968	3.699921	2.653268
C	4.669547	1.546985	4.388923
C	1.767797	4.518885	0.971168
C	-0.04015	5.899576	1.669206
H	-0.60152	6.824275	1.600167
C	4.039364	0.482725	-1.71218
H	4.700812	0.877768	-2.47065
C	4.658493	2.368388	-0.13501
H	5.556664	2.054796	0.401293
H	4.982286	2.920593	-1.02077
C	1.088796	5.709005	0.848037
H	1.406909	6.461486	0.139976
C	6.793465	2.616049	4.588306
H	7.745813	2.745309	5.08667
C	4.774941	4.026432	1.693273
H	4.187126	4.856776	2.090264
H	5.616034	4.454284	1.142036
C	6.484903	3.384405	3.459887
H	7.18325	4.11178	3.069777
C	3.322001	-0.71288	-1.91082
H	3.435011	-1.25664	-2.84168
H	0.859533	1.456283	3.308777
H	1.439865	0.090606	2.45512
H	2.960452	0.664972	4.270163
O	1.643116	0.825032	3.137534

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