Electronic Structures and Reactivity Profiles of Aryl Nitrenoid–Bridged Dicopper Complexes

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Materials and Methods.

General Considerations. All manipulations were carried out in the absence of water and dioxygen using standard Schlenk techniques or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere, unless specified otherwise. All glassware was oven dried at 150 ºC for a minimum of 12 h and cooled in an evacuated antechamber for a minimum of 15 minutes prior to use in the drybox. Benzene, diethyl ether, dichloromethane (DCM), acetonitrile (MeCN), hexanes, pentane, toluene, and tetrahydrofuran (THF) were dried over 4 Å molecular sieves (Strem) prior to use. When applicable, solvents were tested with a deep violet solution of sodium benzophenone ketyl in tetrahydrofuran (prepared by stirring 10 mg benzophenone in 10 mL THF with excess metallic sodium for 12 h) to confirm effective oxygen and moisture removal. Chloroform-d_1 was purchased from Cambridge Isotope Labs and stored over anhydrous potassium carbonate with exclusion of light. Benzene-d_6 and tetrahydrofuran-d_8 were purchased from Cambridge Isotope Labs, degassed, and stored over 4 Å molecular sieves prior to use. Reagents 2-Mesityl-1*H*-pyrrole,[1] 4,5-diformyl-9,9-dimethylxanthene,[2] 3,5-bis(trifluoromethyl) phenyl azide,[3] 4-methoxyphenyl azide,[4] Gomberg's dimer,[5] potassium graphite (KC_8),[6] 2-azaadamantane-*N*-oxyl (AZADO)[7], iodobenzene dichloride,[8] and ($^{t\text{Bu}}$L)H[9] were synthesized according to literature protocols. Mesitylcopper was prepared according to a literature protocol and recrystallized three times from slow cooling of a warm toluene solution, followed by a cold diethyl ether wash.[10] Reagents silver trifluoromethanesulfonate, copper bromide dimethyl sulfide complex, anhydrous cuprous chloride, *N*,*N*-dimethylaminopyridine (DMAP), 1,2-diphenylhydrazine, cryptand 222c (C_{222}), and 2-hydroxy-2-azaadamantane (AZADOL) were purchased from Aldrich and used as received. Potassium bis(trimethylsilyl)amide was purchased from Aldrich and recrystallized from slow cooling of a warm toluene solution prior to use. Reagents styrene, 1,4-cyclohexadiene, *tert*-butyl isocyanide, trimethylphosphine, and pyridine were purchased from Aldrich and dried over molecular sieves prior to use. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. Activated alumina was dried in a Schlenk flask for 48 h under dynamic vacuum at 200 ºC prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received. Reactions involving heating solvents above their reported boiling point in a sealed Schlenk tube were conducted behind a blast shield. ***Caution!*** Organic azides are known to be potentially explosive compounds.[11,12] While we did not encounter any issues during their

synthesis, proper precautions were taken. All reactions involving organic azides at elevated temperatures were conducted behind a blast shield. All organic azides were stored under nitrogen in a –35 ºC freezer and filtered through silica prior to use.

Characterization and Physical Measurements. ^{1}H, $^{13}C\{^{1}H\}$, ^{31}P, and ^{19}F NMR spectra were recorded on Varian Unity/Inova 400, 500, or 600 MHz spectrometers. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts are reported relative to $SiMe_4$ using the chemical shift of residual solvent peaks as reference. ^{19}F NMR chemical shifts are reported relative to an external standard of neat $BF_3(OEt_2)$ (δ –153.00 ppm). ^{31}P NMR chemical shifts are referenced to an external standard of 85 % H_3PO_4 (δ 0.00 ppm). Multiplicity assignments are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, v. br = very broad.

UV/Visible/NIR spectra were recorded on a Varian Cary 50 UV/Vis spectrometer using air-free quartz cuvettes (0.10 mm path length) and a scan rate of 600 nm/min. Samples were prepared in the drybox using serial dilution with volumetric glassware to obtain accurate concentrations. Extinction coefficients were determined from a minimum of three concentrations per sample and were calculated by a linear regression fit of the absorbance vs. concentration data.

EPR spectra were obtained on a Bruker EleXsys E-500 CW-EPR spectrometer. Spectra containing *ca.* 5–10 mg sample were measured as frozen toluene glasses, frozen 2-methyltetrahydrofuran glasses, and/or in solution at a microwave power of 0.6325–2 mW. Effective g-values (g), g-strain (σ), and hyperfine coupling constants (A) were obtained from spectral simulations of $S = {}^{1}/_{2}$ systems using the program SpinCount.

Cyclic voltammetry and differential pulse voltammetry measurements were performed with a CHI660d potentiostat using a three-electrode cell with a glassy carbon working electrode, a platinum wire as the counter electrode, and a $Ag/AgNO_3$ reference electrode. All of the potentials are referenced to the $[Cp_2Fe]^{+/0}$ couple. Saturated tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solutions of 0.2 M in tetrahydrofuran were prepared before each experiment. All measurements were conducted under a dinitrogen atmosphere. No background reaction upon addition of excess $TBAPF_6$ in tetrahydrofuran was observed for all complexes.

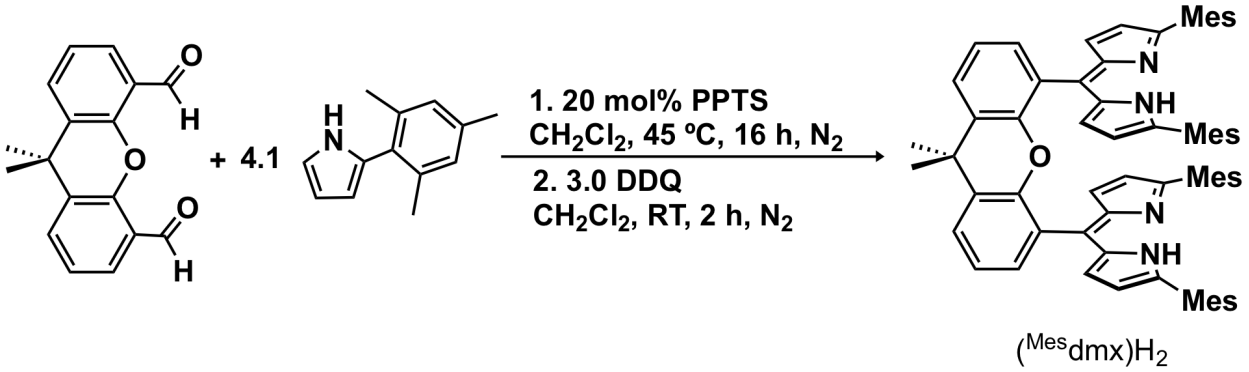
Elemental analysis (%CHN) was conducted at Harvard University on a PerkinElmer 2400 Series II CHNS/O Analyzer using bulk recrystallized compounds. In several cases, satisfactory elemental analyses were obtained by considering the presence of solvent molecules

intercalated within the unit cell as ascertained by single-crystal X-ray diffraction and ^{1}H NMR spectroscopy.

XAS Data Collection. All data were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) under ring conditions of 3.0 GeV and 500 mA. All samples were prepared in an inert-atmosphere glovebox and were measured as solids. For Cu K-edge measurements, samples were ground with BN to a final concentration of 10 weight % Cu, pressed into 1 mm aluminum spacers and sealed with 37 μm Kapton tape. For Cu L-edge and N K-edge measurements, samples were ground to a fine powder and spread in a thin layer on carbon tape affixed to an Al sample rod. Cu K-edge measurements were collected using beam line 7-3. Samples were maintained at 10 K in a liquid He cryostat during data collection. Spectra were collected in transmission mode, with X-rays detected by ionization chambers immediately downstream and upstream of the sample. A Cu foil and a third ionization chamber upstream of the sample were used for internal energy calibration, setting the first inflection point of the Cu foil scan to 8980.3 eV. Data were collected from 8660.0 to 9380.0 eV. Three scans of each sample were collected and averaged. Spectra were processed using Sixpack and Igor Pro. The region below 8960 eV was used to fit a linear background, while the region above 9010 eV was flattened with a piecewise spline and set to an average intensity of unity. Cu $L_{2,3}$-edge XAS measurements were collected on the 31-pole wiggler beam line 10–1 with a 1000 lines/mm spherical grating monochromator and 29 μm entrance and exit slits. Data were measured by monitoring the change in sample current through detection of the total electron yield (TEY). The drain current was normalized to incident photon flux with a gold-grid reference monitor. Incident beam energy was calibrated to the L_3 edge position at 930.65 eV of a $(nmph)_2[CuCl_4]$ (nmph = *N*–methylphenethylammonium) standard spectra collected before and after each sample.[13] Samples were maintained at room temperature under an ultra-high vacuum (10^{-9} Torr) during collection. Data were collected from 910.0 to 990.0 eV. Four scans were measured and averaged for each compound. Processing was done using PyMCA . Background subtraction was achieved by fitting a line to the pre-edge region below 925.0 eV and subtracting from the entire spectrum. The post edge region from 975.0 eV to 990.0 eV was fit to a line and normalized to 1.0. The edge jumps at L_3 and L_2 were subtracted using a statistics-sensitive non-linear iterative peak-clipping algorithm (SNIP)[14] as implemented in PyMCA. Data were processed with Igor 6.37. N K-edge XAS measurements were collected on the 31-pole wiggler beam line 10–1 with a 600

lines/mm spherical grating monochromator and 20 μm entrance and exit slits. Data were measured by monitoring the change in sample current through detection of the total electron yield (TEY). The drain current was normalized to incident photon flux with a gold-grid reference monitor. Incident beam energy was calibrated by comparison of the Ni L_3 second order transition at 426.35 eV in a reference sample placed upstream of the sample chamber. Samples were maintained at room temperature under an ultra-high vacuum (10^{-9} Torr) during collection. Data were collected from 380.0 to 450.0 eV. Seven scans were measured and averaged for each compound. Processing was done using PyMCA. Background subtraction was achieved by fitting a line to the pre-edge region below 395.0 eV and subtracting from the entire spectrum. The post edge region above 410.0 eV was fit to a flattened polynomial and normalized to 1.0.

Ligand Syntheses.



(^{Mes}dmx)H$_2$. In the drybox, 2-mesityl-1*H*-pyrrole[1] (8.6 g, 0.046 mol, 4.1 equiv.) and 4,5-diformyl-9,9-dimethylxanthene[2] (3.0 g, 0.011 mol, 1.0 equiv.) were dissolved in dichloromethane (60 mL), followed by addition of pyridinium *p*-toluenesulfonate (PPTS; 0.57 g, 2.3 mmol, 0.2 equiv.). The mixture was loaded into a pressure vessel, removed from the drybox, and heated to 45 ºC for 16 h during which a gradual color change from off-yellow to deep red-orange was noted. The mixture was cooled to room temperature, exposed to air, and filtered through a plug of silica on top of a coarse porosity frit, followed by extensive rinsing with dichloromethane (500 mL) until the eluant became colorless. Solvent was removed *in vacuo* to afford a flocculent peach solid, which was subsequently dissolved in anhydrous dichloromethane (300 mL). Under an atmosphere of nitrogen, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 7.70 g, 0.034 mol, 3.0 equiv.) was added as a solid, resulting in an immediate color change to purple-red. After 2 h, the solution was concentrated *in vacuo* and filtered through a plug of basic alumina with dichloromethane/triethylamine (99:1) as the eluant, collecting the rapidly eluting red-orange fraction. Removal of solvent *in vacuo* followed by trituration of the solid in methanol and isolation by filtration with cold methanol afforded (^{Mes}dmx)H$_2$ (8.6 g, 79 %) as a red-orange powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.44 (br, 2*H,* dipyrrin N–*H*), 7.56 (dd*, J* = 7.8, 1.6 Hz, 2*H*, xanthene C–*H*), 7.25 – 7.30 (m, 2*H*, xanthene C–*H*), 7.15 (t, *J* = 7.6 Hz, 2*H,* xanthene C–*H*), 6.69 (s, 8*H*, mesityl aryl C–*H*), 6.30 (dd, *J* = 4.1, 1.0 Hz, 4*H*, dipyrrin C–*H*), 6.01 (dd, *J* = 4.1, 1.0 Hz, 4*H*, dipyrrin C–*H*), 2.26 (s, 12*H*, mesityl para-methyl C–*H*), 1.95 (s, 24*H*, mesityl ortho-methyl C–*H*), 1.82 (s, 6 *H*, xanthene methyl C–*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 153.98, 148.96, 141.20, 136.72, 136.64, 135.10, 131.47, 131.02, 120.18, 128.54, 126.98, 125.94, 125.69, 122.02, 119.48, 34.45, 31.61, 20.85, 20.73. HRMS (ESI$^+$) *m/z* Calc. 966.5237 [$C_{69}H_{65}N_4O + H^+$], Found 966.5377 [M + H]$^+$.

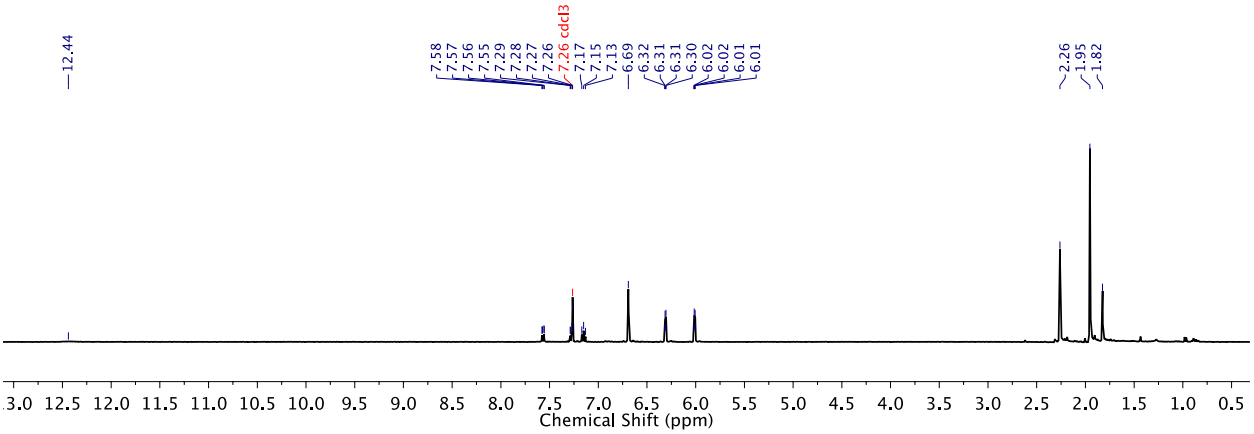


Figure S–1. ^{1}H NMR spectrum of (^{Mes}dmx)H_2 (600 MHz, $CDCl_3$).

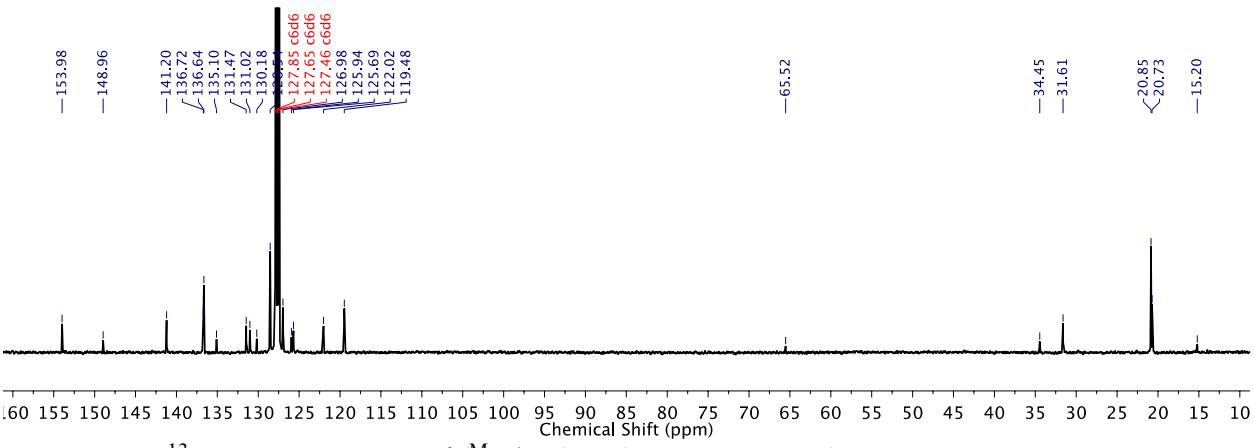
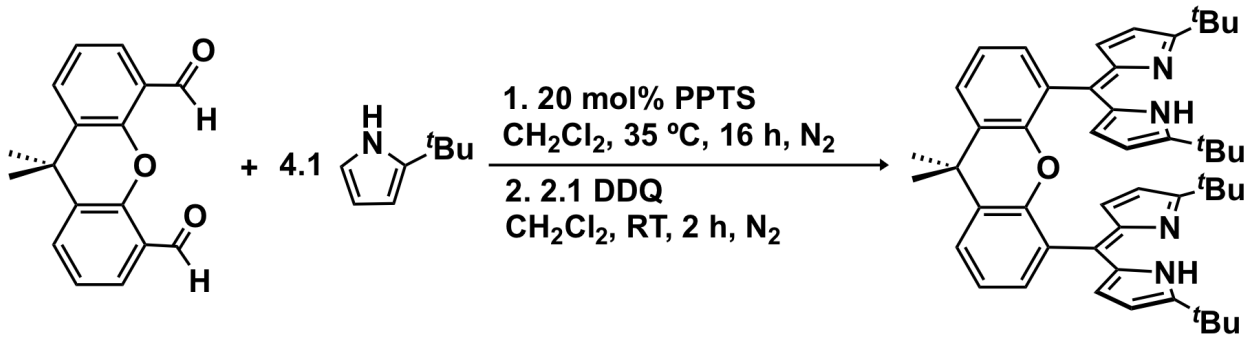


Figure S–2. ^{13}C NMR spectrum of (^{Mes}dmx)H_2 (125 MHz, C_6D_6).



($^{t\text{Bu}}$dmx)H_2

($^{t\text{Bu}}$dmx)H_2. Adapting from a literature procedure,[15] in the drybox, crystalline 2-(*tert*-butyl)-1*H*-pyrrole[16] (5.25 g, 0.041 mol, 4.1 equiv.) and 4,5-diformyl-9,9-dimethylxanthene[2] (2.77 g, 0.010 mol, 1.0 equiv.) were dissolved in dichloromethane (70 mL), followed by addition of pyridinium *p*-toluenesulfonate (PPTS; 0.53 g, 2.11 mmol, 0.2 equiv.). The mixture was loaded into a pressure vessel, removed from the drybox, and heated to 35 ºC with exclusion of light for 16 h during which a gradual color change from faint orange to deep red-orange was noted. The mixture was cooled to room temperature, exposed to air, and filtered through a plug of silica on top of a coarse porosity frit, followed by extensive rinsing with dichloromethane (500 mL) until the eluant became colorless. Solvent was removed *in vacuo* to afford a flocculent light yellow solid, which was subsequently dissolved in anhydrous dichloromethane (300 mL). Under an atmosphere of nitrogen, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 4.95 g, 0.021 mol, 2.1 equiv.) was added as a solid, resulting in an immediate color change from red-orange to purple-red with visible precipitant. After 2 h, the solution was quenched with 1.0 M NaOH (100 mL), following by extraction and dessication of the organic phase with brine and magnesium sulfate. After filtration, the solution was concentrated *in vacuo* and filtered through a plug of basic alumina, eluting slowly with dichloromethane/triethylamine (99:1). The first (*bright orange*) and second (*dark red*) fractions were together collected and triturated three times in methanol to remove residual triethylamine. The resulting bright orange solid was suspended in minimal methanol and held at –20 ºC for two hours, following by collection of the orange solid by filtration. After rinsing with thawing methanol (2 x 50 mL), the bright orange solid was suspended in boiling methanol (*ca.* 250 mL), to which dichloromethane (*ca.* 40 mL) was added until the solution became homogeneous. The mixture was allowed to cool to room temperature and held at –20 ºC for 48 h. Subsequent isolation by filtration afforded ($^{t\text{Bu}}$dmx)H_2 (8.40 g, 51 %) as a thin orange needles. ^{1}H NMR (500 MHz, C_6D_6): δ 13.25 (br, 2*H*, dipyrrin N–*H*), 7.17 (dd, *J*

= 7.9, 1.6 Hz, 2*H,* xanthene C–*H*), 7.09 (dd, *J* = 7.5, 1.6 Hz, 2H, xanthene C–*H*), 6.79 (t, *J* = 15.3 Hz, 2*H*, xanthene C–*H*), 6.54 (dd, *J* = 4.1, 0.8 Hz, 4*H*, dipyrrin C–*H*), 6.07 (dd, *J* = 4.1, 1.2 Hz, 4*H*, dipyrrin C–*H*), 1.50 (s, 9*H*, xanthene methyl C–*H*), 1.40 (s, 36*H*, *tert*-butyl C–*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 165.05, 148.87, 140.28, 135.09, 132.40, 130.43, 128.59, 128.35, 126.51, 126.21, 122.40, 113.61, 34.69, 33.48, 32.29, 30.21. HRMS (ESI+) *m/z* Calc. 719.4689 [$C_{49}H_{58}N_4O$ + H^+], Found 719.4718 $[M+H]^+$.

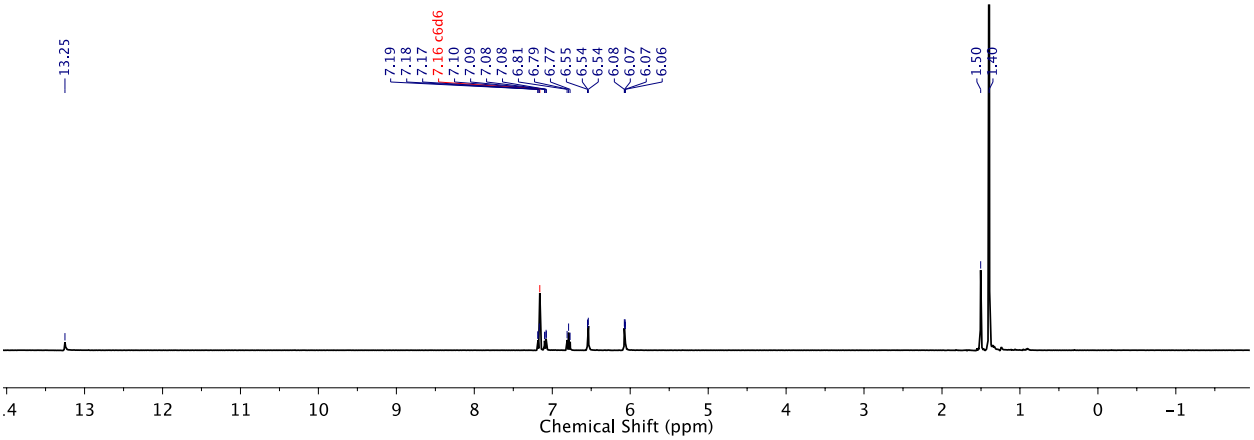


Figure S–3. ^{1}H NMR spectrum of ($^{t\text{Bu}}$dmx)H_2 (600 MHz, C_6D_6).

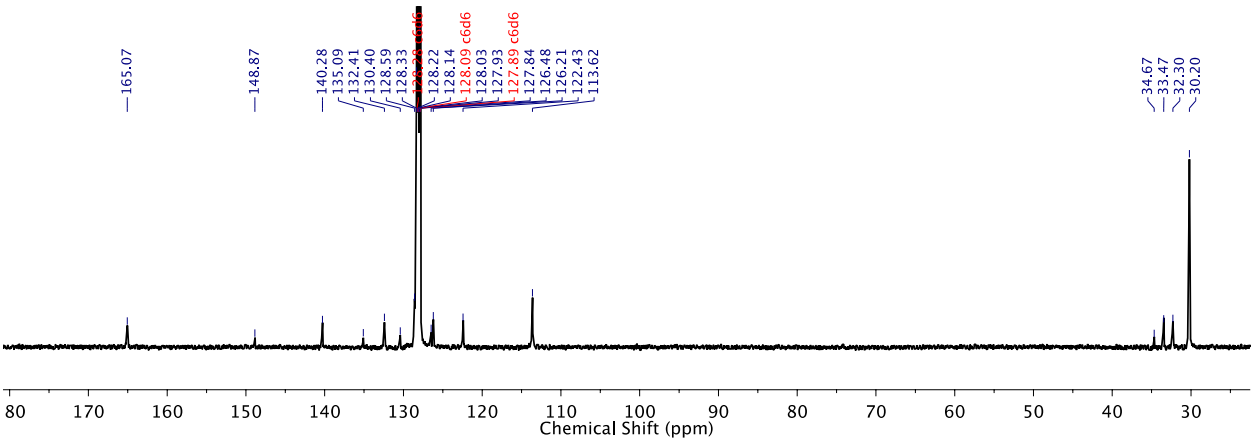
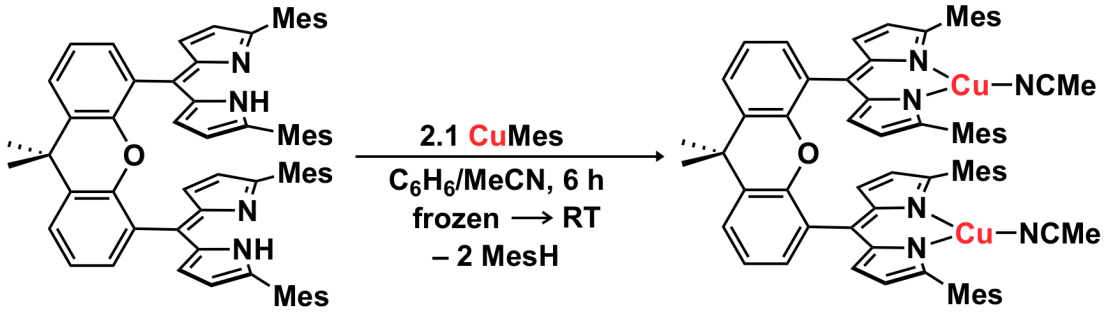


Figure S–4. ^{13}C NMR spectrum of ($^{t\text{Bu}}$dmx)H_2 (125 MHz, C_6D_6).

Metal Complex Syntheses.



(**1**)

(^{Mes}dmx)Cu$_2$(NCMe)$_2$ (**1**). In the drybox, to a thawing benzene solution (20 mL) of (^{Mes}dmx)H$_2$ (0.710 g, 0.734 mmol, 1.0 equiv.) in benzene (5 mL) was added a thawed solution of mesitylcopper[10] (CuMes; 0.282 g, 1.54 mmol, 2.1 equiv.) in a benzene/acetonitrile mixture (5 mL C_6H_6, 0.25 mL CH_3CN). Over the course of 6 h, the reaction gradually thickened and changed color from red-orange to red-pink. The reaction was lyophilized, followed by an additional lyophilization to remove residual mesitylene. The red-pink powder was suspended in acetonitrile (5 mL) and stirred rapidly for 2 h. The slurry was placed in a –35 ºC freezer for 1 h and subsequently filtered over a pad of Celite on top of a coarse porosity frit. The red solid was rinsed with cold acetonitrile (3 x 5 mL) and cold pentane (10 mL). The remaining solid was eluted with warm benzene and lyophilized to afford (^{Mes}dmx)Cu$_2$(NCMe)$_2$ (**1**) as a red solid (0.710 g, 82 %). Single crystals of **1** suitable for X-ray diffraction were obtained by layering acetonitrile with a diethyl ether solution of **1** at –35 ºC overnight. ^{1}H NMR (600 MHz, C_6D_6): δ 7.35 (d, *J* = 7.4 Hz, 2*H*, dipyrrin C–*H*), δ 7.26 (d, *J* = 7.4 Hz, 2*H,* dipyrrin C–*H*), 6.83 – 6.84 (m, 6*H*, xanthene C–*H*), 6.74 – 6.77 (d, *J* = 17.4 Hz, 8*H,* mesityl aryl C–*H*), 6.31 (d, *J* = 4.0 Hz, 4*H*, dipyrrin C–*H*), 2.37 (d, *J* = 11.5 Hz, 24*H*, mesityl ortho-methyl C–*H*), 2.10 (s, 12*H* mesityl para-methyl C–*H*), 1.61 (s, 6*H*, xanthene methyl C–*H*), 0.40 (s, 6 *H*, acetonitrile C–*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 143.15, 141.22, 138.23, 137.44, 136.19, 135.02, 132.72, 131.27, 130.37, 129.42, 128.10, 127.85, 127.29, 124.50, 121.23, 117.78, 114.143, 34.49, 31.17, 21.91, 21.33, 20.83. Calculated for $C_{73}H_{70}Cu_2N_6O$: C 74.65 H 6.01 N 7.16; Found: C 74.26 H 5.76 N 7.16.

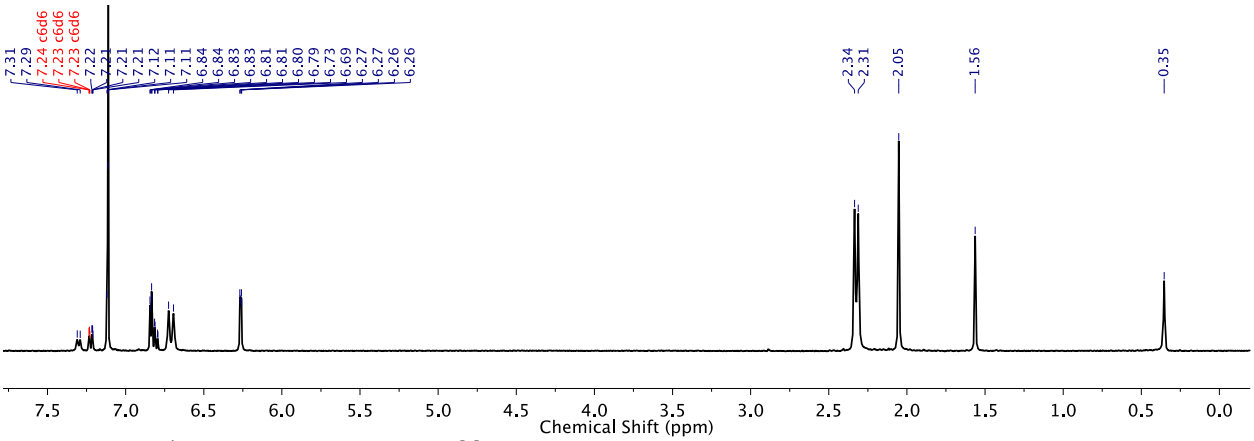


Figure S–5. ^{1}H NMR spectrum of (^{Mes}dmx)$Cu_2(NCMe)_2$ (**1**), (600 MHz, C_6D_6).

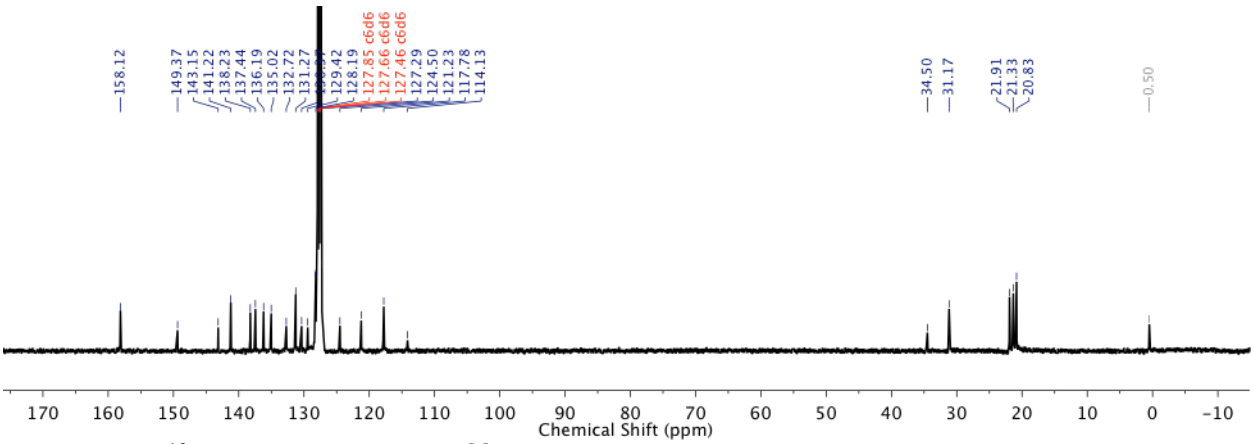
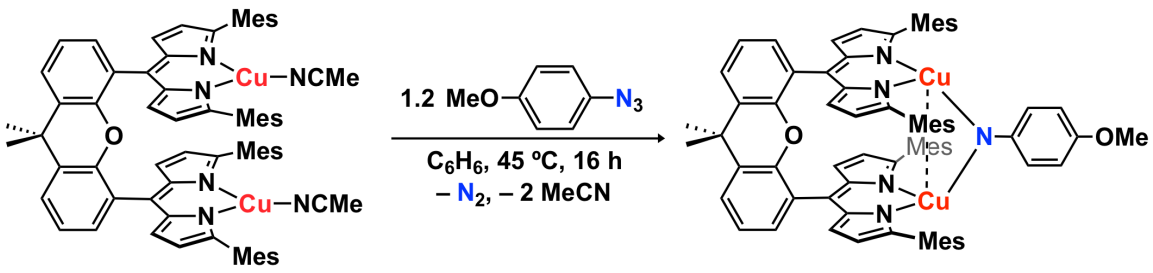


Figure S–6. ^{13}C NMR spectrum of (^{Mes}dmx)$Cu_2(NCMe)_2$ (**1**), (125 MHz, C_6D_6).



(**1**) (**2**)

(^Mes^dmx)Cu~2~(μ^2^–N(C~6~H~4~OMe)) (**2**). In the drybox, to a Schlenk tube charged with a benzene solution (5 mL) of **1** (0.25 g, 0.22 mmol, 1.0 equiv.) was added a benzene solution (5 mL) of 4-methoxyphenyl azide[4] (0.04 g, 0.26 mmol, 1.2 equiv.). The Schlenk tube was sealed, removed from the drybox, and heated to 45 ºC for 16 h, during which a color change from red-pink to deep violet was noted, and precipitate formed. The reaction was returned into the drybox and lyophilized. The residual powder was slurried in diethyl ether for 1 h and filtered over a pad of Celite on top of a coarse porosity frit. The residual powder was rinsed with a copious volume of diethyl ether (*ca*. 10 mL) and acetonitrile (*ca*. 5 mL) until the washings were faint purple. The product was eluted with boiling tetrahydrofuran (*ca.* 3 mL) to afford (^Mes^dmx)Cu~2~(μ^2^–N(C~6~H~4~OMe)) (**2**) as a deep violet solid (0.24 g, 92 %). Single crystals of **2** suitable for X-ray diffraction were obtained by allowing diethyl ether to diffuse into a dichloromethane solution of **2** at –35 ºC over several days. ^{1}H NMR (600 MHz, C_6D_6): δ 7.74 (dd, *J* = 10.2, 2.1 Hz, 2*H*, aryl imide C–*H*), 7.30 (dd, *J* = 7.4, 1.5 Hz, 2*H*, dipyrrin C–*H*), 7.21 (dd, *J* = 7.9, 1.6 Hz, 2*H*, dipyrrin C–*H*), 6.99 (br, 4*H*, mesityl aryl C–*H*), 6.83 – 6.89 (m, 6*H*, xanthene C–*H*), 6.31 (d, *J* = 4.0 Hz, 4*H*, dipyrrin C–*H*), δ 6.27 (br, 4*H*, mesityl aryl C–*H*), 6.06 (dd, *J* = 10.3, 2.1 Hz, 2*H*, aryl imide C–*H*), 3.06 (s, 3*H*, imide methoxy C–*H*), 2.73 (br, 24 *H*, mesityl ortho-methyl C–*H*), 2.06 (s, 12*H* mesityl para-methyl C–*H*), 1.55 (s, 6*H,* xanthene methyl C–*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 161.50, 159.14, 149.25, 143.05, 140.86, 137.24, 137.09, 136.12, 135.21, 133.64, 130.75, 129.84, 128.94, 127.46, 126.74, 121.58, 115.73, 54.79, 34.24, 33.35, 20.77. Calculated for $C_{76}H_{71}Cu_2N_5O_2$•$CH_3CH_2OCH_2CH_3$: C 74.62 H 6.34 N 5.44; Found: C 74.64 H 6.22 N 5.46 (one molecule of diethyl ether is present from bulk recrystallization).

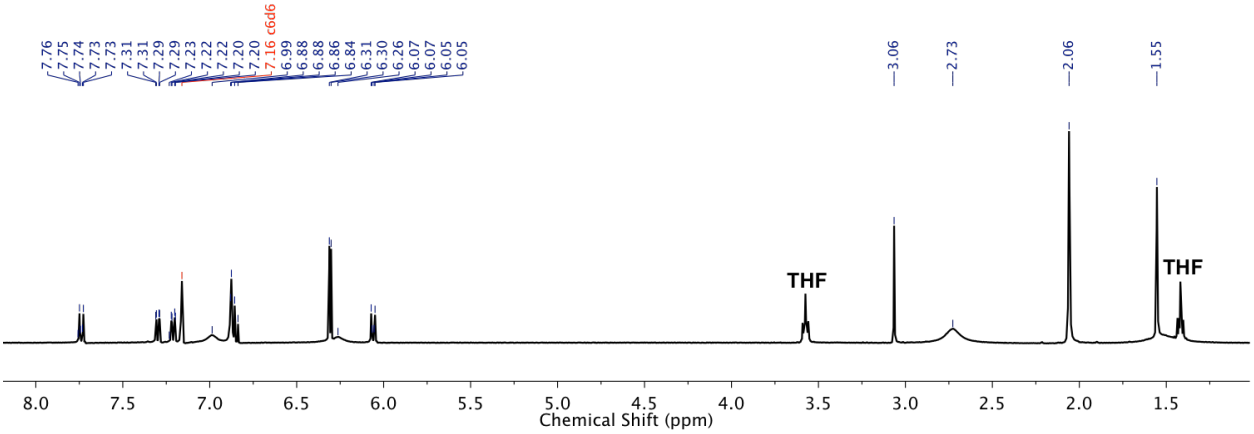


Figure S–7. ^{1}H NMR spectrum of (^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**2**), (600 MHz, C$_6$D$_6$).

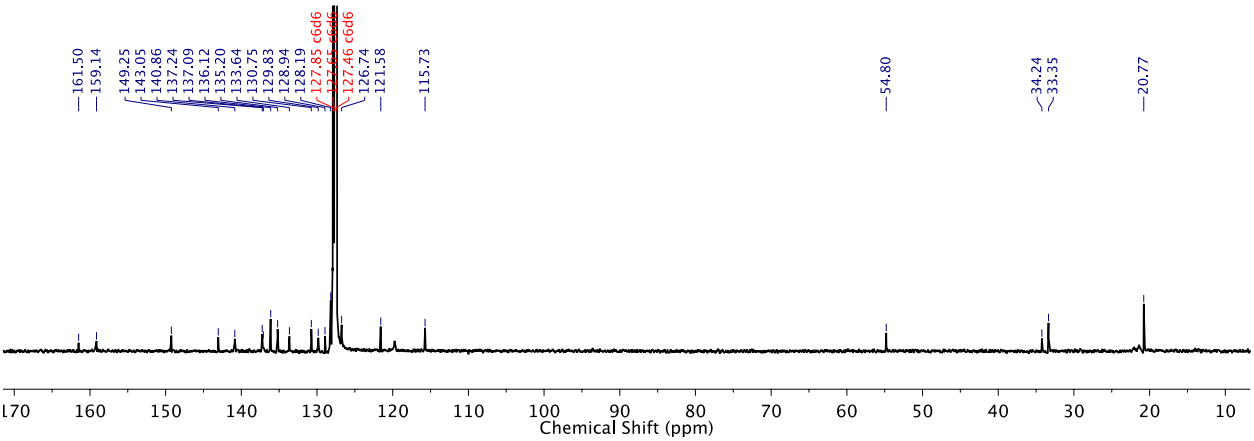
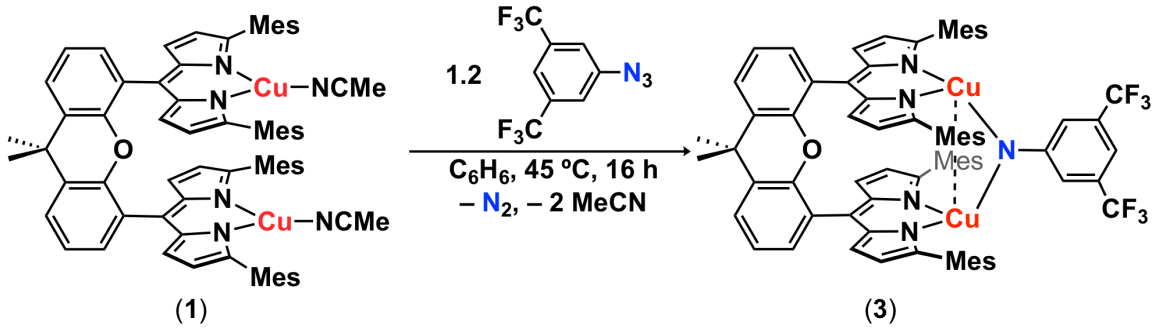


Figure S–8. ^{13}C NMR spectrum of (^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**2**), (125 MHz, C$_6$D$_6$).



(**1**) (**3**)

(**[Mes]dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)**) (**3**). In the drybox, to a Schlenk tube charged with a benzene solution (10 mL) of **1** (0.20 g, 0.17 mmol, 1.0 equiv) was added a benzene solution (5 mL) of 3,5-bis(trifluoromethyl)phenyl azide[3] (0.05 g, 0.21 mmol, 1.2 equiv). The Schlenk tube was sealed, removed from the drybox, and heated to 45 ºC for 16 h, during which a color change from magenta to pink-purple was noted. The reaction was returned into the drybox and lyophilized. The residual powder was slurried in minimal acetonitrile for 2 h and placed in a –35 ºC freezer for 2 h, then filtered over a pad of Celite on top of a coarse porosity frit. The residual powder was rinsed with a copious volume of thawing acetonitrile (*ca*. 10 mL) until the washings were faint pink. The product was eluted with benzene and lyophilized to afford ([Mes]dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**3**) as a dark purple solid (0.16 g, 79 %). Single crystals of **3** suitable for X-ray diffraction were obtained by layering acetonitrile with a diethyl solution of **1** at –35 ºC overnight. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ 8.26 (s, 2 *H*, aryl imide C–*H*), 8.01 (s, 1*H,* aryl imide C–*H*), 7.18 – 7.21 (m, 4*H,* dipyrrin C–*H*), 7.00 (br, 8*H*, mesityl aryl C–*H*), 6.85 (t, *J* = 7.6 Hz, 6*H*, xanthene C–*H*), 6.20 (d, *J* = 4.0 Hz, 4*H*, dipyrrin C–*H*), 2.76 (br*,* 24*H*, mesityl ortho-methyl C–*H*), 2.08 (s, 12 *H,* mesityl para-methyl C–*H*), 1.55 (s, 6*H*, xanthene methyl C–*H*), ^{19}F NMR (470 MHz, C$_6$D$_6$): δ –62.8 (s, aryl imide C*F*$_3$). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): δ 148.95, 142.74, 139.63, 137.20, 132.33, 130.93, 130.50, 129.34, 128.22, 127.22, 126.40, 121.82, 119.87, 118.45, 67.70, 34.58, 33.60, 31.56, 25.54, 22.62, 20.37, 13.84. Calculated for C$_{77}$H$_{67}$Cu$_2$F$_6$N$_5$O: C 70.09 H 5.12 N 5.31; Found: C 69.73 H 5.14 N 5.65.

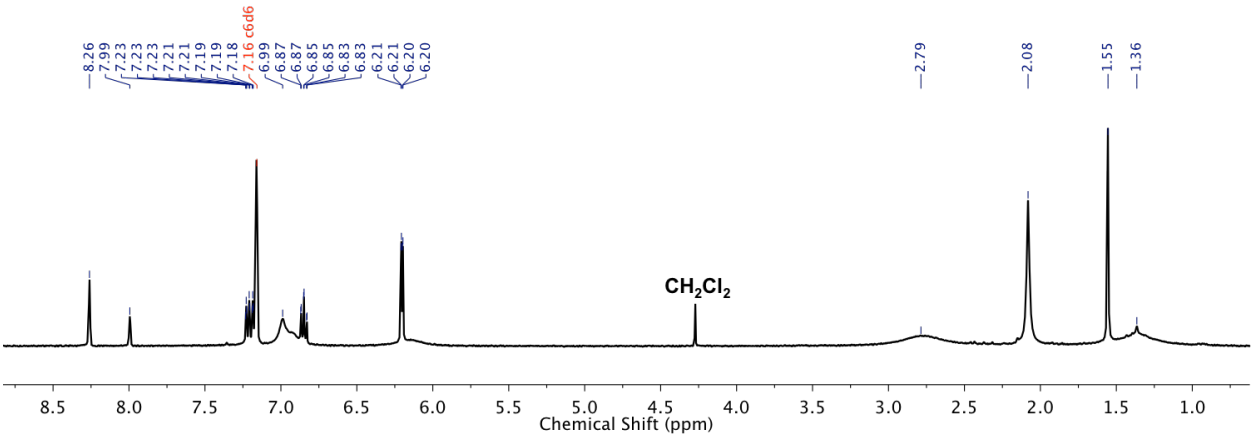


Figure S–9. ^{1}H NMR spectrum of (^{Mes}dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**3**), (600 MHz, C$_6$D$_6$).

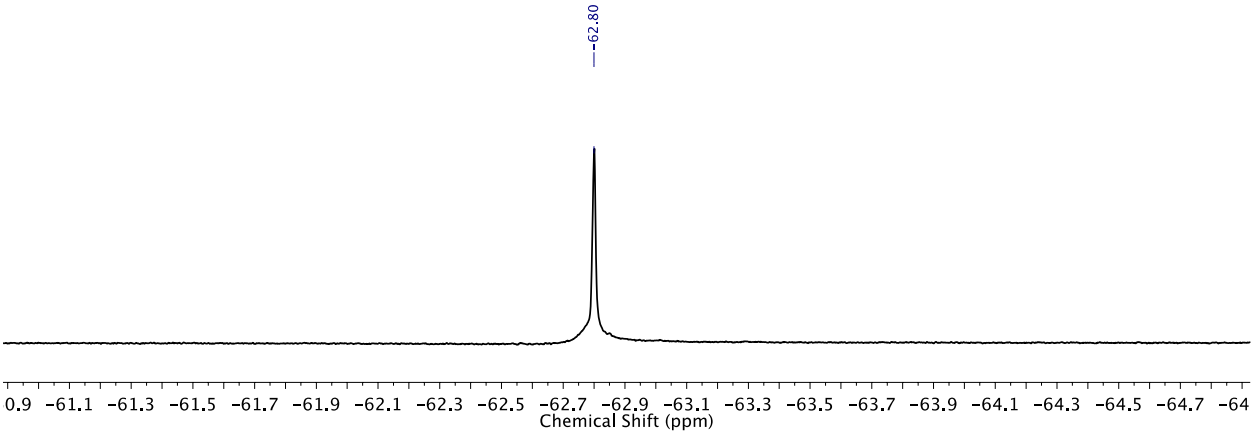
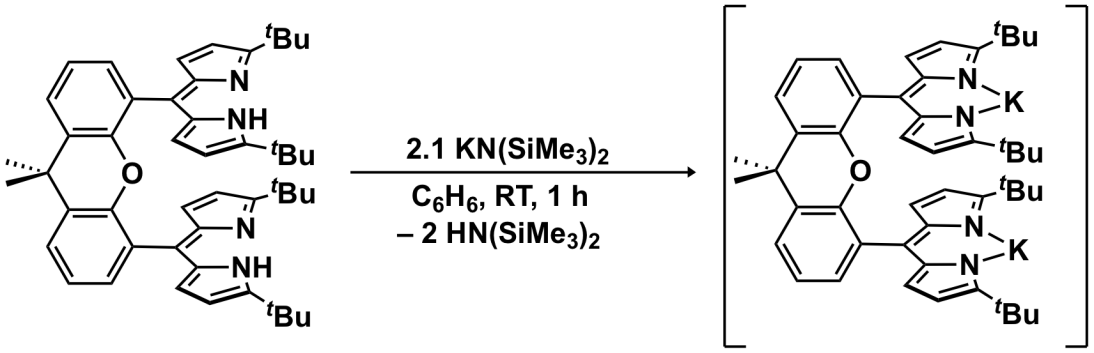


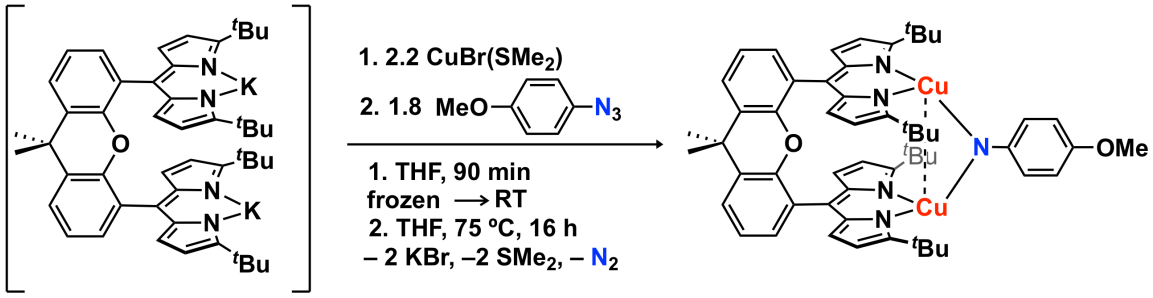
Figure S–10. ^{19}F NMR spectrum of (^{Mes}dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**3**), (375 MHz, C$_6$D$_6$).



(**4**)

(*t*^{Bu}dmx)K$_2$ (**4**). In the drybox, to a rapidly stirring solution of (*t*^{Bu}dmx)H$_2$ (1.01 g, 1.40 mmol, 1.0 equiv.) in benzene (20 mL) was added dropwise potassium bis(trimethylsilyl)amide (0.590 g, 2.95 mmol, 2.1 equiv.) as a solution in benzene (10 mL). Within seconds, formation of a thick orange slurry was observed. The reaction was stirred for an additional 45 minutes, followed by addition of hexanes (50 mL) and removal of solvent *in vacuo*. The resulting powder was suspended in hexanes, loaded onto a medium porosity glass frit, and rinsed with boiling toluene (3 x 5 mL) and ample hexanes (3 x 5 mL). The remaining solid – putatively assigned as (*t*^{Bu}dmx)K$_2$ (**4**) – was collected as a deep orange powder (1.04 g, 93 %) and employed without further purification. Due to the insolubility of **9** in anhydrous non-polar (*e.g.,* hexanes, toluene) and polar aprotic organic solvents (*e.g.,* dichloromethane, tetrahydrofuran), further characterization by ^{1}H NMR, ^{13}C NMR, or elemental analysis was not conducted.

Note: An alternative formulation of **4** is a coordination polymer in which bridging potassium ions between different (*t*^{Bu}dmx) units engender low solubility.



(**4**) (**5**)

($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**5**). In the drybox, to a thawing suspension of **4** (0.300 g, 0.373 mmol, 1.0 equiv.) in tetrahydrofuran (20 mL) was added copper bromide dimethylsulfide complex (0.170 g, 0.828 mmol, 2.2 equiv.) as a solid. Over 90 minutes, the reaction became a homogeneous red-orange solution. The reaction was subsequently filtered through a plug of Celite, followed by the addition of 4-methoxyphenyl azide[4] (0.100 g, 0.679 mmol, 1.8 equiv.) in tetrahydrofuran (10 mL) to the filtrate. The mixture was transferred to a Schlenk tube, sealed, removed from the drybox, and heated to 75 ºC for 16 h. The deep purple solution was returned into the drybox and dried *in vacuo*. The resulting solid was dissolved in minimal benzene, filtered through a plug of Celite, and lyophilized. The resulting dark purple powder was dissolved in minimal acetonitrile and stirred rapidly for 2 h, accompanied by formation of a thick purple slurry. The mixture was place in a –35 ºC freezer for 1 h. The mixture was filtered through a pad of Celite on top of a coarse porosity frit, followed by rinsing of the residual solids with thawing acetonitrile (2 x 3 mL). The filtrate was discarded, and the residual purple powder was eluted with benzene and lyophilized to afford ($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**5**) as a dark purple solid (0.235 g, 65 %). Single crystals suitable for X-ray diffraction were obtained by layering acetonitrile with a concentrated solution of **5** in diethyl ether. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ 9.33 (dd, *J* = 6.7, 2.3 Hz, 2*H*, aryl imide C–*H*), 7.20 (dd, *J* = 7.9, 1.6 Hz, 2*H*, dipyrrin C–*H*), 6.97 (dd, *J* = 7.3, 1.6 Hz, 2*H*, dipyrrin C–H), 6.78 (m, 6 *H*, xanthene C–*H*), 6.68 (dd, *J* = 5.6, 1.9 Hz, 4*H*, aryl imide C–*H*), 6.62 (d, *J* = 4.4 Hz, 4*H*, dipyrrin C–*H*), 3.08 (s, 3*H*, imide methoxy C–*H*), δ 1.58 (s, 6*H*, xanthene methyl C–*H*), δ 1.37 (s, 36*H, tert*-butyl C–*H*). ^{13}C NMR (150 MHz, C$_6$D$_6$): 173.19, 164.89, 161.38, 151.83, 144.85, 142.41, 141.69, 134.52, 133.82, 131.93, 128.38, 124.21, 119.55, 117.43, 57.77, 37.03, 36.32, 34.94, 33.58. NIR/UV-vis (THF), λ_{max}/nm (ε/M^{-1} cm^{-1}): 1330 (430), 780 (8,200), 600 (32,000), 480 (101,000), 350 (18,200), 300 (22,100). Calculated for C$_{56}$H$_{63}$Cu$_2$N$_5$O: C 69.68 H 6.58 N 7.26; Found: C 69.69 H 6.60 N 7.34.

Note: The putative intermediate species ($^{t\text{Bu}}$dmx)$Cu_2(SMe_2)_2$ was noted to be unstable upon workup or isolation attempts.

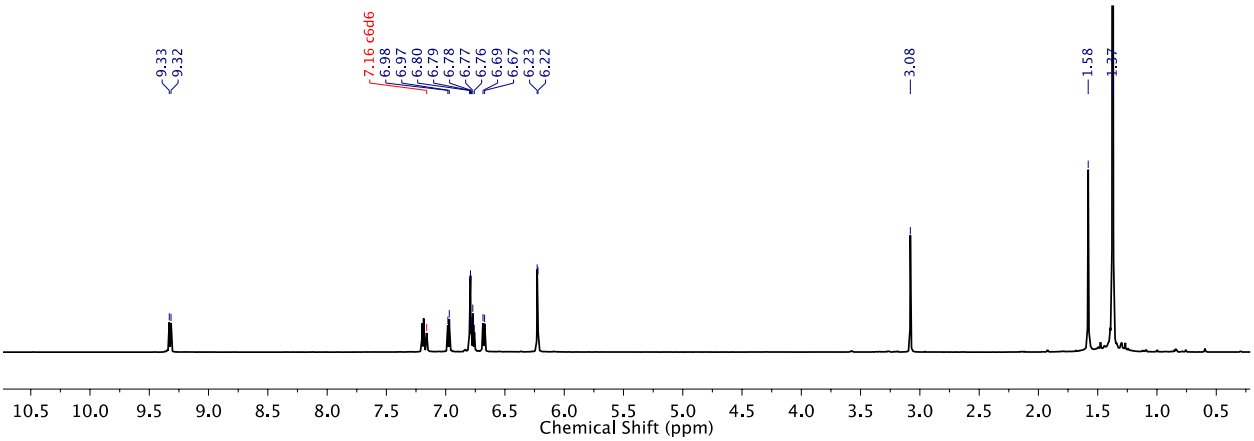


Figure S–11. ^{1}H NMR spectrum of ($^{t\text{Bu}}$dmx)$Cu_2(\mu^2\text{–}N(C_6H_4OMe))$ (**5**), (600 MHz, C_6D_6).

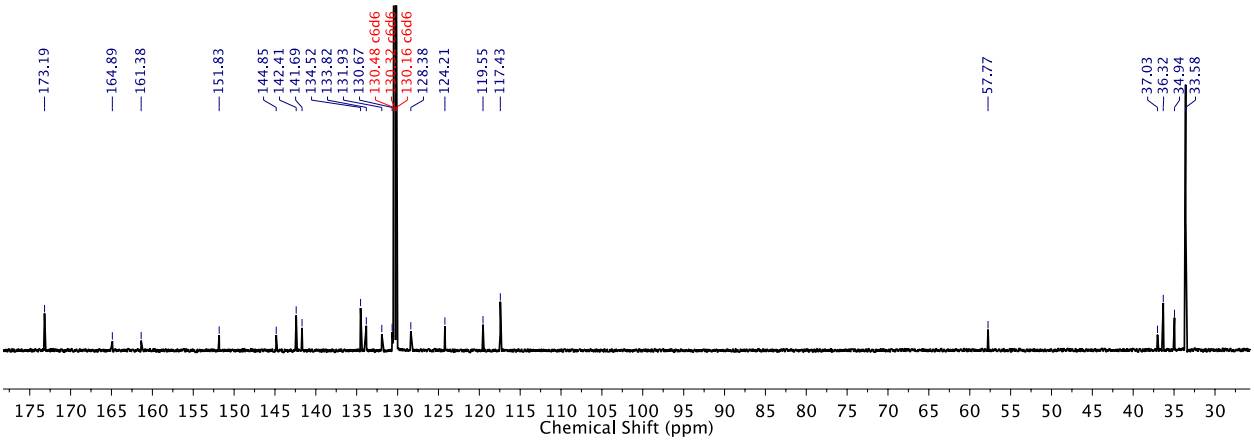
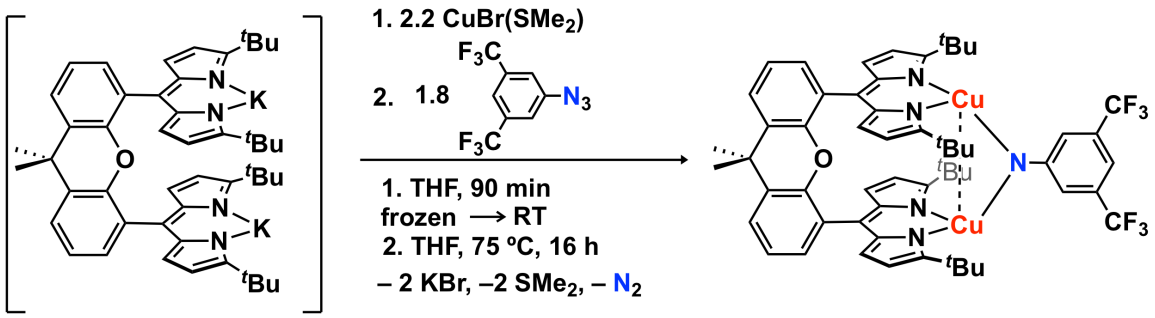


Figure S–12. ^{13}C NMR spectrum of ($^{t\text{Bu}}$dmx)$Cu_2(\mu^2\text{–}N(C_6H_4OMe))$ (**5**), (125 MHz, C_6D_6).



($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**6**). In the drybox, to a thawing suspension of **4** (0.070 g, 0.096 mmol, 1.0 equiv.) in tetrahydrofuran (5 mL) was added copper bromide dimethylsulfide complex (0.040 g, 0.21 mmol, 2.2 equiv.) as a solid. Over 90 minutes, the reaction became a homogeneous red-orange solution. The reaction was subsequently filtered through a plug of Celite, followed by the addition of 3,5-bis(trifluoromethyl)phenyl azide[3] (0.040 g, 0.17 mmol, 1.8 equiv.) in tetrahydrofuran (5 mL) to the filtrate. The mixture was transferred to a Schlenk tube, sealed, exported from the drybox, and heated to 70 ºC for 16 h. The subsequent dark purple solution was returned to drybox and dried *in vacuo*. The resulting solid was dissolved in minimal benzene, filtered through a plug of Celite, and lyophilized. The resulting dark purple powder was dissolved in minimal acetonitrile and stirred rapidly for 2 h to form a thick slurry. The vial was transferred to the freezer for 2 h. The mixture was filtered through a pad of Celite on top of a coarse porosity frit, followed by rinsing of the residual solids on top of the frit with minimal thawing acetonitrile (2 x 10 mL) until the filtrate became faint pink. The filtrate was discarded, and the remaining deep purple solids were eluted with benzene and lyophilized to afford ($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**6**) as a dark purple solid (0.050 g, 49 %). Single crystals suitable for X-ray diffraction were obtained by layering acetonitrile with a concentrated solution of **11** in diethyl ether at –35 ºC overnight. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ 9.48 (s, 2*H*, aryl imide C–*H*), 8.08 (s, 1*H*, aryl imide C–*H*), 7.19 (d, *J* = 8.0 Hz, 2*H*, dipyrrin C–*H*), 6.77 (m, 6*H*, xanthene C–*H*), 6.09 (d, *J* = 4.0 Hz, 4H, dipyrrin C–*H*), 1.57 (s, 6*H*, xanthene methyl C–*H*), 1.33 (s, 36*H*, *tert*-butyl C–*H*). ^{19}F NMR (470 MHz, C$_6$D$_6$): δ -62.50 (s, aryl imide C*F*$_3$). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 171.84, 163.37, 149.00, 142.39, 138.97, 134.14, 133.88, 133.62, 133.36, 132.93, 131.53, 131.07, 129.40, 127.06, 126.22, 124.38, 122.20, 121.79, 118.17, 115.51, 34.36, 33.31, 32.44, 30.53. NIR/UV-vis (THF), λ_{max}/nm (ε/M^{-1} cm^{-1}): 1430 (600), 1120 (300), 760

(13,500), 670 (13,000), 480 (140,000), 360 (23,500), 310 (33,300). Calculated for $C_{57}H_{59}Cu_2F_6N_5O$: C 63.91 H 5.55 N 6.54; Found: C 63.90 H 5.51 N 6.47.

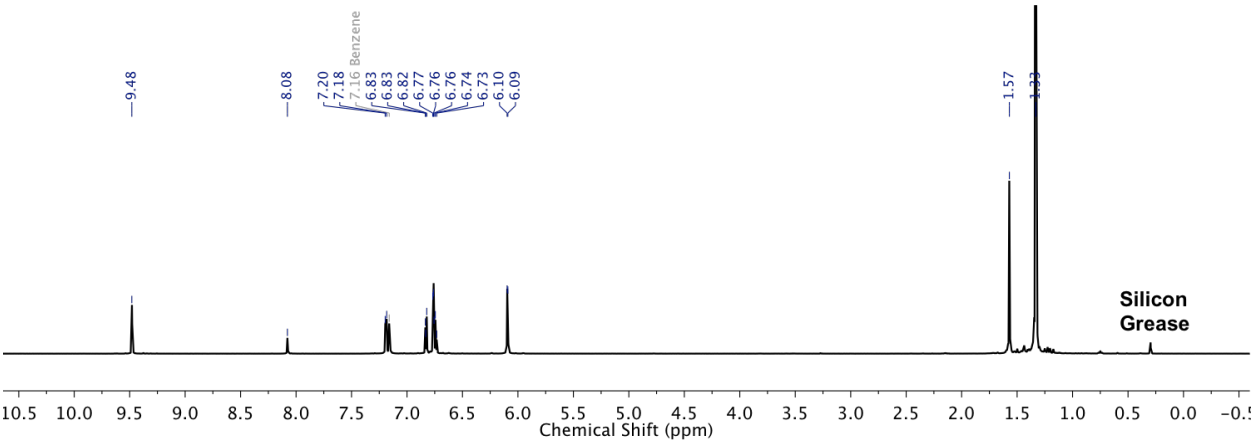


Figure S–13. ^{1}H NMR spectrum of ($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(F_3C)_2C_6H_3$)) (**6**), (600 MHz, C_6D_6).

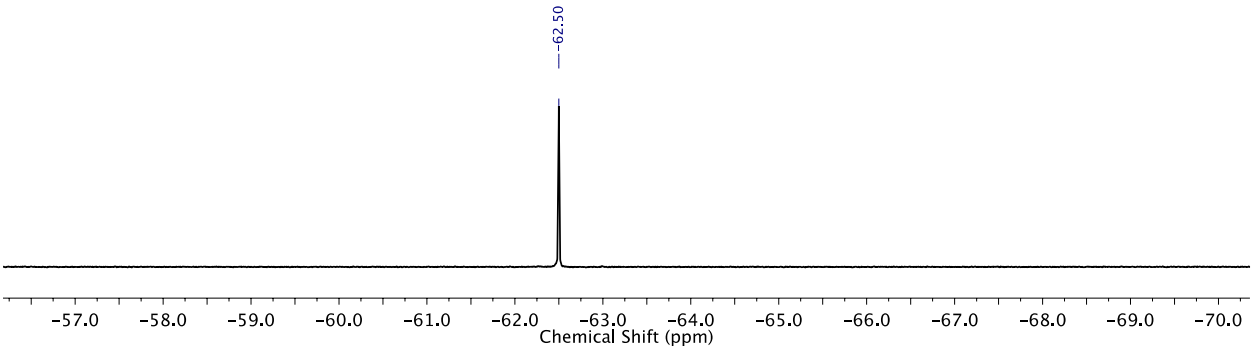


Figure S–14. ^{19}F NMR spectrum of ($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(F_3C)_2C_6H_3$)) (**6**), (375 MHz, C_6D_6).

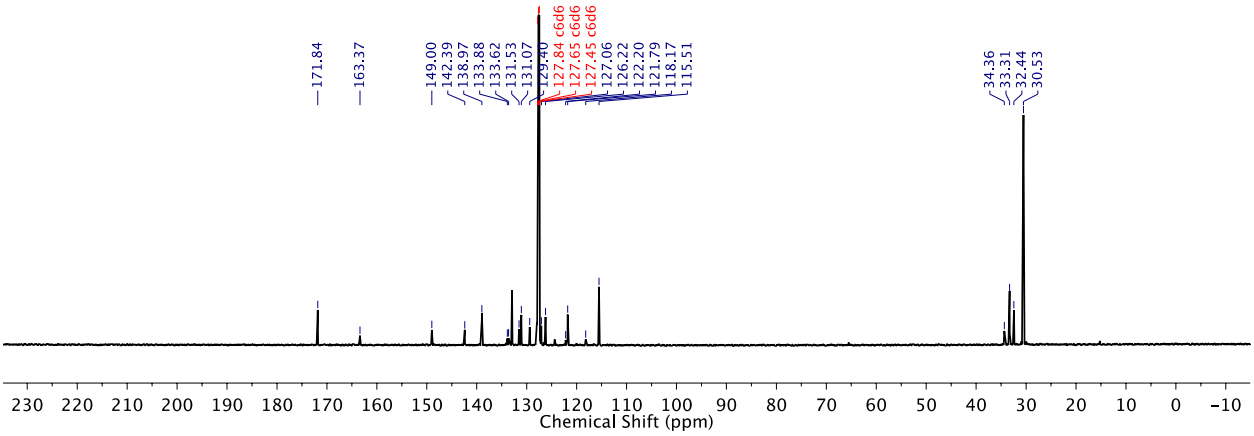
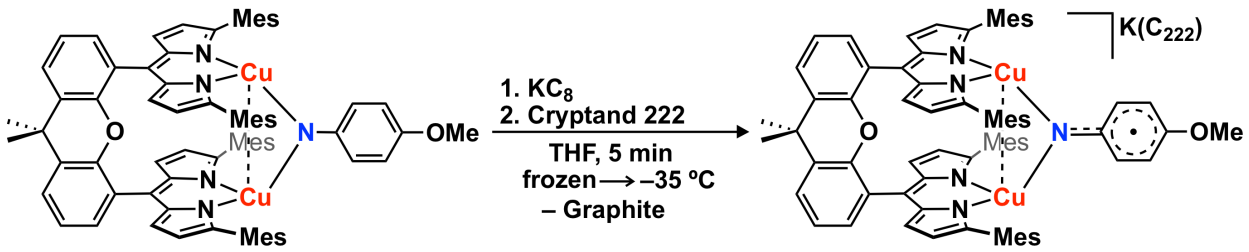


Figure S–15. ^{13}C NMR spectrum of ($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(F_3C)_2C_6H_3$)) (**6**), (125 MHz, C_6D_6).



(**2**) (**7**)

[K(C$_{222}$)][(^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (**7**). *Due to the thermal instability of 7, all manipulations were performed at –35 ºC or below –35 ºC. Allowing 7 to stand at room temperature in solution or the solid state affords a marked color change to deep red, accompanied by complete consumption of* **7** *as ascertained by* ^{1}*H NMR spectroscopy.* In the drybox, a thawing suspension of KC$_8$ (0.003 g, 0.021 mmol, 1.05 equiv.) in tetrahydrofuran (0.5 mL) was added to solid **2** (0.025 g, 0.020 mmol, 1.0 equiv.), resulting in a rapid color change from violet to pink upon thawing. The mixture was physically agitated for ten seconds and placed into a liquid-nitrogen chilled cold well to solidify the mixture. The solid suspension was layered with a thawing solution of Cryptand 222 (222c; 0.008 g, 0.021 mmol, 1.05 equiv.) in tetrahydrofuran (0.3 mL) and allowed to thaw. The thawed solution was physically agitated for ten seconds – resulting in a darkening of the solution – and filtered through a pad of cold Celite within a pre-chilled pipette to afford [K(C$_{222}$)][(^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (**7**) accompanied by quantitative consumption of **2** by ^{1}H NMR spectroscopy. The resulting brown-pink solution was layered with a thawing 1:3 benzene/hexane mixture (2 mL) and placed in a –35 ºC freezer over two days to afford crystals suitable for X-ray diffraction. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.56 (br), δ 7.25 (br), δ 7.16 (br), δ 6.46 (br), 2.56 (br). *Note:* Although an isolated yield of **7** could not be obtained, treatment of **7** generated in situ with stoichiometric silver trifluoromethanesulfonate re-afforded **2** quantitatively, suggesting the formation of **7** to proceed in quantitative yield. Due to the thermal instability of the complex in the solid-state, a satisfactory elemental analysis could not be obtained.

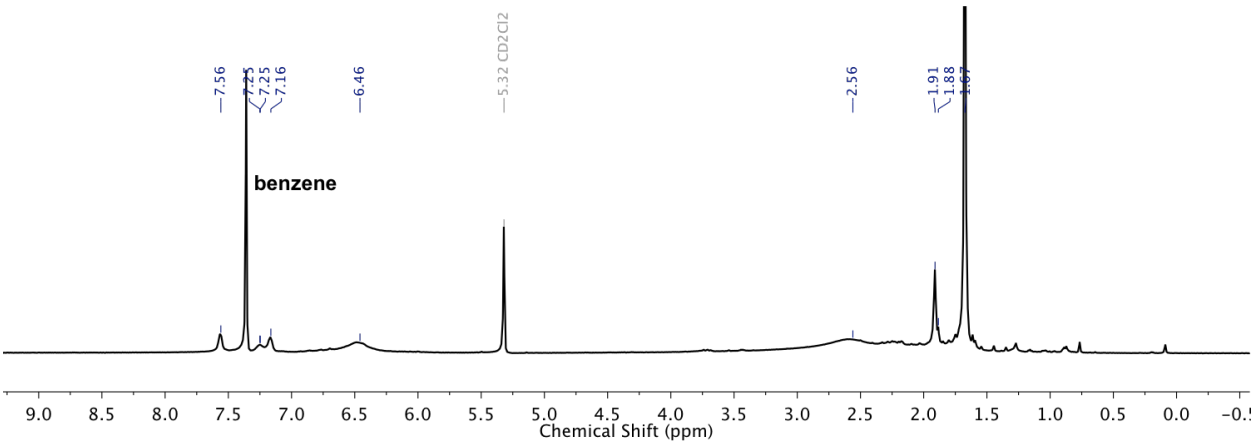


Figure S–16. ^{1}H NMR spectrum of *in situ* generated [K(C_{222})][(^{Mes}dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**7**), (600 MHz, CD_2Cl_2) on a just-thawed sample prior to thermal decomposition.

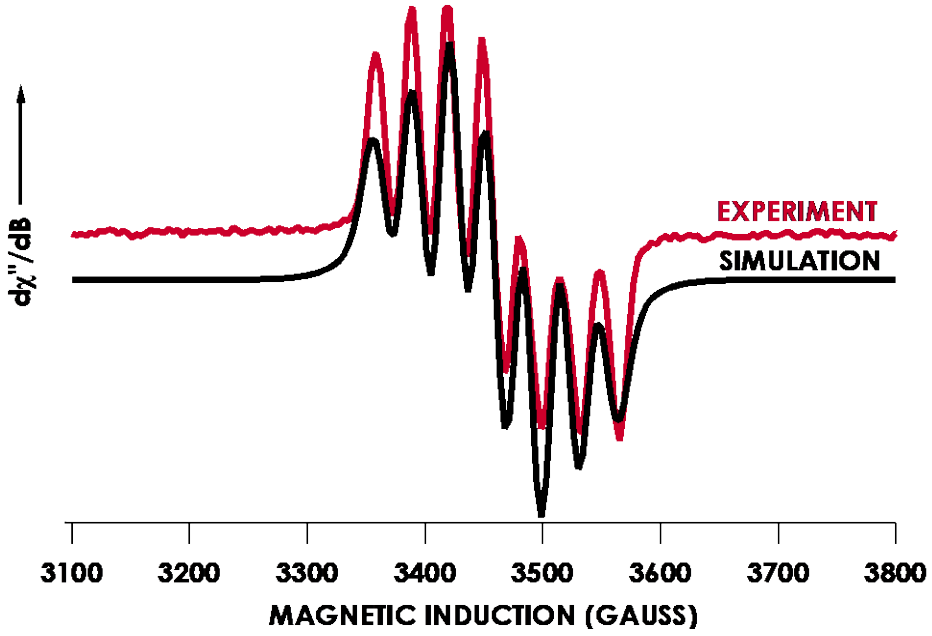


Figure S–17. Solution 2-methyltetrahydrofuran EPR spectrum of [K(C_{222})] [(^{Mes}dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**7**) obtained from a just-thawed solution with microwave frequency of 9.843 GHz and 0.6325 mW microwave power, expanded to show an isotropic S = $^1/_2$ signal (red) simulated using SpinCount (black) with the following parameters: g_{iso} = 2.033, σg_x = 0.0277, σg_y = 0.0039, σg_z = 0.0051; $^{63}Cu_2$ A_{iso} = 87.4 MHz; ^{14}N A_{iso} = 17.8 MHz. *Note*: EPR resonances for **7** disappear when the reaction mixture is left to stand at room temperature over 1 h due to thermal decomposition to diamagnetic species.

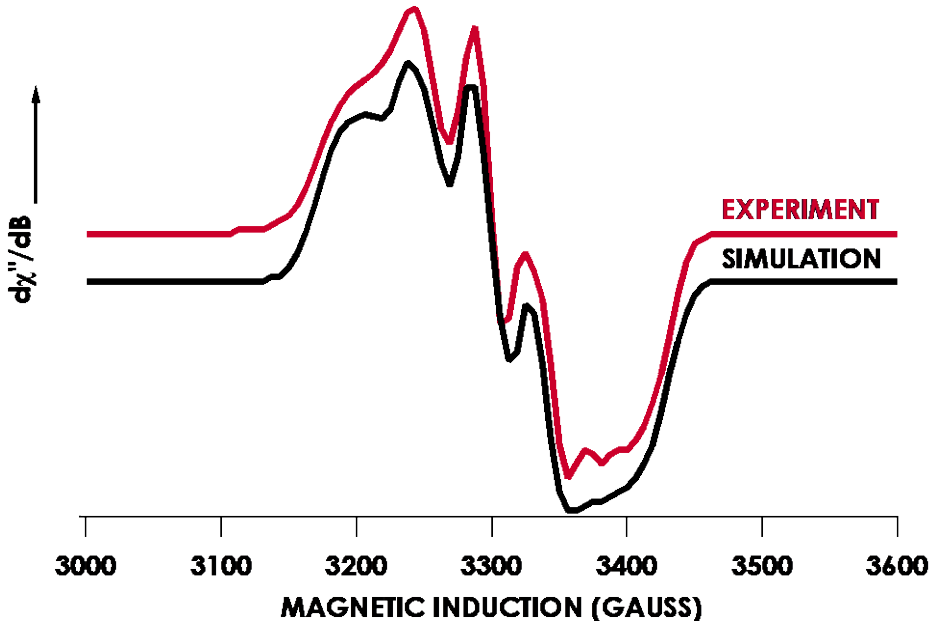


Figure S–18. Frozen 2-methyltetrahydrofuran EPR spectrum of [K(C_{222})][(^{Mes}dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**7**) obtained at 4 K with microwave frequency of 9.378 GHz and 0.6325 mW microwave power expanded to show an anisotropic $S = {}^1/_2$ signal (red) simulated using SpinCount (black) with the following parameters: $g_x = 1.979$, $g_y = 2.032$, $g_z = 2.074$; $\sigma g_x = 0.0080$, $\sigma g_y = 0.0014$, $\sigma g_z = 0.0098$; $^{63}Cu_2$ $A_x = 9.3$ MHz, $A_y = 43.9$ MHz, $A_z = 9.7$ MHz; ^{14}N $A_x = 86.6$ MHz, $A_y = 125.6$ MHz, $A_z = 130.3$ MHz.

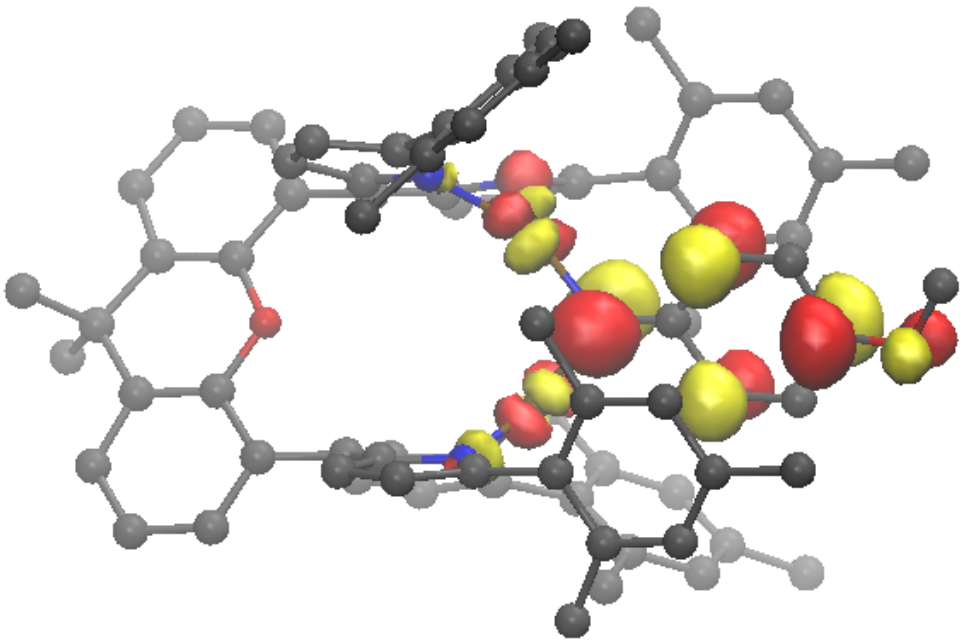
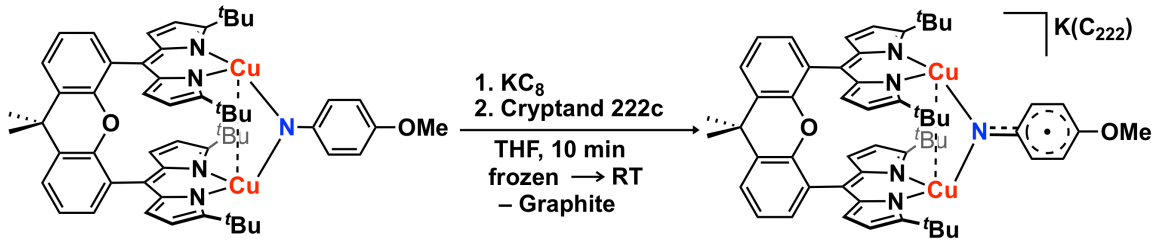


Figure S–19. Singly occupied molecular orbital (SOMO) of [K(C_{222})][(^{Mes}dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**7**), displaying pronounced radical character delocalized across both copper centers and the bridging nitrene motif. Calculated orbital coefficient values exceeding 0.05: Cu_1 (0.11), Cu_2 (0.09), N_{imide} (0.43), C_{ipso} (-0.16), C_{ortho} (0.28, 0.23), C_{meta} (-0.13, -0.11) C_{ipso} (0.21). Orbital resolution plotted at an isolevel of 0.03 au. See computational section for calculation details.



(**5**) (**8**)

[K(C$_{222}$)][(*t*^{Bu}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (**8**). In the drybox, to a thawing solution of **5** (0.041 g, 0.042 mmol, 1.0 equiv.) in tetrahydrofuran (2 mL) was added KC_8 (0.006 g, 0.043 mmol, 1.03 equiv.), accompanied by a rapid color change from purple to yellow-brown. The reaction was stirred at room temperature for ten minutes, followed by addition of Cryptand 222 (222c; 0.015 g, 0.054 mmol, 1.3 equiv.). A rapid color change to pink-brown was noted. The solution was filtered through a pad of Celite, followed by removal of solvent *in vacuo*. The resulting power was suspended in diethyl ether and filtered through a pad of Celite. The residual power was eluted with minimal tetrahydrofuran, layered with diethyl ether, and placed in a –35 ºC freezer overnight to afford large pink-brown crystals of [K(C$_{222}$)][(*t*^{Bu}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (**8**), (0.045 g, 78 %). Single crystals suitable for X-ray diffraction were grown by layering a solution of **8** in tetrahydrofuran with diethyl ether at –35 ºC overnight. ^{1}H NMR (600 MHz, d$_8$-THF): δ 9.36 (v. br) 7.45 (br), 6.98 (br), 3.44 (br), 3.40 (br), 2.57 (v. br), 2.42 (br), 1.77 (br). NIR/UV-vis (THF), λ_{max}/nm (ε/M^{-1} cm^{-1}): 1300 (200), 770 (3,500), 600 (12,000), 490 (140,000), 390 (24,000), 290 (44,400). Calculated for $C_{74}H_{99}Cu_2KN_7O_8$: C 64.37 H 7.23 N 7.10; Found: C 64.17 H 7.30 N 6.89.

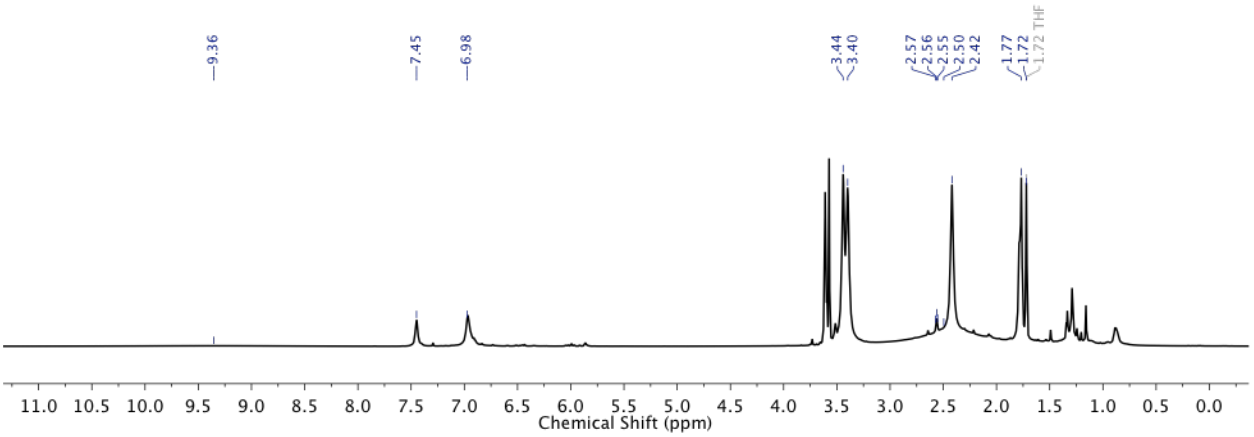


Figure S–20. ^{1}H NMR spectrum of [K(C_{222})][($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**8**), (600 MHz, d_8-THF).

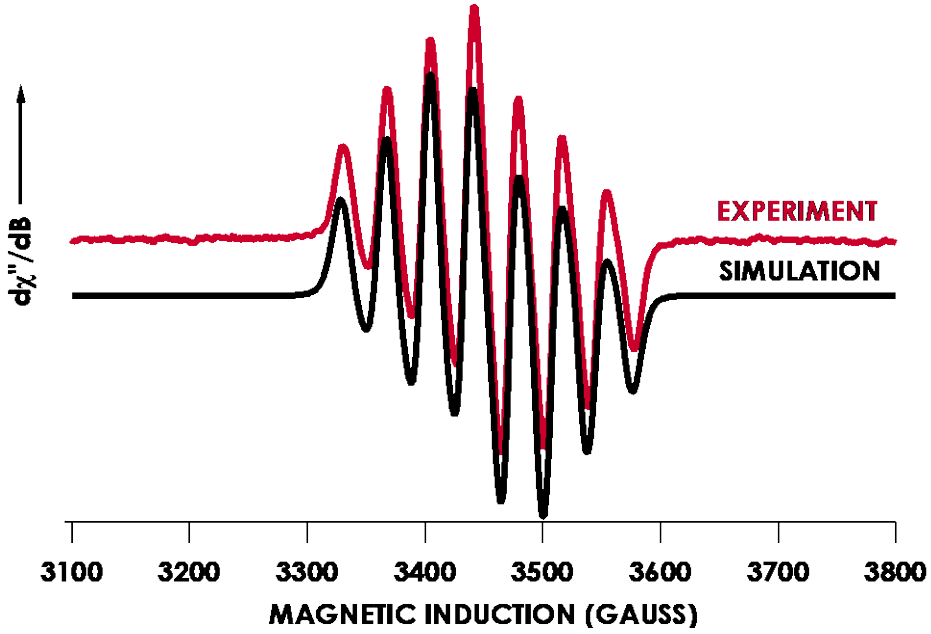


Figure S–21. Solution 2-methyltetrahydrofuran EPR spectrum of [K(C_{222})][($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**8**) obtained at 298 K with microwave frequency of 9.849 GHz and 0.6325 mW microwave power, expanded to show an isotropic $S = {}^1/_2$ signal (red) simulated using SpinCount (black) with the following parameters: g_{iso} = 2.038, σg_x = 0.0106, σg_y = 0.0020, σg_z = 0.0042; $^{63}Cu_2$ A_{iso} = 105.5 MHz; ^{14}N A_{iso} = 29.3 MHz.

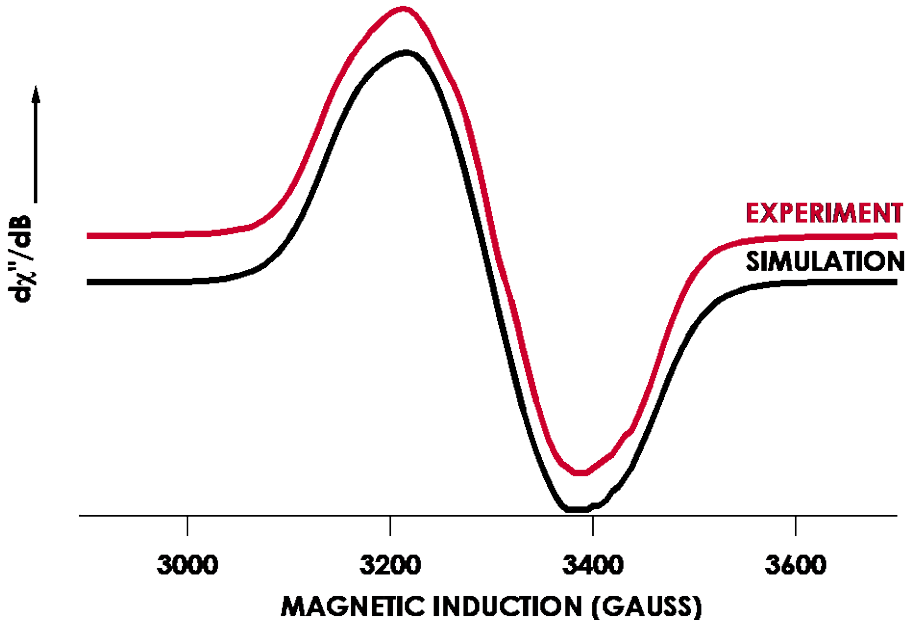
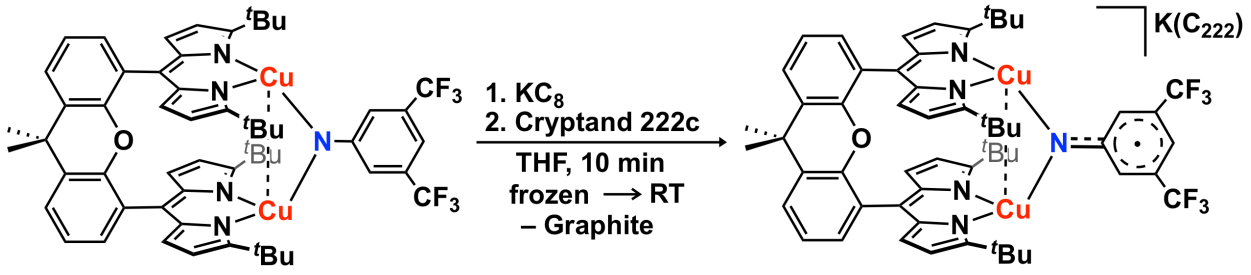


Figure S–22. Frozen 2-methyltetrahydrofuran EPR spectrum of [K(C_{222})][($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**8**) obtained at 4 K with microwave frequency of 9.381 GHz and 0.6325 mW microwave power expanded to show an isotropic $S = {}^1/_2$ signal (red) simulated using SpinCount (black) with the following parameters: g_{iso} = 2.029; σg_x = 0.0465, σg_y = 0.0370, σg_z = 0.0190; $^{63}Cu_2$ A_{iso} = 115.9 MHz; ^{14}N A_{iso} = 29.3 MHz.



[K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] (**9**). In the drybox, to a thawing solution of **6** (0.047 g, 0.044 mmol, 1.0 equiv) in tetrahydrofuran (2 mL) was added KC_8 (0.006 g, 0.044 mmol, 1.0 equiv.), accompanied by a rapid color change from purple to yellow-brown. The reaction was stirred at room temperature for ten minutes, followed by addition of Cryptand 222 (0.017 g, 0.052 mmol, 1.2 equiv). A rapid color change to red-brown was noted. After stirring for 30 minutes, the solution was filtered through a pad of Celite, followed by removal of solvent *in vacuo*. The resulting power was suspended in diethyl ether and filtered through a pad of Celite. The residual power was eluted with minimal tetrahydrofuran, layered with diethyl ether, and placed in a –35 ºC freezer overnight to afford large brown crystals of [K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] (**9**) (0.040 g, 63 %). Single crystals suitable for X-ray diffraction were grown by layering a solution of **15** in tetrahydrofuran with diethyl ether at –35 ºC overnight. ^{1}H NMR (600 MHz, d$_8$-THF): δ 9.42 (br) 7.44 (br), 6.96 (br), 3.49 (br), 3.45 (br), 2.46 (br), 1.78 (br). ^{19}F NMR (470 MHz, d$_8$-THF): no resonances. UV/vis (THF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 490 (130,000), 420 (23,000), 300 (28,000). Calculated for $C_{75}H_{95}Cu_2F_6KN_7O_7$: C 60.59 H 6.44 N 6.59; Found: C 60.39 H 6.49 N 6.81.

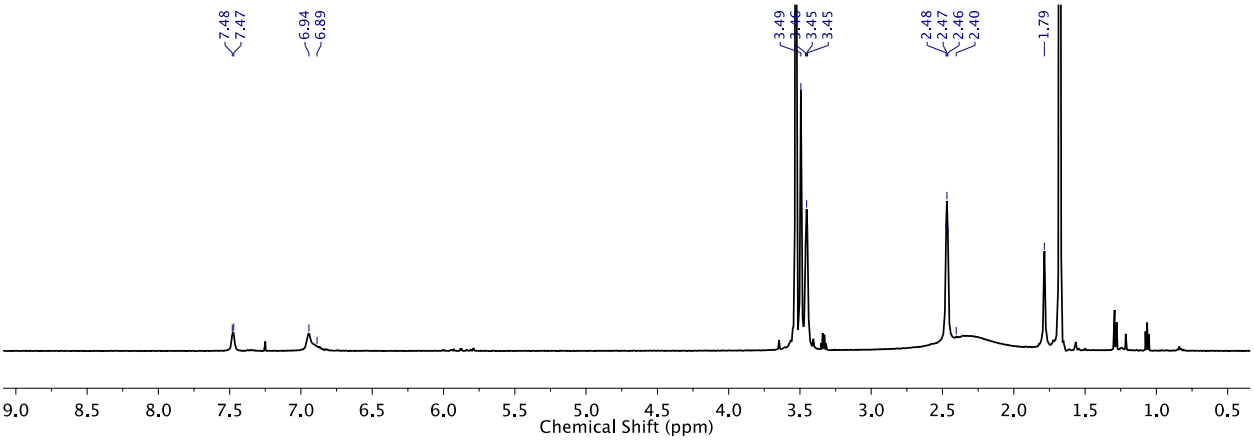


Figure S–23. ^{1}H NMR spectrum of [K(C_{222})][($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(CF_3)_2C_6H_3$))] (**9**), (600 MHz, d_8-THF).

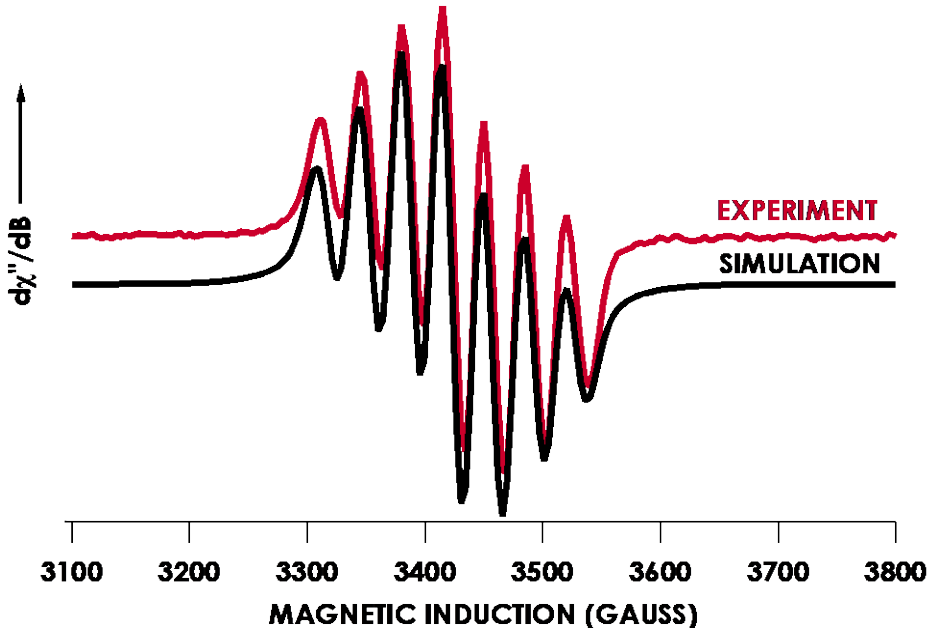


Figure S–24. Solution 2-methyltetrahydrofuran EPR spectrum of [K(C_{222})][($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(CF_3)_2C_6H_3$))] (**9**) obtained at 298 K with microwave frequency of 9.847 GHz and 0.6325 mW microwave power, expanded to show an isotropic $S = {}^1/_2$ signal (red) simulated using SpinCount (black) with the following parameters: $g_{iso} = 2.055$, $\sigma g_x = 0.0065$, $\sigma g_y = 0.0089$, $\sigma g_z = 0.0422$; $^{63}Cu_2$ $A_{iso} = 99.4$ MHz; ^{14}N $A_{iso} = 5.7$ MHz.

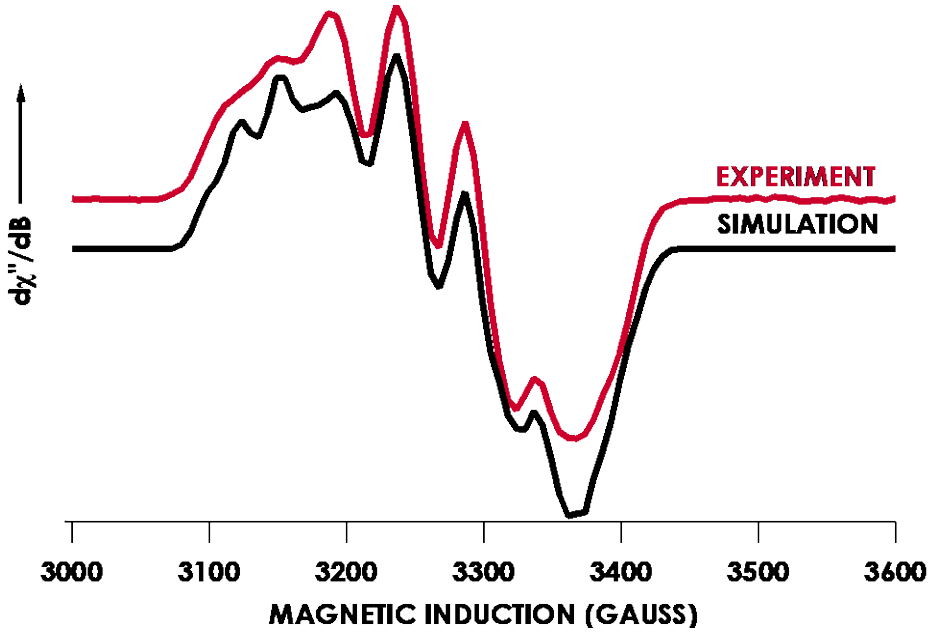
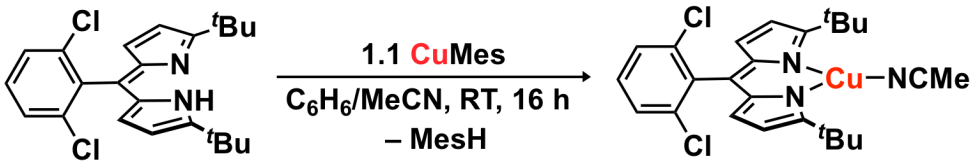


Figure S–25. Frozen 2-methyltetrahydrofuran EPR spectrum of [K(C_{222})][($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(CF_3)_2C_6H_3$))] (**9**) obtained at 4 K with microwave frequency of 9.377 GHz and 0.6325 mW microwave power expanded to show an anisotropic $S = {}^1/_2$ signal (red) simulated using SpinCount (black) with the following parameters: g_x = 1.987, g_y = 2.043, g_z = 2.128; σg_x = 0.0019, σg_y = 0.0038, σg_z = 0.0038; $^{63}Cu_2$ A_x = 35.7 MHz, A_y = 41.0 MHz, A_z = 25.0 MHz; ^{14}N A_x = 26.3 MHz, A_y = 70.9 MHz, A_z = 96.2 MHz.



(**10**)

($^{t\text{Bu}}$L)Cu(NCMe) (**10**). In the drybox, to a solution of ($^{t\text{Bu}}$L)H (0.133 g, 0.331 mmol, 1.0 equiv.) in a benzene/acetonitrile mixture (3.0 mL C_6H_6, 0.5 mL MeCN) was added mesitylcopper[10] (0.067 mg, 0.365 mmol, 1.1 equiv.). The reaction was stirred for 16 h, during which a gradual color change from deep orange to red-pink was observed. Following removal of solvent *in vacuo*, the resulting red-pink powder was dissolved in minimal acetonitrile, filtered through a pad of Celite, and allowed to stand at –35 ºC overnight to furnish large red crystals suitable for single crystal X-ray diffraction. The mother liquor was decanted, and the crystals were rinsed with cold acetonitrile to afford ($^{t\text{Bu}}$L)Cu(NCMe) (**10**) (0.095 g, 57 %). ^{1}H NMR (500 MHz, C_6D_6): δ 7.00 (d, *J* = 8.1 Hz, 2*H*, dipyrrin C–*H*), 6.65 (d, *J* = 4.2 Hz, 2*H*, aryl C–*H*), 6.61 (t, *J* = 7.8 Hz, 1*H*, aryl C–*H*), 6.56 (d, *J* = 4.2 Hz, 2*H*, dipyrrin C–*H*), 1.55 (s, 18*H*, *tert*-butyl C–*H*), 0.64 (s, 3*H*, acetonitrile C–*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 170.57, 139.41, 136.42, 130.08, 128.80, 127.30, 116.09, 114.66, 34.02, 30.96, 0.26. Calculated for $C_{25}H_{28}Cl_2CuN_3$•0.5CH_3CN: C 59.43 H 5.66 N 9.33; Found: C 59.50 H 5.56 N 9.23 (the molecule of acetonitrile is present from bulk recrystallization). *Note*: Although **16** demonstrates no signs of decomposition by ^{1}H NMR spectroscopy over several months in the solid state, room temperature solutions of **16** in C_6D_6 in the absence of excess acetonitrile will gradually convert (< 10 % per 24 h) to ($^{t\text{Bu}}$L)$_2$Cu$_2$ (**18**).

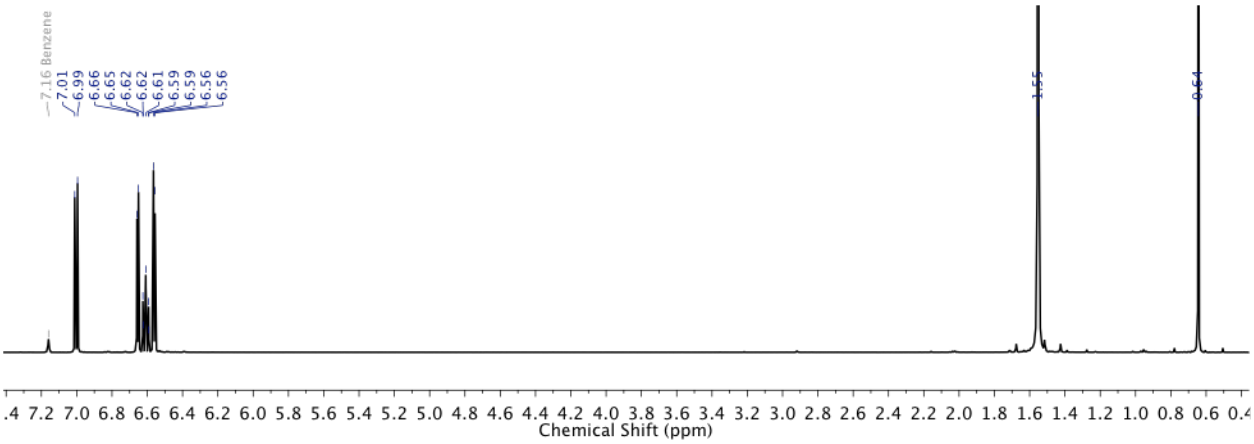


Figure S–26. ^{1}H NMR spectrum of ($^{t\text{Bu}}$L)Cu(NCMe) (**10**), (500 MHz, C_6D_6).

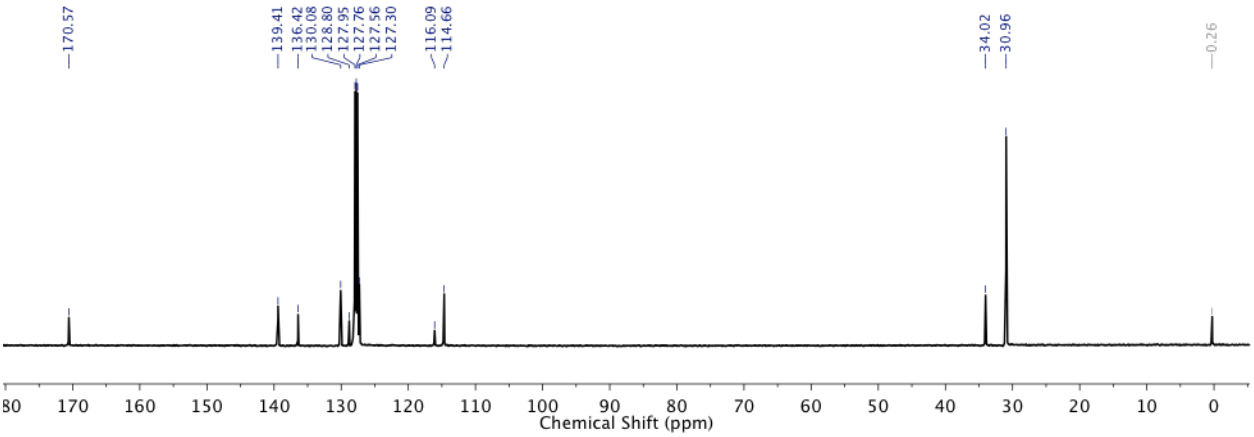
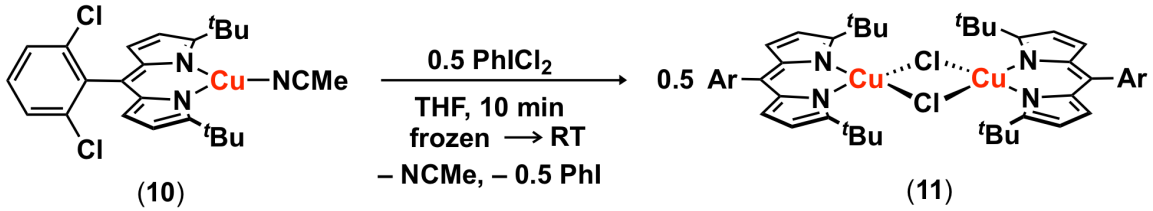


Figure S–27. ^{13}C NMR spectrum of ($^{t\text{Bu}}$L)Cu(NCMe) (**10**), (125 MHz, C_6D_6).



(**10**) (**11**)

[(*t*^{Bu}L)CuCl]$_2$ (**11**). In the drybox, to a thawing solution of **10** (0.056 g, 0.100 mmol, 1.0 equiv.) in tetrahydrofuran (1 mL) was added iodobenzene dichloride[8] ($PhICl_2$; 0.015 mg, 57 μmol, 0.55 equiv.), accompanied by a rapid darkening of the solution. After ten minutes, solvent was removed *in vacuo*. The residual solid was dissolved in a 2:1 hexane/benzene mixture, filtered, and allowed to stand at –35 ºC overnight. The mother liquor was decanted, and the residual solids were rinsed with hexanes to afford [(*t*^{Bu}L)CuCl]$_2$ (**11**) as a dark red solid (0.041 g, 74 %). Single crystals suitable for X-ray diffraction were obtained by allowing a concentrated pentane/benzene solution of **11** to stand overnight at –35 ºC. ^{1}H NMR (500 MHz, C_6D_6): δ 37.44 (br), 6.51 (br). Calculated for $C_{46}H_{50}Cl_6Cu_2N_4$•$2C_6H_6$: C 60.32, 5.41, 4.85; Found: C 60.16, H 5.51, N 5.04 (two molecules of benzene are present from bulk recrystallization).

Note: Preparation of **11** by salt metathesis of (*t*^{Bu}L)Li with either anhydrous $CuCl_2$ or $CuBr_2$ is accompanied by partial halogenation of the dipyrrin β-position as ascertained from single-crystal X-ray diffraction (*unpublished*), ^{1}H NMR spectroscopy, and mass spectrometry.

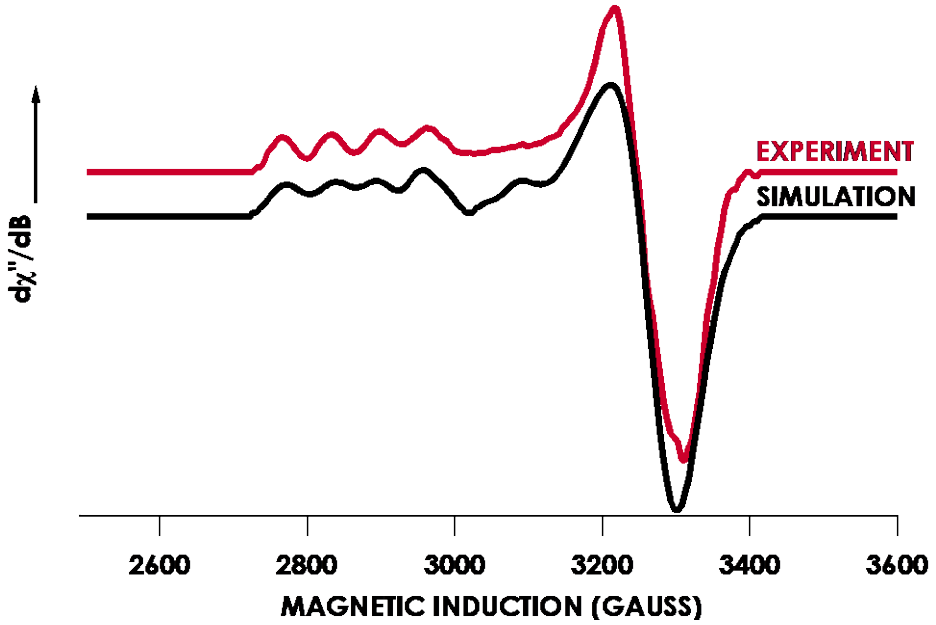
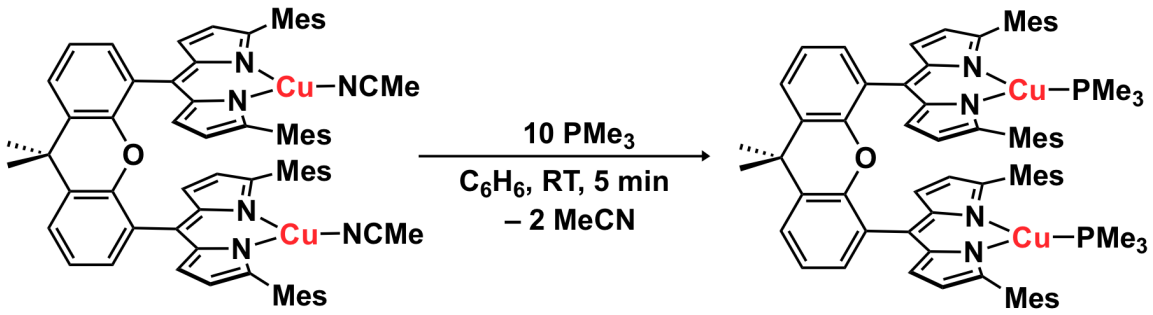


Figure S–28. Frozen toluene EPR spectrum of $[(^{t\text{Bu}}\text{L})\text{CuCl}]_2$ (**11**) obtained at 77 K with microwave frequency of 9.454 GHz and 0.6325 mW microwave power expanded to show the axial signal (red) simulated using SpinCount (black) with the following parameters: $g_{\perp} = 2.061$, $g_{\parallel} = 2.365$; $\sigma g_x = 0.0301$, $\sigma g_y = 0.0296$, $\sigma g_z = 0.0180$; $^{63}\text{Cu}\ A_{\parallel} = 199.3$ MHz.



(**1**) (**12**)

(^{Mes}**dmx)Cu$_2$(PMe$_3$)$_2$** (**12**). In the drybox, to a thawing solution of **1** (0.050 g, 0.040 mmol, 1.0 equiv.) in benzene (2 mL) was added dropwise excess trimethylphosphine (PMe_3; 0.030 g, 0.40 mmol, 10 equiv.), during which a rapid color change from red-pink to translucent pink was noted. The reaction was stirred for 10 minutes, followed by removal of solvent *in vacuo*. The residue was dissolved in benzene, filtered through a pad of Celite, and lyophilized to afford (^{Mes}dmx)$Cu_2(PMe_3)_2$ (**12**) as a bright pink solid (0.050 g, 98 %). Single crystals of **4** suitable for X-ray diffraction were obtained by allowing a concentrated tetrahydrofuran/hexanes solution of **12** to stand at –35 ºC for one week. ^{1}H NMR (600 MHz, C_6D_6): δ 7.40 (dd, *J* = 7.3, 1.7 Hz, 2*H*, dipyrrin C–*H*), 7.27 (dd, 7.3, 1.7 Hz, 2*H,* dipyrrin C–*H*), 6.92 (d, *J* = 4.4 Hz, 4*H,* xanthene C–*H*), 6.85 (t, *J* = 7.6 Hz, 2*H,* xanthene C–*H*), 6.81 (s, 4*H*, mesityl aryl C–*H*), δ 6.75 (s, 4*H*, mesityl aryl C–*H*), 6.28 (d, *J* = 3.9 Hz, 4*H*, dipyrrin C–*H*), 2.43 (s, 12*H*, mesityl ortho-methyl C–*H*), 2.32 (s, 12*H*, mesityl ortho-methyl C–*H*), 2.14 (s, 12*H,* mesityl para-methyl C–*H)* 1.61 (s, 6*H*, xanthene methyl C–*H*), 0.23 (d, *J* = 6.5 Hz, 18*H*, trimethylphosphine C–*H*). ^{31}P NMR (160 MHz, C_6D_6): δ -46.8 (s, *P*Me_3). ^{13}C NMR (125 MHz, C_6D_6): δ 158.40, 149.48, 143.83, 140.98, 137.88, 137.29, 136.74, 135.90, 133.35, 131.46, 130.82, 129.40, 124.48, 121.36, 118.14, 67.43, 34.59, 30.99, 25.43, 22.13, 21.23, 20.72, 14.52, 14.34. Calculated for $C_{75}H_{82}Cu_2N_4OP_2$•CH_3CN: C 71.94 H 6.66 N 5.45; Found: C 72.24 H 6.67 N 5.13 (one molecule of acetonitrile is present from bulk recrystallization from a diethyl ether/acetonitrile recrystallization for elemental analysis).

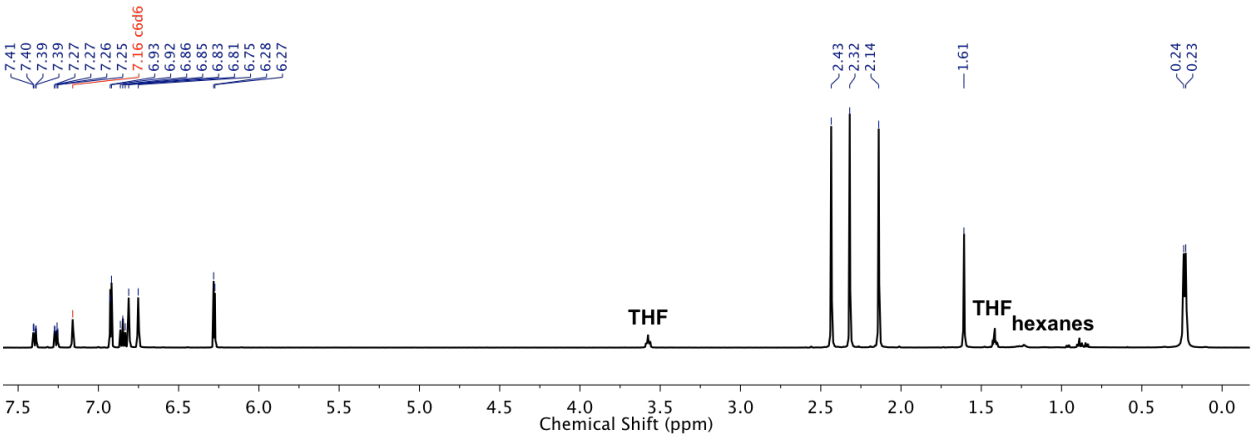


Figure S–29. ^{1}H NMR spectrum of (^{Mes}dmx)$Cu_2(PMe_3)_2$ (**12**), (600 MHz, C_6D_6).

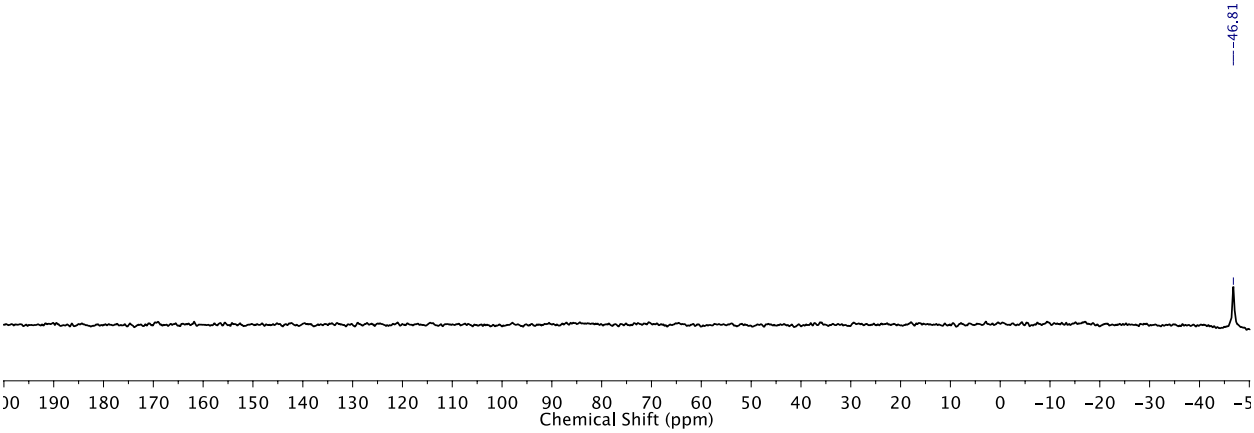


Figure S–30. ^{31}P NMR spectrum of (^{Mes}dmx)$Cu_2(PMe_3)_2$ (**12**), (160 MHz, C_6D_6).

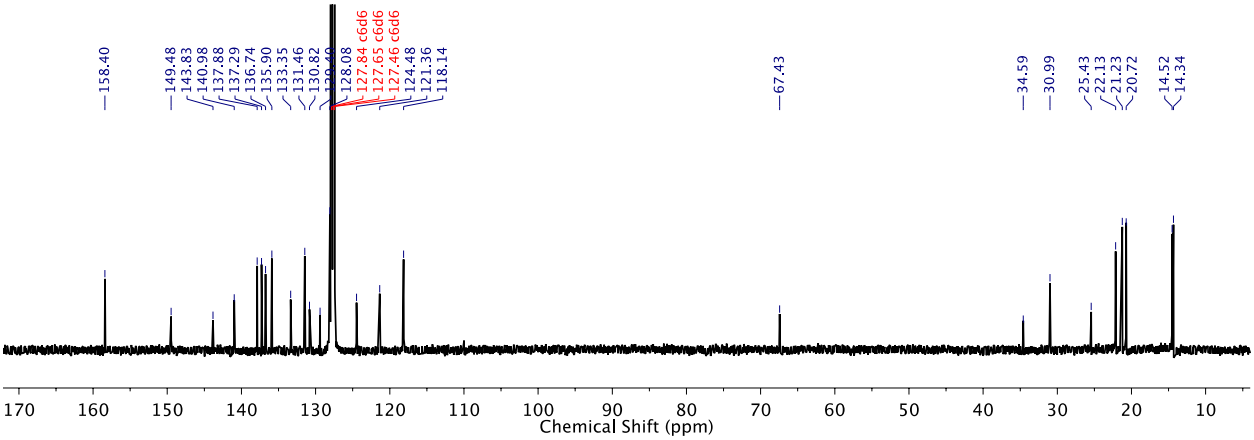
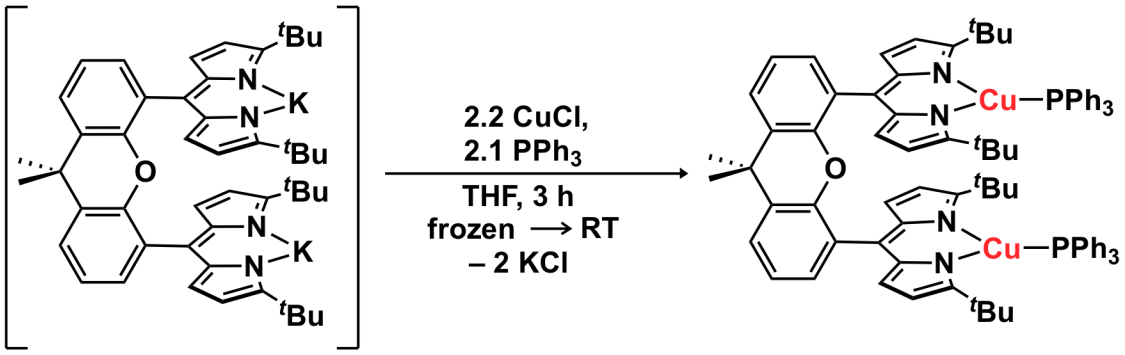


Figure S–31. ^{13}C NMR spectrum of (^{Mes}dmx)$Cu_2(PMe_3)_2$ (**12**), (125 MHz, C_6D_6).



(**4**) (**13**)

($^{t\text{Bu}}$dmx)Cu$_2$(PPh$_3$)$_2$ (**13**). In the drybox, to a thawing suspension of **4** (0.500 g, 0.629 mmol, 1.0 equiv.) in tetrahydrofuran (10 mL) was added solid triphenylphosphine (PPh$_3$; 0.350 g, 1.320 mmol, 2.1 equiv.) followed by cuprous chloride (0.137 g, 1.383 mmol, 2.2 equiv.). Over 2 h, homogenization and a color change to red-pink were noted. The solution was filtered through a pad of Celite and dried *in vacuo*. The residual solids were dissolved in benzene (5 mL) and lyophilized. The resulting powder was suspended in hexanes and filtered through a pad of Celite, followed by rinsing with hexanes (*ca.* 2 mL) and acetonitrile (*ca*. 2 mL). The residual powder was eluted with benzene and lyophilized to afford ($^{t\text{Bu}}$dmx)Cu$_2$(PPh$_3$)$_2$ (**13**) as a bright pink solid (0.800 g, 93 %). Single crystals suitable for X-ray diffraction were obtained by allowing a concentrated solution toluene/hexanes solution of **13** to stand overnight at –35 ºC. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ 7.25 (m, 14*H*, overlapping dipyrrin C–*H* and triphenylphosphine C–*H*), 6.97 (m, 20*H*, triphenylphosphine C–*H*), 6.87 (m, 6*H*, xanthene C–*H*), 6.38 (dd, *J* = 4.1, 1.0 Hz, dipyrrin C–H), 1.60 (s, 6*H*, xanthene methyl C–H), 1.44 (s, 36*H*, *tert*-butyl C–*H*). ^{31}P NMR (160 MHz, C$_6$D$_6$): δ -0.46 (s, *P*Ph$_3$). ^{13}C NMR (125 MHz, C$_6$D$_6$, δ/ppm): δ 167.98, 148.59, 142.85, 140.01, 133.81, 133.69, 133.41, 132.74, 130.54, 130.08, 129.62, 129.46, 128.55, 128.47, 124.69, 121.27, 113.36, 34.45, 33.55, 31.64, 30.80, 30.76. Calculated for C$_{85}$H$_{86}$Cu$_2$N$_4$OP$_2$: C 74.59 H 6.33 N 4.09; Found: C 75.57 H 6.20 N 4.15.

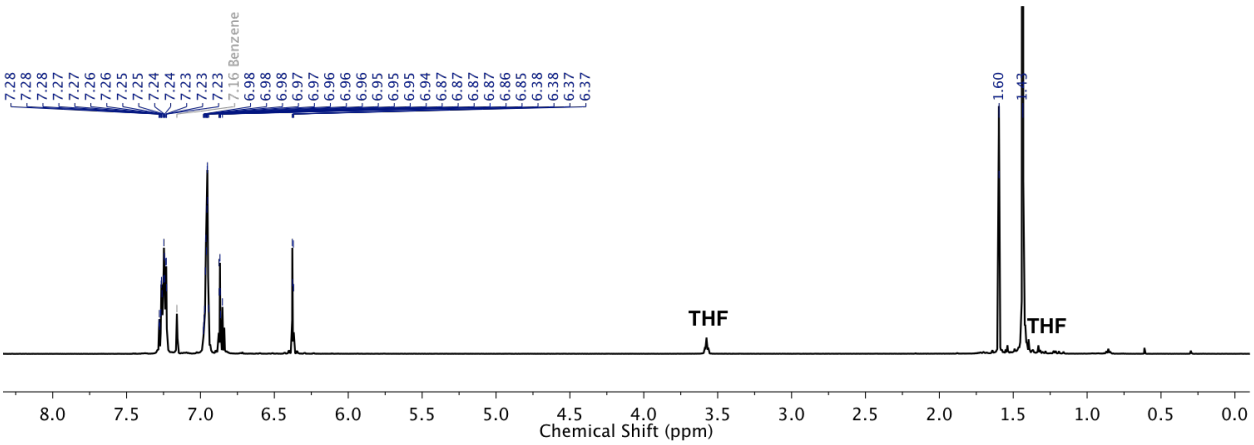


Figure S–32. ^{1}H NMR spectrum of ($^{t\text{Bu}}$dmx)$Cu_2(PPh_3)_2$ (**13**), (600 MHz, C_6D_6).

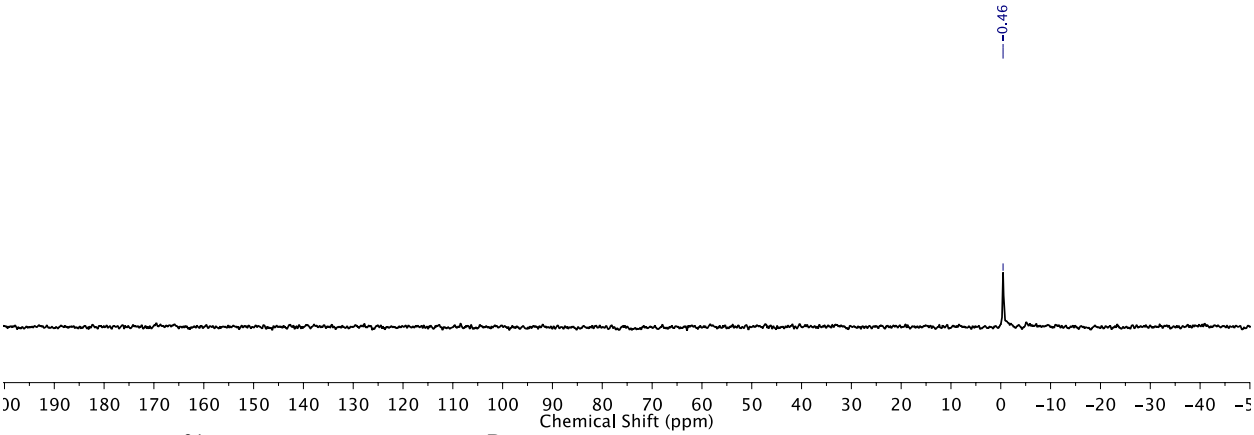


Figure S–33. ^{31}P NMR spectrum of ($^{t\text{Bu}}$dmx)$Cu_2(PPh_3)_2$ (**13**), (160 MHz, C_6D_6).

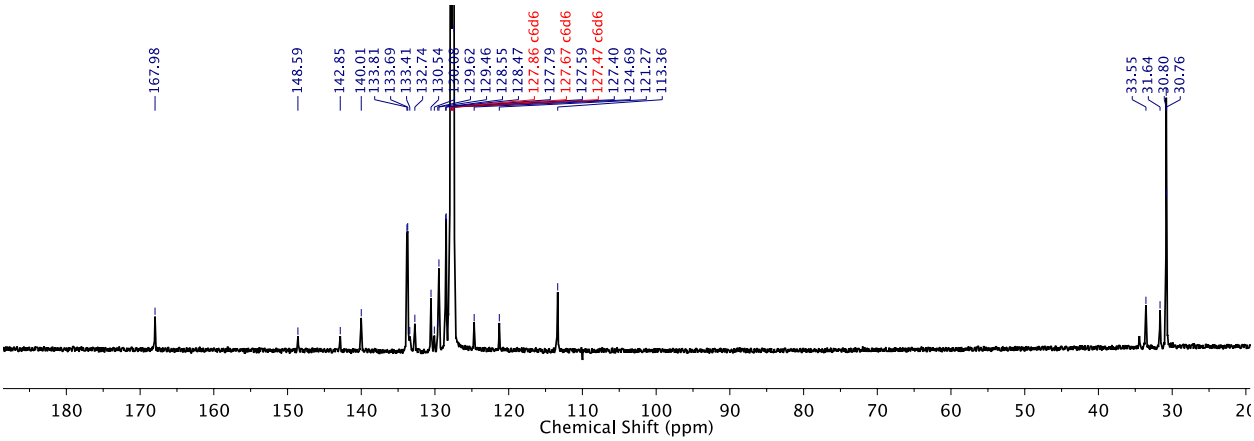
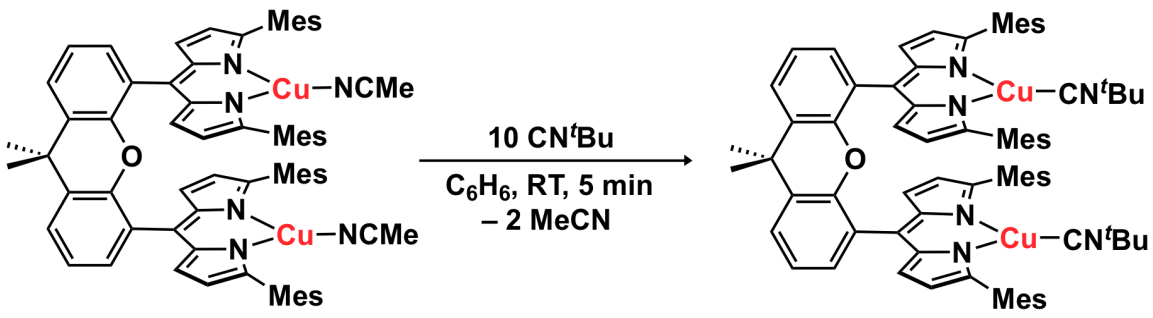


Figure S–34. ^{13}C NMR spectrum of ($^{t\text{Bu}}$dmx)$Cu_2(PPh_3)_2$ (**13**), (125 MHz, C_6D_6).



(**1**) (**14**)

(^{Mes}dmx)Cu$_2$(CN^{t}Bu)$_2$ (**14**). In the drybox, to a thawing solution of **1** (0.03 g, 0.025 mmol, 1.0 equiv) in benzene (2 mL) was added excess *tert*-butyl isocyanide (CN^{t}Bu; 0.02 g, 0.250 mmol, 10 equiv), during which a rapid color change from red-pink to orange was noted. The reaction was stirred for 20 minutes, followed by removal of solvent *in vacuo*. The residue was dissolved in benzene, filtered through a pad of Celite, and lyophilized to afford (^{Mes}dmx)Cu$_2$(CN^{t}Bu)$_2$ (**14**) as a bright orange powder (0.03 g, quant.). Single crystals of **14** suitable for X-ray diffraction were obtained by allowing a concentrated tetrahydrofuran/diethyl ether solution of **14** to stand overnight at –35 ºC. ^{1}H NMR (600 MHz, C_6D_6): δ 7.33 (dd, *J* = 7.5, 1.3 Hz, 2*H*, dipyrrin C–*H*), 7.26 (dd, *J* = 7.8, 1.4 Hz, 2*H,* dipyrrin C–*H*), 6.86 (m, 6*H,* xanthene C–*H*), 6.77 (d, *J* = 5.2 Hz, 8 *H*, mesityl aryl C–*H*), 6.30 (dd, *J* = 4.1, 0.9 Hz, 4*H*, dipyrrin C–*H*), 2.33 (s, 24*H*, mesityl ortho-methyl C–*H*), 2.30 (s, 12*H*, mesityl ortho-methyl C–*H*), 1.60 (s, 6*H*, xanthene methyl C–*H*), 0.85 (s, 18*H*, tert-butyl C–*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 159.06, 149.28, 143.12, 140.67, 138.11, 137.37, 136.37, 134.96, 132.56, 131.12, 130.33, 128.94, 124.58, 121.28, 117.75, 54.10, 34.46, 31.57, 31.19, 29.29, 22.05, 21.39, 20.93. Calculated for $C_{79}H_{82}Cu_2N_6O$•0.50CH_3CN: C 75.12 H 6.58 N 7.12; Found: C 75.51 H 6.66 N 7.25 (the molecule of acetonitrile is present from bulk recrystallization from acetonitrile/diethyl ether vapor diffusion).

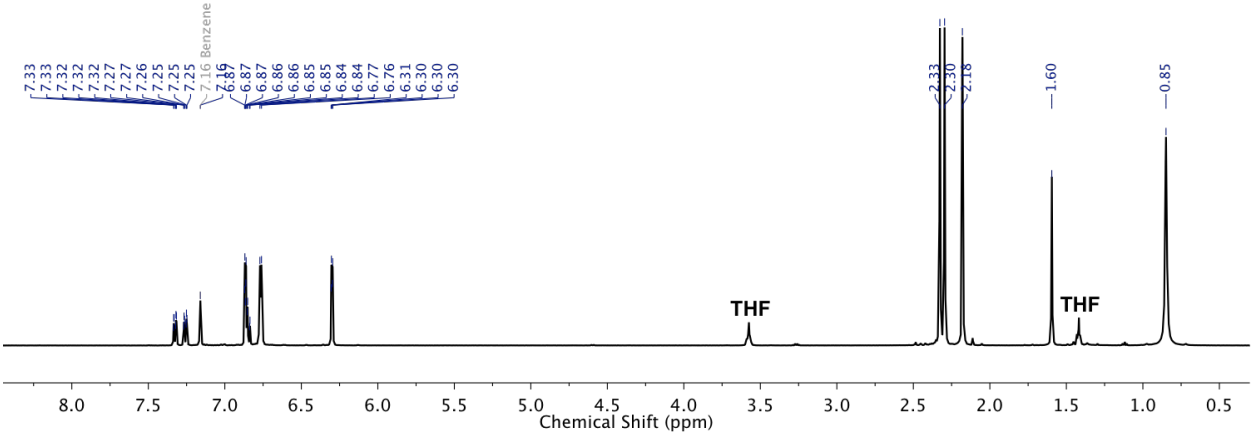


Figure S–35. ^{1}H NMR spectrum of (^{Mes}dmx)Cu$_2$(CN^{t}Bu)$_2$ (**14**), (600 MHz, C_6D_6).

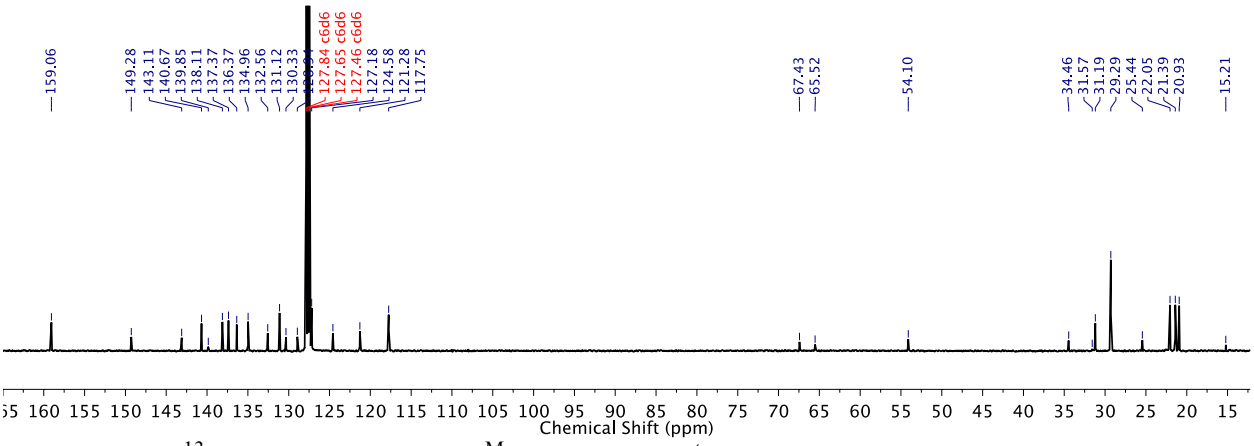
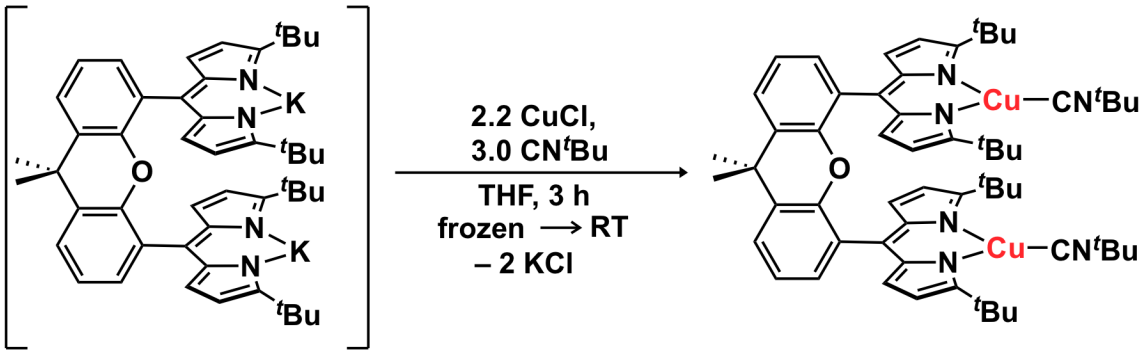


Figure S–36. ^{13}C NMR spectrum of (^{Mes}dmx)Cu$_2$(CN^{t}Bu)$_2$ (**14**), (125 MHz, C_6D_6).



(**4**) (**15**)

($^{t\text{Bu}}$dmx)Cu$_2$(CN^{t}Bu)$_2$ (15). In the drybox, to a thawing suspension of **9** (0.100 g, 0.126 mmol, 1.0 equiv.) in tetrahydrofuran (2 mL) was added *tert*-butyl isocyanide (CN^{t}Bu; 0.0310 g, 0.378 mmol, 3.0 equiv.) followed by rapid addition of cuprous chloride (0.0270 g, 0.277 mmol, 2.2 equiv.). Over 1 h, homogenization and a color change to bright orange were noted. The solution was filtered through a pad of Celite and dried *in vacuo*. The residual solids were dissolved in benzene (2 mL) and lyophilized. The resulting powder was suspended in hexanes and filtered through a pad of Celite, followed by rinsing with hexanes (*ca.* 1 mL) and acetonitrile (*ca*. 3 mL). The residual powder was eluted with benzene and lyophilized to afford ($^{t\text{Bu}}$dmx)Cu$_2$(CN^{t}Bu)$_2$ (**15**) as a bright orange solid (0.121 g, 87 %). Single crystals suitable for X-ray diffraction were obtained by allowing a concentrated solution tetrahydrofuran/hexanes solution of **15** to stand overnight at –35 ºC. ^{1}H NMR (600 MHz, C_6D_6): δ 7.19 (ddd, *J* = 13.0, 7.5, 1.6 Hz, dipyrrin C–*H*), 6.77 (t, *J* = 7.5 Hz, xanthene C–*H*), 6.66 (d, *J* = 4.1 Hz, 4*H,* xanthene C–*H*), 6.36 (dd, *J* = 4.1, 0.7 Hz, 4*H,* dipyrrin C–*H*), 1.71 (s, 36*H*, dipyrrin *tert*-butyl C–*H*), 1.56 (s, 6*H*, xanthene methyl C–*H*), 0.95 (s, 18*H*, isocyanide *tert*-butyl C–*H*). ^{13}C NMR (150 MHz, C_6D_6): δ 171.62, 151.54, 144.44, 143.19, 134.92, 134.03, 132.58, 132.14, 127.36, 123.70, 115.99, 36.77, 34.43, 32.00. Calculated for $C_{59}H_{74}Cu_2N_6O$: C 70.14 H 7.38 N 8.32; Found: C 70.18 H 7.50 N 8.14.

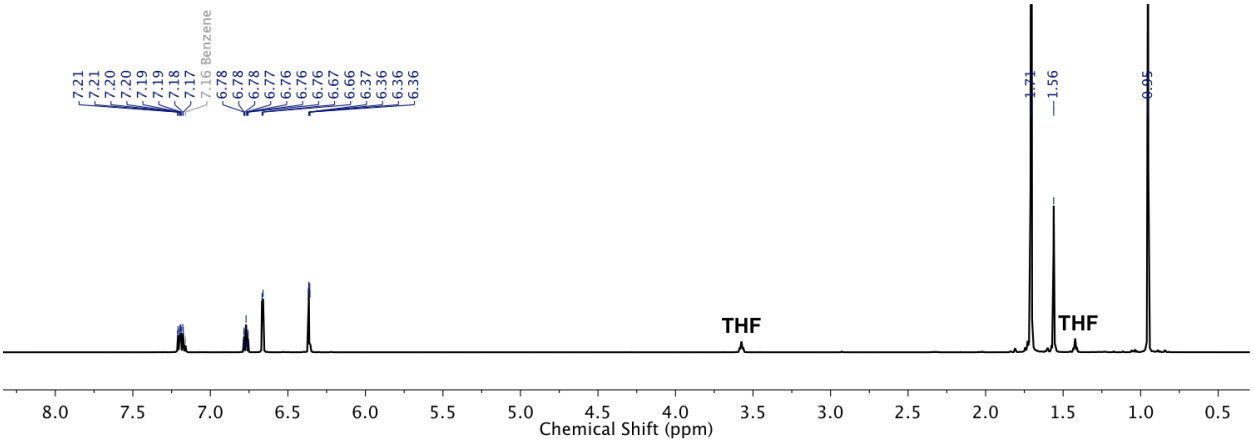


Figure S–37. ^{1}H NMR spectrum of ($^{t\text{Bu}}$dmx)Cu$_2$(CN^{t}Bu)$_2$ (**15**), (600 MHz, C_6D_6).

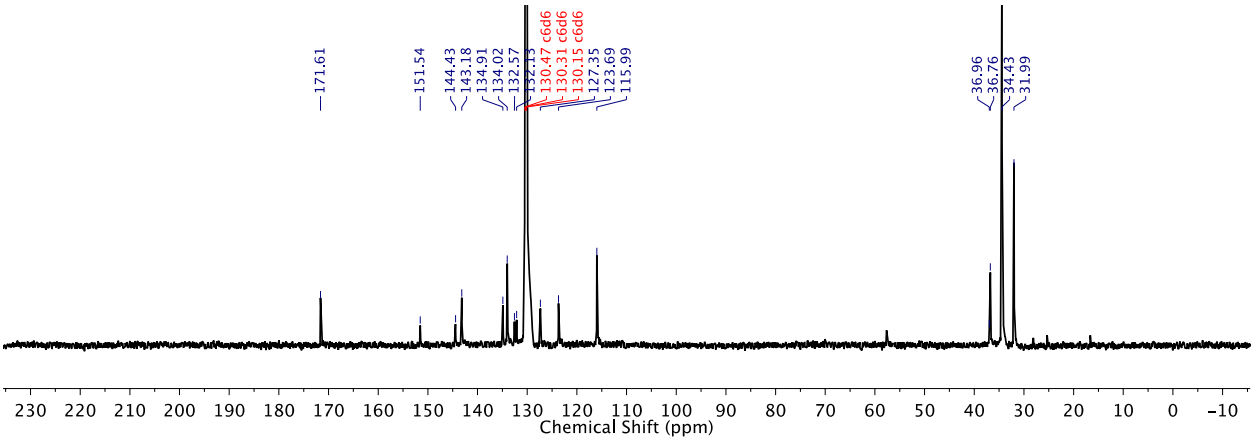
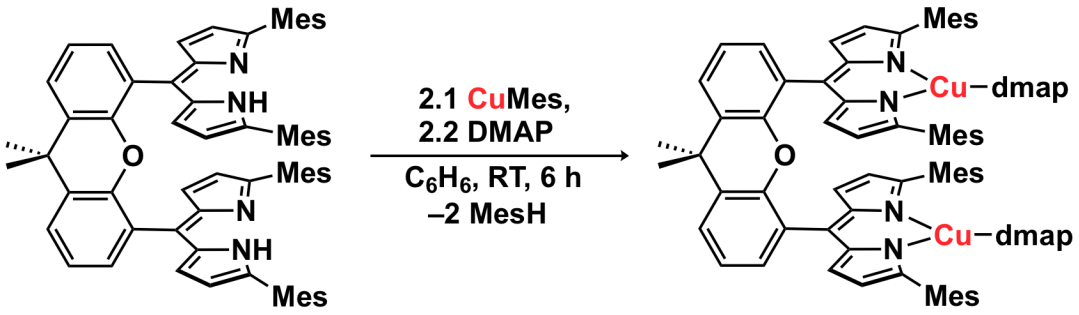


Figure S–38. ^{13}C NMR spectrum of ($^{t\text{Bu}}$dmx)Cu$_2$(CN^{t}Bu)$_2$ (**15**), (125 MHz, C_6D_6).



(**16**)

(^{Mes}dmx)Cu$_2$(dmap)$_2$ (16). In the drybox, mesitylcopper[10] (CuMes; 0.029 g, 0.153 mmol, 2.1 equiv) and 4-dimethylaminopyridine (DMAP; 0.020 g, 0.160 mmol, 2.2 equiv.) were combined in benzene to produce an off-yellow suspension. To this mixture was added (^{Mes}dmx)H$_2$ (0.070 mg, 0.073 mmol, 1.0 equiv.) as a solid. Over 6 h, homogenization and color change from red-orange to maroon was noted. The reaction was filtered through a pad of Celite and lyophilized. The resulting powder was suspended in hexanes and filtered over a pad of Celite, following by rinsing with hexanes (*ca*. 5 mL). The residual powder was eluted with benzene and lyophilized to afford (^{Mes}dmx)Cu$_2$(dmap)$_2$ (**16**) as a deep red solid (0.090 g; 85 %). Single crystals suitable for X-ray diffraction were obtained by allowing a concentrated diethyl ether/hexanes solution of **6** to stand overnight at –35 ºC. ^{1}H NMR (600 MHz, C_6D_6): δ 7.49 (dd, *J* = 7.4, 1.7 Hz, 2*H*, dipyrrin C–*H*), 7.26 (dd, *J* = 7.8, 1.7 Hz, 2*H*, dipyrrin C–H), 7.01 (dd, *J* = 4.0, 0.7 Hz, 4*H*, xanthene C–*H*), 6.93 (t, *J* = 7.48 Hz, 2*H*, xanthene C–*H*), 6.62 – 6.66 (m, 12*H*, overlapping mesityl aryl C–*H* and pyridine C–*H*), 6.35 (dd, *J* = 4.0, 0.7 Hz, 4*H,* dipyrrin C–*H*), 5.54 (d, *J* = 6.1 Hz, 4*H*, pyridine C–H), 2.41 (s, 12*H*, dimethylamino C–*H*) 2.26 (s, 12*H*, mesityl para-methyl C–*H*), 2.04 – 2.06 (s, 24*H*, mesityl ortho-methyl C–*H*), 1.63 (xanthene methyl C–*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 157.74, 152.35, 150.44, 149.55, 143.31, 141.60, 138.39, 137.57, 136.96, 135.11, 132.86, 131.28, 130.43, 130.18, 124.23, 121.17, 117.50, 105.04, 37.66, 34.57, 31.57, 31.18, 22.03, 21.07, 20.79. Calculated for $C_{83}H_{84}Cu_2N_8O$: C 74.58 H 6.33 N 8.38; Found: C 74.46 H 6.36 N 8.75.

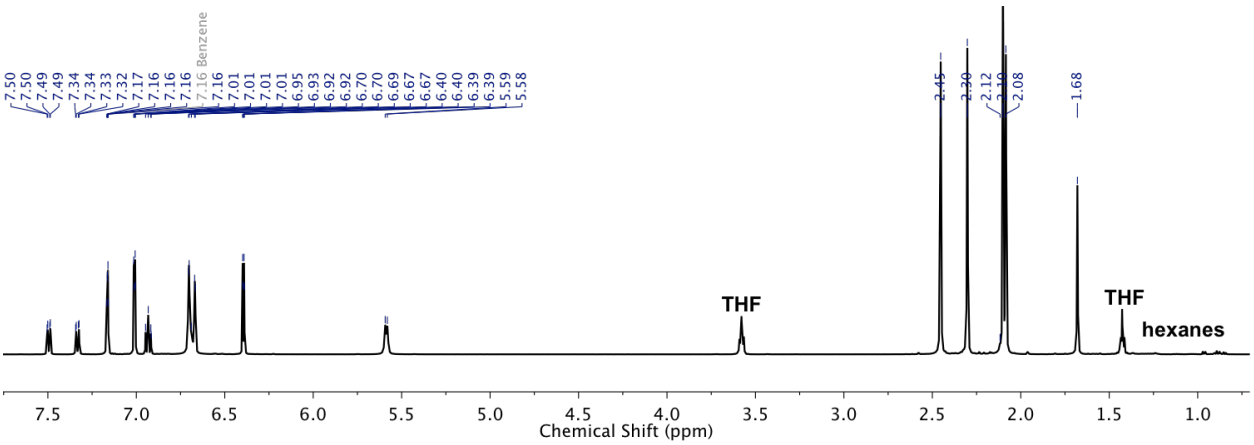


Figure S–39. ^{1}H NMR spectrum of (^{Mes}dmx)Cu_2(dmap)$_2$ (**16**), (600 MHz, C_6D_6).

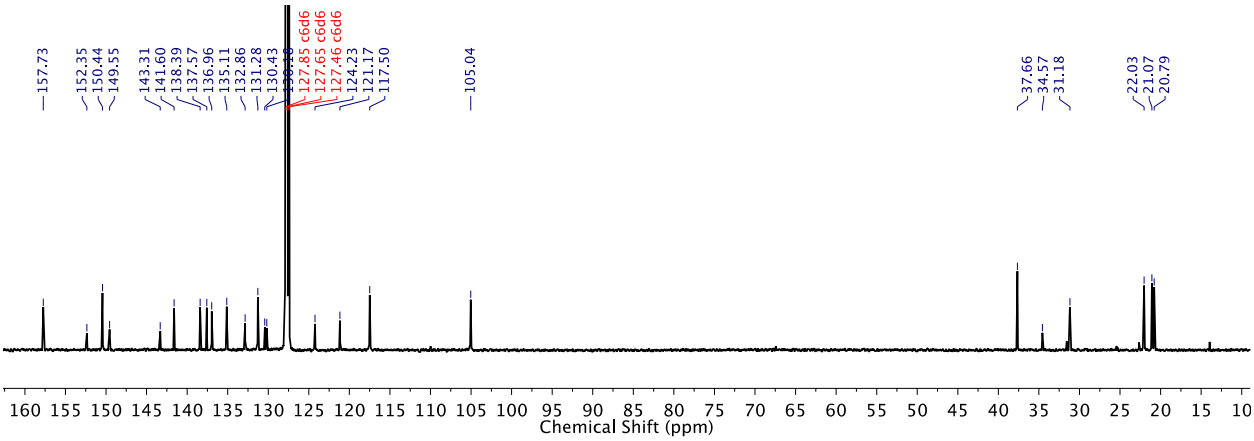


Figure S–40. ^{13}C NMR spectrum of (^{Mes}dmx)Cu_2(dmap)$_2$ (**16**), (125 MHz, C_6D_6).

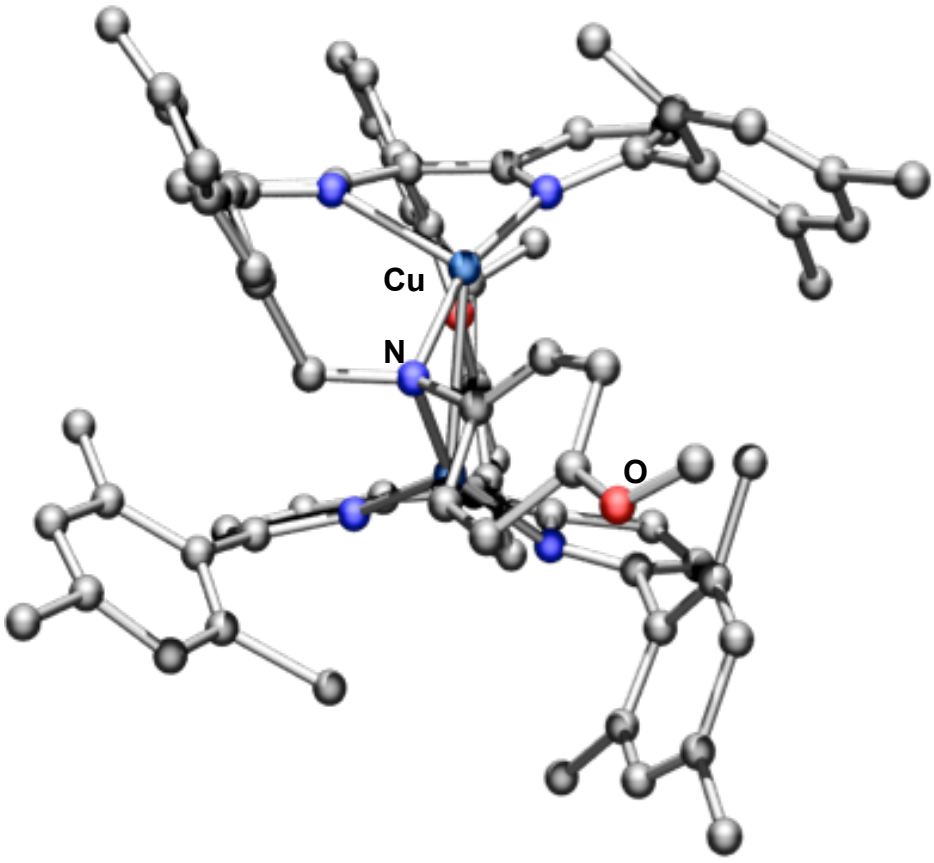


Figure S–41. Solid-state molecular structure of benzylic C–H aminated complex (**17**) from thermal decomposition of **7**, crystallized from vapor diffusion of diethyl ether into a concentrated solution of **7** in tetrahydrofuran at room temperature over one week. Hydrogen atoms, K(C_{222}) counterion, and solvent molecules in the unit cell are omitted for clarity.

Note I: The existence of multi-component non-Merohedral twinning prevents full anisotropic refinement of all atoms, which was prevalent over multiple data set collections. Nonetheless, this structure establishes intramolecular C–H amination of a proximal benzylic C–H bond to have occurred. *Unit Cell Parameters: Triclinic* ($P\bar{1}$), a = 19.197(3) Å, b = 19.206(3) Å, c = 26.465(5) Å, α = 100.707(6) º, β = 108.207(4) º, γ = 95.461(4) º; V = 8984(3) Å^3.

Note II: formation of **17** proceeds with loss of a hydrogen atom. Due to the inability of the dipyrrin ligand platform to support zero-valent copper, we propose C–N bond formation proceeds by initial H-atom abstraction from a benzylic methyl group, followed by loss of a hydrogen atom and radical recombination.

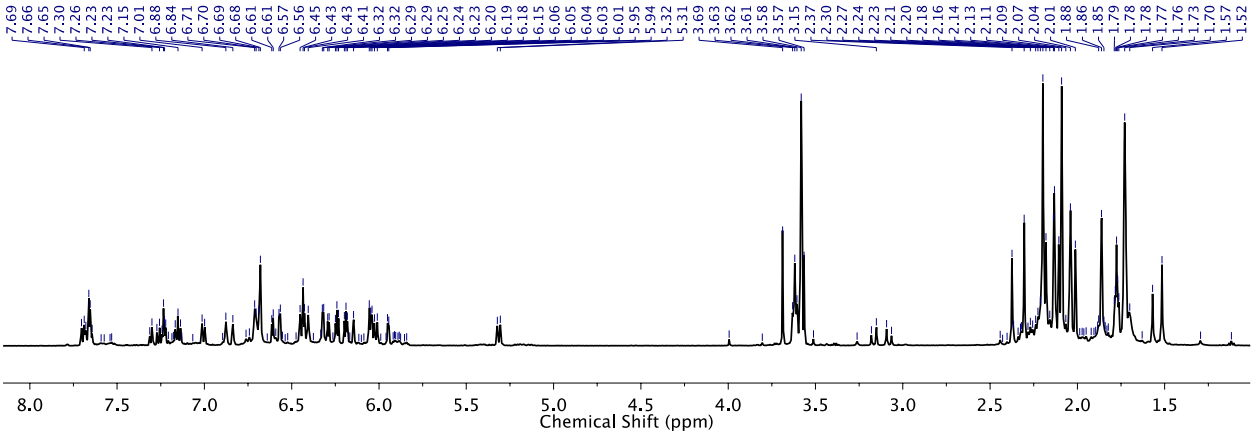
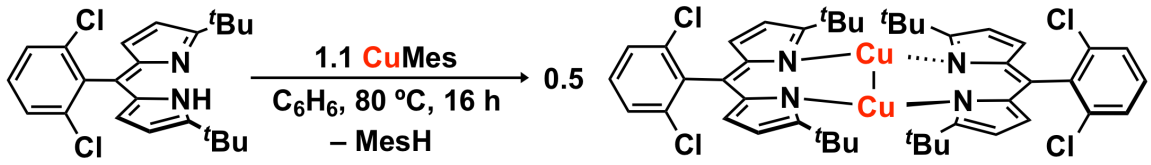


Figure S–42. ^{1}H NMR spectrum of intramolecular benzylic C–H amination decomposition from **7** to furnish **17** alongside minor components of unidentified species (500 MHz, d_8–THF).



(**18**)

($^{t\mathrm{Bu}}$L)$_2$Cu$_2$ (18). In the drybox, to a Schlenk tube charged with a solution of ($^{t\mathrm{Bu}}$L)H (0.256 g, 0.632 mmol, 1.0 equiv.) in benzene (2.0 mL) was added mesitylcopper[10] (0.127 g, 0.696 mmol, 1.1 equiv.). The reaction vessel was sealed, exported from the drybox, and heated to 100 ºC for 16 h, accompanied by a gradual color change from red-orange to red-pink. The Schlenk tube was subsequently removed from heat and allowed to stand at room temperature undisturbed for 8 h, during which precipitation of a crystalline solid was noted. The Schlenk tube was imported into the drybox, and the resulting solids were collected and rinsed with thawing benzene (*ca.* 5 mL) and cold hexanes (*ca*. 2 mL) to afford ($^{t\mathrm{Bu}}$L)$_2$Cu$_2$ (**18**) as dark red crystals (0.225 g, 77 %). Single crystals suitable for X-ray diffraction were obtained by allowing a concentrated 2:1 hexane/benzene solution of **18** to stand overnight at –35 ºC. ^{1}H NMR (600 MHz, C_6D_6): 6.95 (d, J = 8.1 Hz, 4*H*, dipyrrin C–*H*), 6.53 (t, J = 8.1 Hz, 2*H*, aryl C–*H*), 6.48 (d, J = 4.4 Hz, 4*H*, aryl C–*H*), 6.34 (d, J = 4.4 Hz, 4*H*, dipyrrin C–*H*), 1.35 (s, 36*H*, *tert*-butyl C–*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 175.28, 145.31, 144.53, 142.54, 139.17, 135.56, 131.64, 129.90, 36.49, 33.38. Calculated for $C_{46}H_{50}Cl_4Cu_2N_4$: C 59.55, H 5.43, N 6.04; Found: C 59.63, H 5.29, N 6.18.

Note: Fragmentation of **18** is reversible, evident by formation of **10** upon treatment of **18** with acetonitrile and by formation of **18** upon heating **10** in the absence of excess acetonitrile.

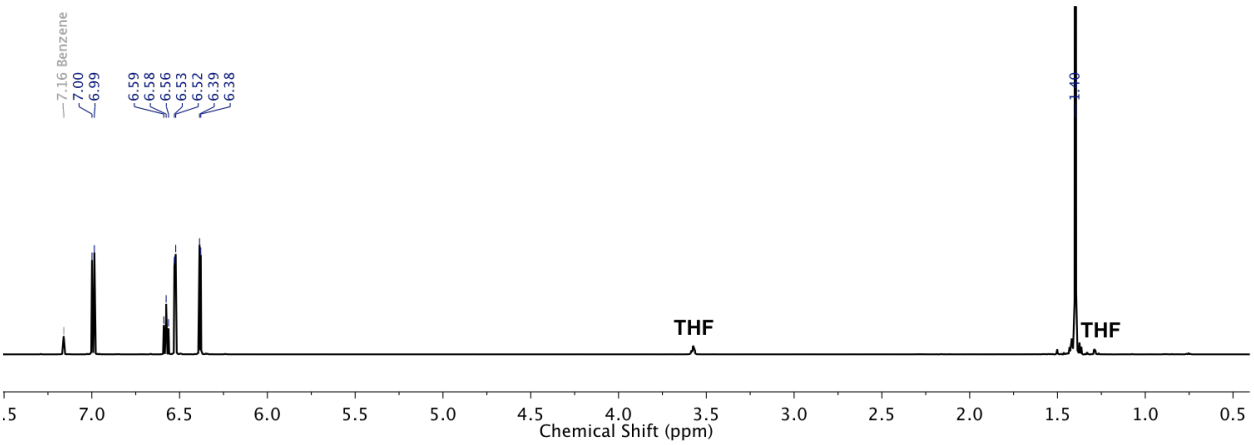


Figure S–43. ^{1}H NMR spectrum of ($^{t\text{Bu}}$L)$_2$Cu$_2$ (**18**), (500 MHz, C_6D_6).

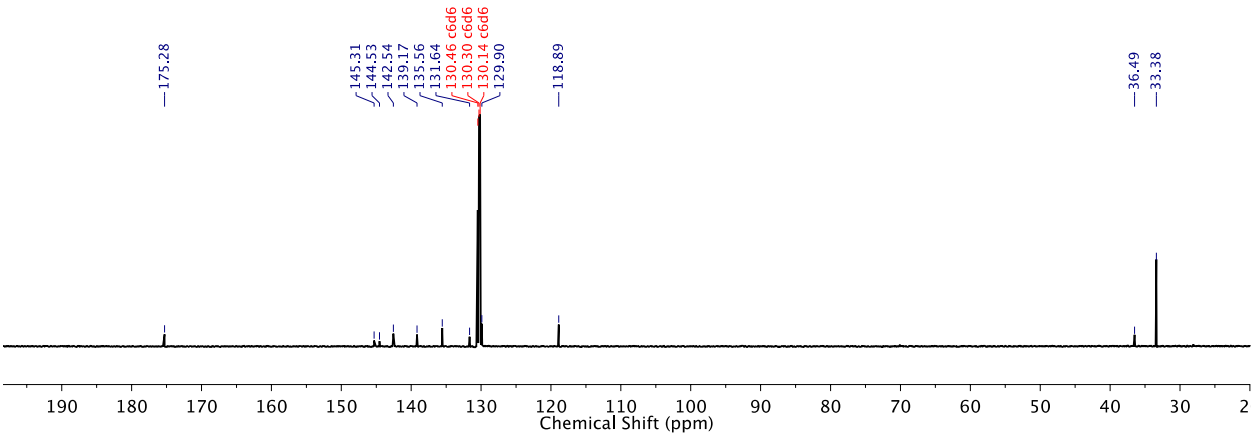
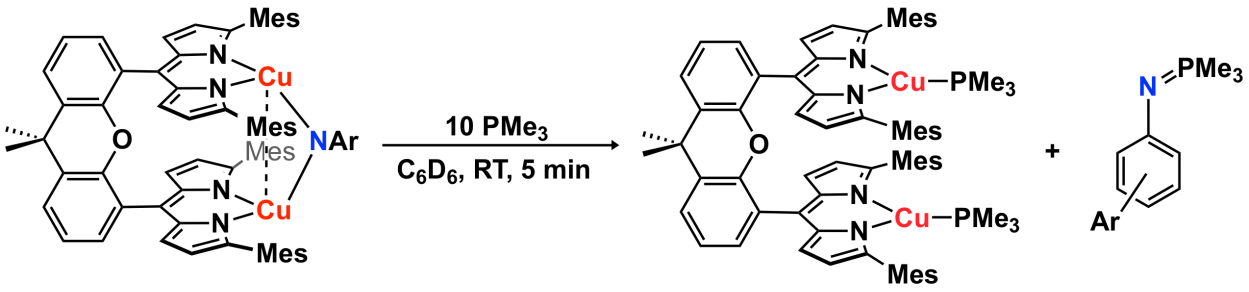


Figure S–44. ^{13}C NMR spectrum of ($^{t\text{Bu}}$L)$_2$Cu$_2$ (**18**), (125 MHz, C_6D_6).

Stoichiometric Reactions.



(**2**): Ar = (4-MeO)C_6H_4
(**3**): Ar = 3,5-$(F_3C)_2C_6H_3$

(**12**)

Trimethylphosphine (PMe_3) Reactivity from 2 and 3. In the drybox, to a benzene solution of either **2** (9.9 mg, 0.008 mmol, 1.0 equiv.) or **3** (9.2 mg, 0.008 mmol, 1.0 equiv.) in a J. Young tube was added neat trimethylphosphine (5.8 mg, 7.8 μL, 0.080 mmol, 10 equiv.). A stark color change from purple to pink was observed upon inversion of the J–Young tube. After 5 minutes, complete consumption of the starting material, quantitative conversion to (^{Mes}dmx)$Cu_2(PMe_3)_2$ (**12**) and formation of the respective phosphinimide (**2**: $Me_3P(N(C_6H_4OMe))$, **3**: $Me_3P(N(3,5\text{-}(CF_3)_2C_6H_3))$) were confirmed by ^{1}H, ^{31}P, and ^{19}F NMR comparison to authentic samples. Featureless EPR spectra confirm the absence of half-integer-spin paramagnetic impurities.

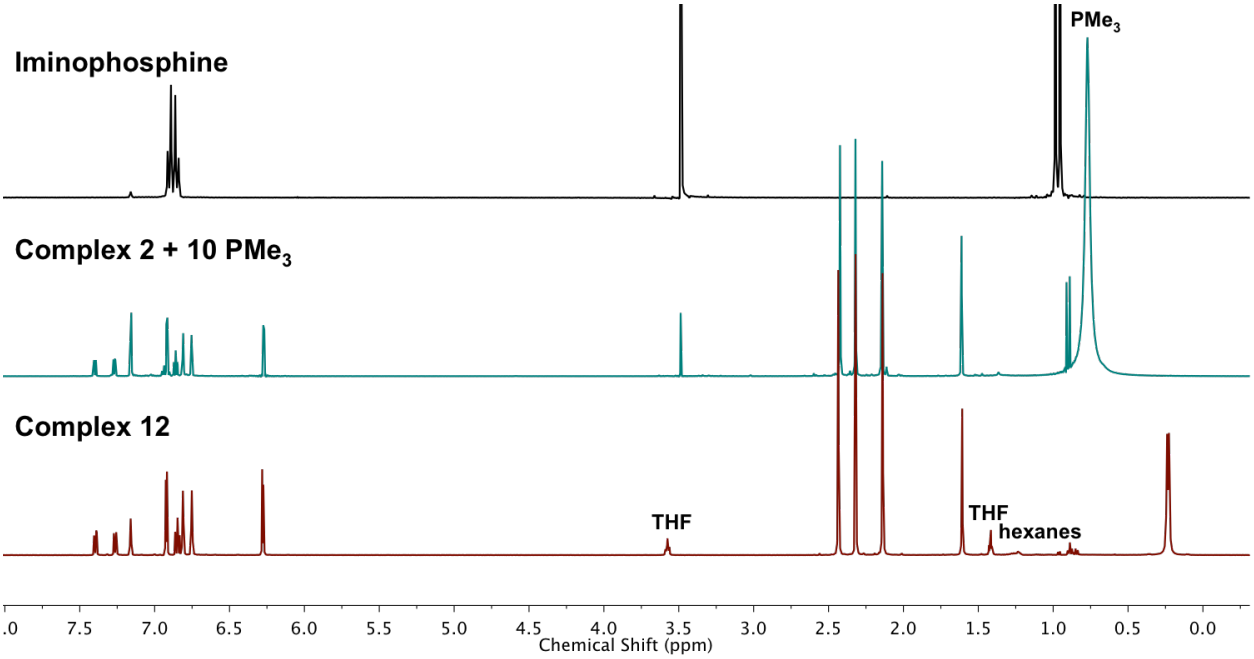
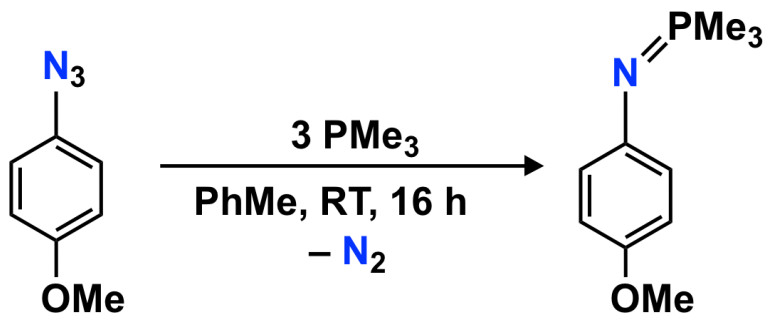


Figure S–45. Representative ^{1}H NMR spectra overlay of authentically prepared (^{Mes}dmx)Cu$_2$(PMe$_3$)$_2$ (**4**, *red*, bottom spectrum), crude reaction mixture of (^{Mes}dmx)Cu$_2$(N(C$_6$H$_4$OMe)) (**2**, *cyan*, middle spectrum) with excess trimethylphosphine, and authentic Me$_3$P(N(C$_6$H$_4$OMe)) (*black*, top spectrum), (600 MHz, C$_6$D$_6$).



N-(4-methoxyphenyl)-1,1,1-trimethyl-λ^5-phosphanimine ($Me_3P(N(4\text{-}OMe\text{-}C_6H_4))$), Adapted from a literature procedure,[17] in the drybox, to a solution of 4-methoxyphenyl azide (0.061 g, 0.41 mmol, 1.0 equiv.) in toluene (2 mL) was added dropwise excess trimethylphosphine (0.094 g, 1.2 mmol, 3.0 equiv.), accompanied by rapid effervescence. The reaction was stirred overnight at ambient temperature, followed by filtration through Celite and removal of solvent *in vacuo* to afford the title compound as a yellow solid (79 mg, 98 %). ^{1}H NMR (400 MHz, C_6D_6): δ 6.84 (m, 4*H*, aryl C–*H*), 3.44 (s, 3*H*, methoxy C–H), 0.93 (dd, 9*H*, *J* = 12.4, 1.4 Hz, trimethylphosphine C–*H*). ^{31}P NMR (160 MHz, C_6D_6): δ 1.60 (s, *P*Me_3). ^{13}C NMR (125 MHz, C_6D_6): δ 151.88, 146.74, 146.71, 123.10, 123.00, 122.95, 114.88, 114.80, 114.76, 55.21, 55.12, 15.97, 15.91, 15.86, 15.43, 15.33. HRMS (ESI$^+$) *m/z* Calc. 198.1042 [$C_{10}H_{16}NOP + H^+$], Found 198.1038 $[M + H]^+$.

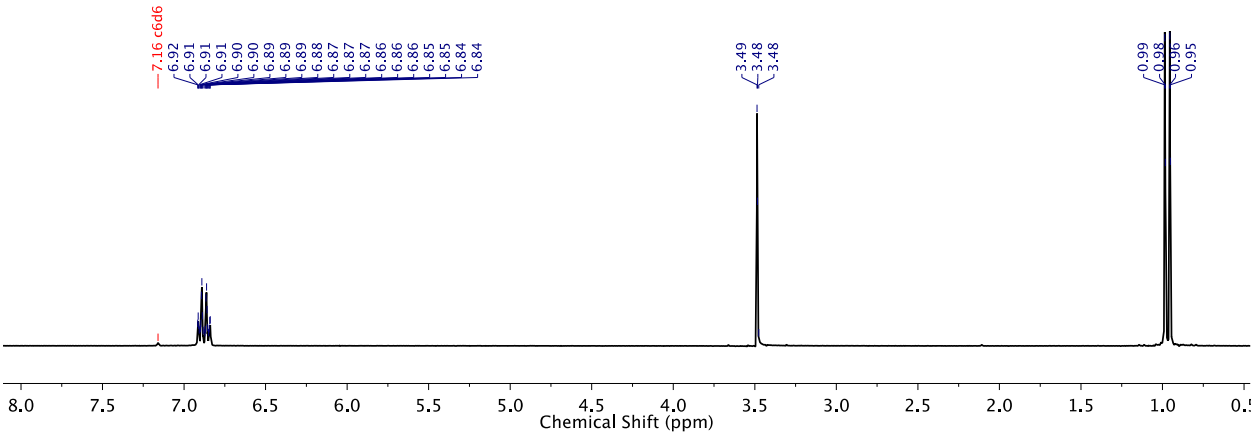


Figure S–46. ^{1}H NMR spectrum of $Me_3P(N(C_6H_4OMe))$, (400 MHz, C_6D_6).

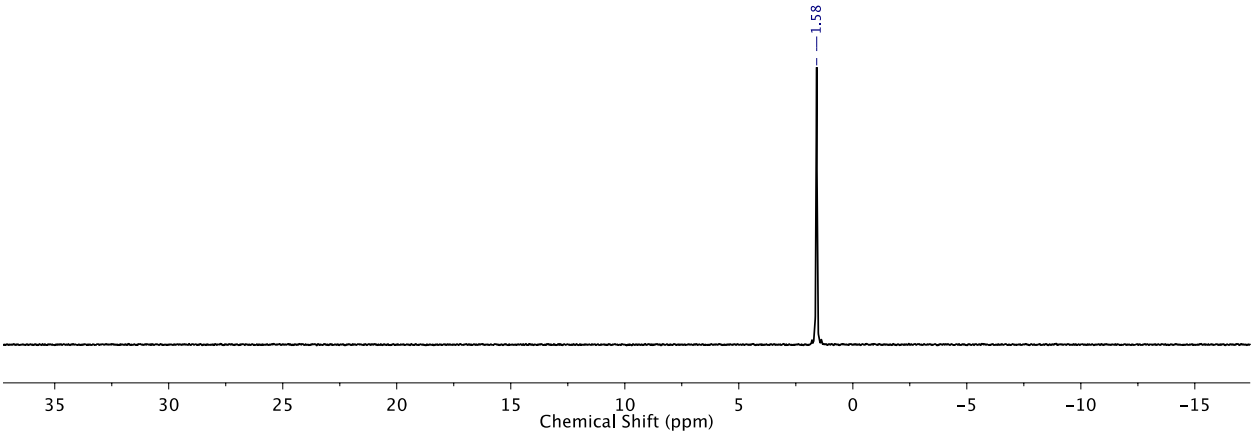


Figure S–47. ^{31}P NMR spectrum of $Me_3P(N(C_6H_4OMe))$, (160 MHz, C_6D_6).

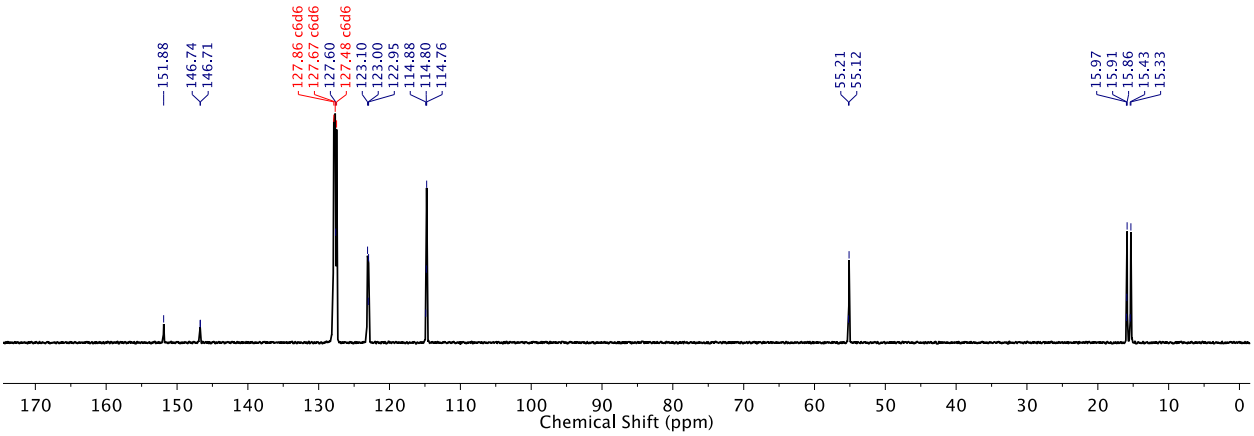
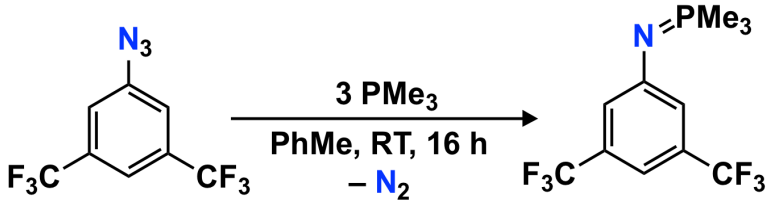


Figure S–48. ^{13}C NMR spectrum of $Me_3P(N(C_6H_4OMe))$, (125 MHz, C_6D_6).



***N*-(3,5-bis(trifluoromethyl)phenyl)-1,1,1-trimethyl-λ^5-phosphanimine (Me$_3$P(N(3,5-(F$_3$C)$_2$C$_6$H$_3$))).** In the drybox, to a thawing solution of 3,5-bis(trifluoromethyl)phenyl azide (0.080 g, 0.31 mmol, 1.0 equiv) in toluene (3 mL) was added dropwise trimethylphosphine (0.072 g, 0.95 mmol, 3.0 equiv), accompanied by effervescence. The reaction was stirred overnight at ambient temperature, followed by filtration through Celite and removal of solvent *in vacuo* to afford the title compound as a white solid (94 mg, 99 %). ^{1}H NMR (400 MHz, C_6D_6): δ 7.28 (s, 1*H*, aryl C–*H*), 7.13 (s, 2*H*, aryl C–*H*), 0.93 (dd, 9*H*, *J* = 12.4, 1.4 Hz, trimethylphosphine C–*H*). ^{31}P NMR (160 MHz, C_6D_6): δ 9.11 (s, *P*Me$_3$). ^{19}F NMR (375 MHz, C_6D_6): δ -62.6 (s, aryl C*F*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 154.69, 132.07, 131.81, 125.56, 123.40, 121.47, 121.31, 108.44, 14.80, 14.26. HRMS (ESI$^+$) *m/z* Calc. 304.0684 [$C_{11}H_{13}F_6NP + H^+$], Found 304.0695 [M + H]$^+$.

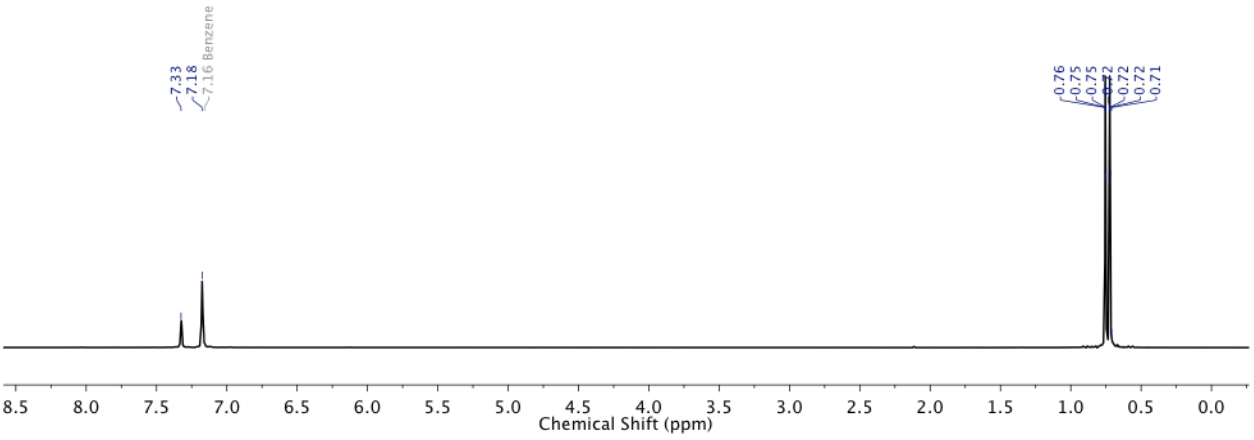


Figure S–49. ^{1}H NMR spectrum of Me$_3$P(N(3,5-(CF$_3$)$_2$C$_6$H$_3$)), (400 MHz, C_6D_6).

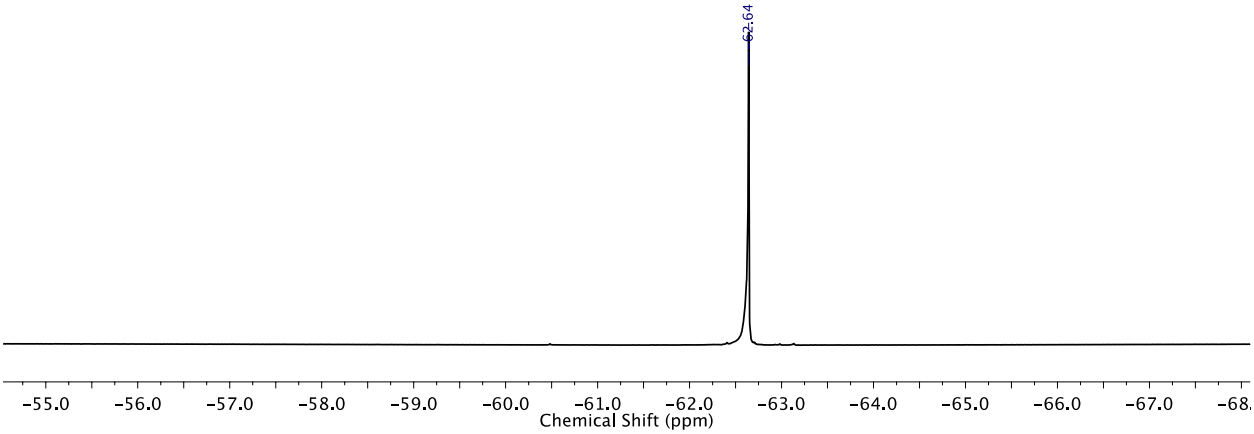


Figure S–50. ^{19}F NMR spectrum of $Me_3P(N(3,5\text{-}(CF_3)_2C_6H_3))$, (375 MHz, C_6D_6).

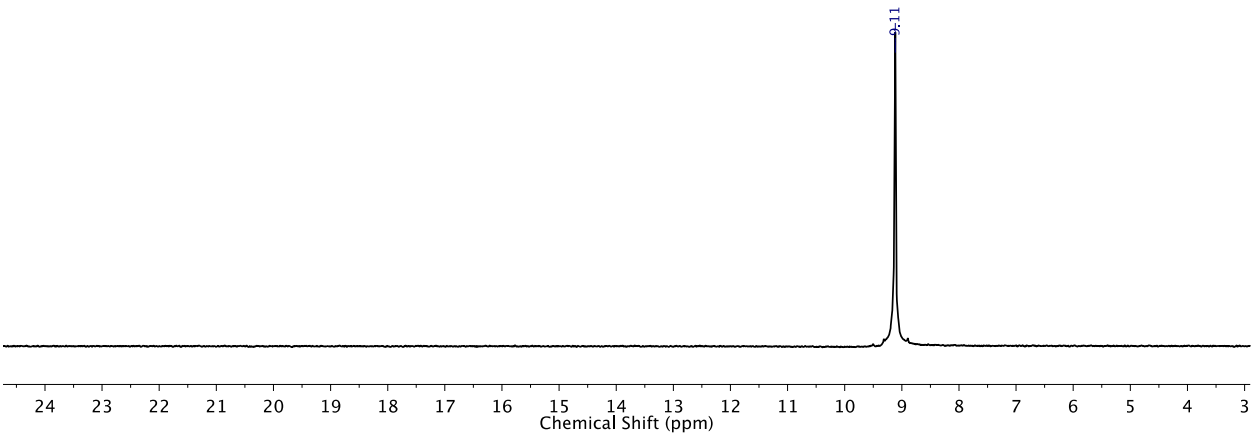


Figure S–51. ^{31}P NMR spectrum of $Me_3P(N(3,5\text{-}(CF_3)_2C_6H_3))$, (160 MHz, C_6D_6).

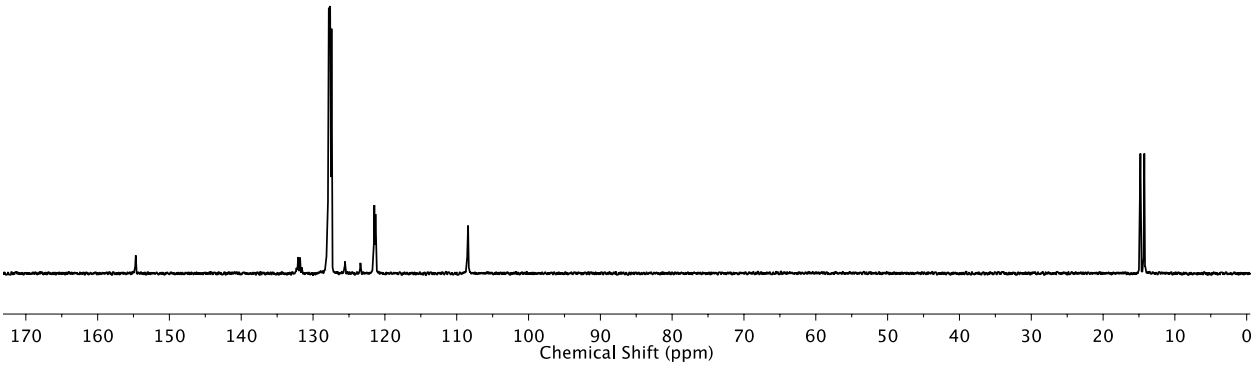
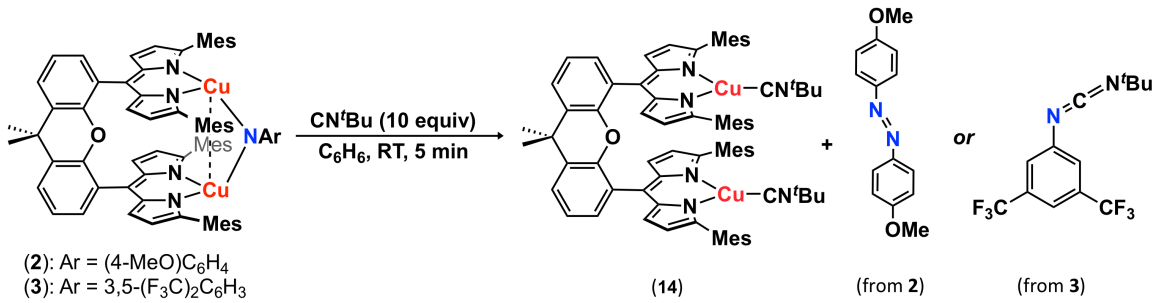


Figure S–52. ^{13}C NMR spectrum of $Me_3P(N(3,5\text{-}(CF_3)_2C_6H_3))$, (125 MHz, C_6D_6).



***Tert*-butyl Isocyanide (CN^{t}Bu) Reactivity from 2 and 3**. In the drybox, to a benzene solution of either **2** (10.0 mg, 0.008 mmol, 1.0 equiv.) or **3** (9.2 mg, 0.008 mmol, 1.0 equiv.) in a J. Young tube was added neat *tert*-butyl isocyanide (6.9 mg, 0.080 mmol, 10 equiv.). A stark color change from purple to orange was observed upon inversion of the J. Young tube. ^{1}H-NMR spectroscopy revealed complete consumption of the starting material and conversion to (^{Mes}dmx)Cu$_2$(CN^{t}Bu)$_2$ (**14**), accompanied by formation of either 1,2-bis(4-methoxyphenyl)diazene (exclusively from **2**) or *N*-(3,5-bis(trifluoromethyl)phenyl)-*N*-(*tert*-butyl)methanediimine (exclusively from **3**). Spectral data of both organic products are consistent with previously reported characterization data.[18,19] *Note*: The reactivity of **3** with excess CN^{t}Bu is accompanied by formation of an unidentified paramagnetic species, which exhibits an EPR spectrum that has not yet been satisfactorily modeled. The presence of a paramagnetic species may account for the non-quantitative yield of azoarene. The yield of carbodiimide from **3** is maximized upon dissolution of **3** in neat CN^{t}Bu, accompanied by partial ligand protonolysis from adventitious water.

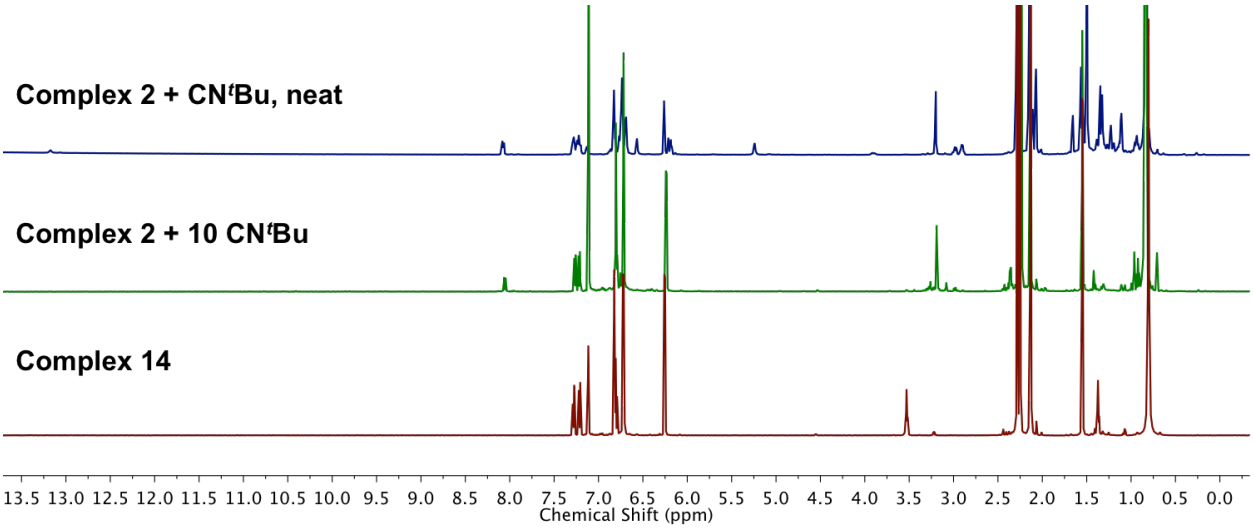
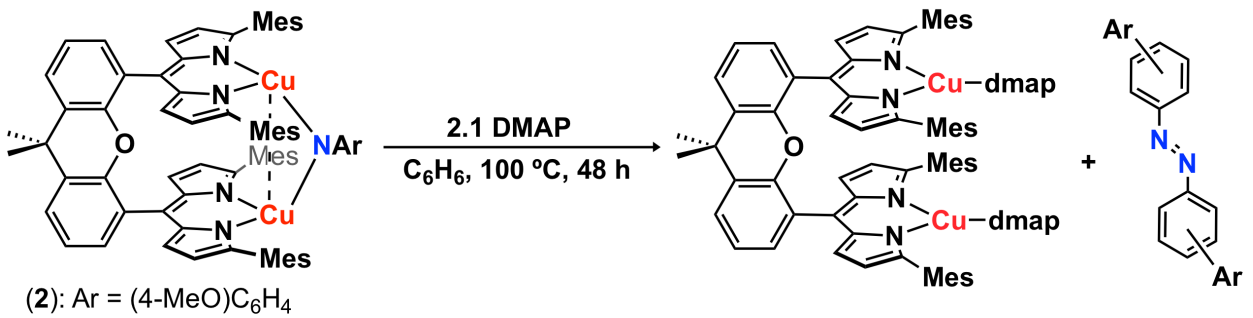


Figure S–53. ^{1}H NMR spectra overlay of authentically prepared (^{Mes}dmx)Cu$_2$(CN^{t}Bu)$_2$ (**14**, *red*, bottom spectrum), crude reaction mixture of (^{Mes}dmx)Cu$_2$(μ^2–N(4-MeOC$_6$H$_4$)) (**2**) with moderate excess of CN^{t}Bu (~10 equiv) (*green*, middle spectrum), crude reaction mixture of (^{Mes}dmx)Cu$_2$(μ^2–N(4-MeOC$_6$H$_4$)) (**2**) dissolved in neat CN^{t}Bu (*blue*, top spectrum), (500 MHz, C$_6$D$_6$). The addition proton resonances in the reaction of **2** with neat CN^{t}Bu (top spectrum) are attributed to formation of (^{Mes}dmx)H$_2$, possibly from adventitious water.



(**2**): Ar = (4-MeO)C_6H_4
(**3**): Ar = 3,5-$(F_3C)_2C_6H_3$

(**16**)

Dimethylaminopyridine (DMAP) Reactivity from 3. In the drybox, to a benzene solution of **3** (11.0 mg, 0.008 mmol, 1.0 equiv.) in a J-Young tube was added dimethylaminopyridine (DMAP; 2.1 mg, 0.017 mmol, 2.1 equiv.). The J-Young was sealed and heated to 100 ºC for two days in which unreacted starting material, (^{Mes}dmx)Cu_2(dmap)$_2$ (**16**), and 1,2-bis(3,5-bis(trifluoromethyl)phenyl)diazene (for **3**) were observed by ^{1}H NMR spectroscopy and ^{19}F NMR spectroscopy. Spectral data of the organic product is consistent with previously reported characterization data.[12] The analogous reactivity profile is observed for **2**.

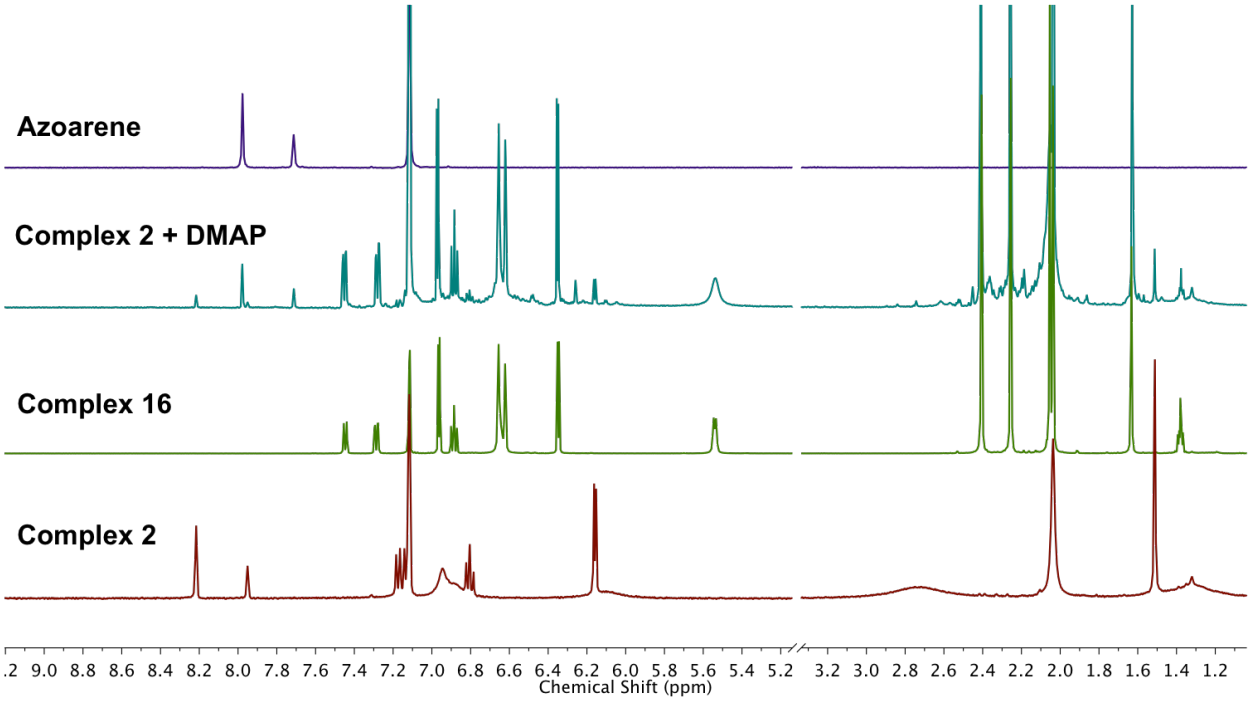
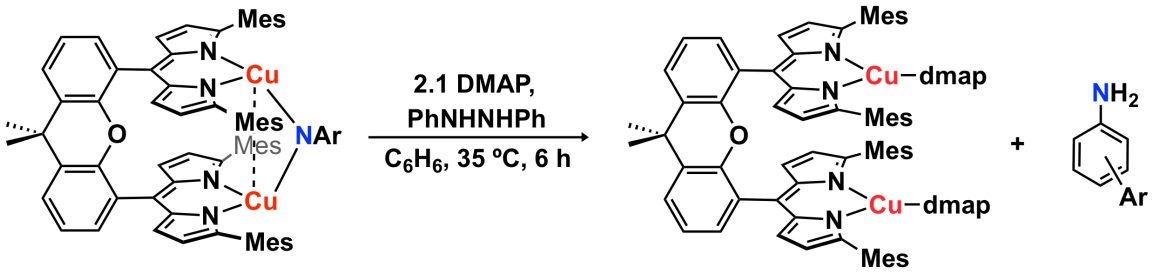


Figure S–54. Representative ^{1}H NMR spectra overlay of (^{Mes}dmx)Cu_2(μ^2–N(3,5-$(F_3C)_2C_6H_3$)) (**3**, *red*, bottom spectrum), (^{Mes}dmx)Cu_2(dmap)$_2$ (**6**, *green*, lower middle), reaction of **3** with DMAP at 100 ºC over two days (*cyan*, upper middle), and authentic azoarene product (*purple*, top).



(**2**): Ar = (4-MeO)C_6H_4
(**3**): Ar = 3,5-$(F_3C)_2C_6H_3$

(**16**)

Dimethylaminopyridine (DMAP) Reactivity from 3 in presence of weak C–H bonds. In the drybox, to a benzene solution of **3** (9.3 mg, 0.007 mmol, 1.0 equiv.) in a J-Young tube was added dimethylaminopyridine (DMAP; 1.8 mg, 0.015 mmol, 2.1 equiv.) and 1,2-diphenylhydrazine (PhNHNHPh; 1.5 mg, 0.008 mmol, 1.1 equiv.). The J-Young was sealed and heated to 35 ºC for six hours in which (^{Mes}dmx)Cu_2(dmap)$_2$ (**16**) and 3,5-bis(trifluoromethyl)aniline were observed by ^{1}H NMR spectroscopy and ^{19}F NMR spectroscopy, accompanied by full consumption of starting material. Spectral data of 3,5-bis(trifluoromethyl)aniline is consistent with authentic commercial samples. The analogous reactivity profile is observed for **2**.

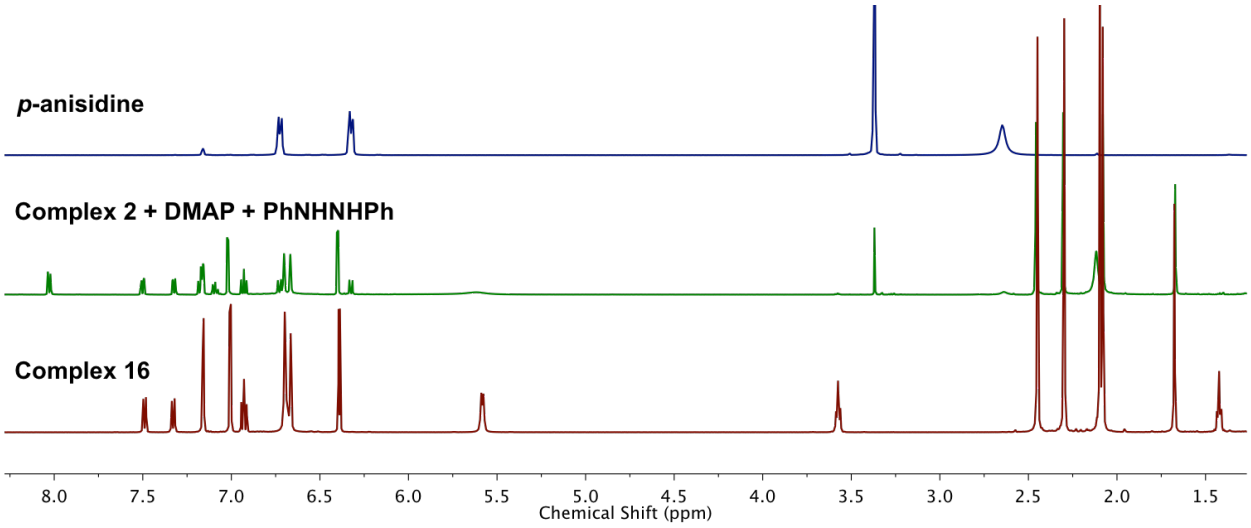
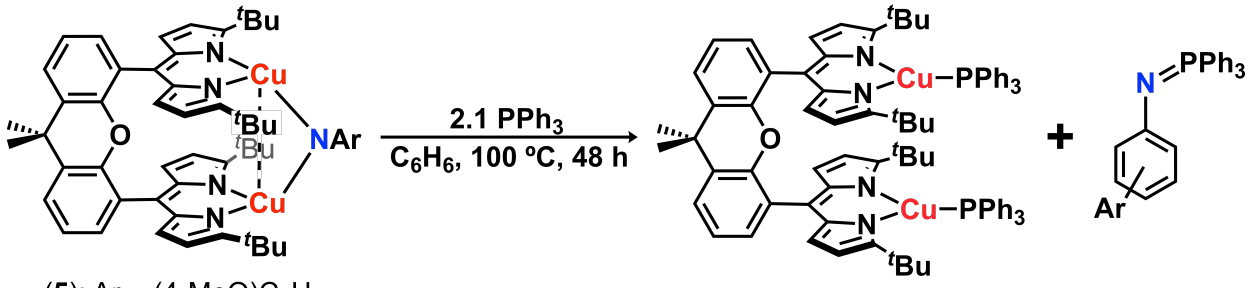


Figure S–55. Representative ^{1}H NMR spectra overlay of (^{Mes}dmx)Cu_2(dmap)$_2$ (**6**, *red*, bottom spectrum), (^{Mes}dmx)Cu_2(μ^2–N(C_6H_3OMe)) (**2**) treated with dimethylaminopyridine (DMAP), and 1,2-diphenylhydrazine (PhNHNHPh) at 60 ºC overnight (*green*, middle), and p–anisidine (blue, top).



(**5**): Ar = (4-MeO)C_6H_4
(**6**): Ar = 3,5-$(F_3C)_2C_6H_3$

(**13**)

Triphenylphosphine (PPh_3) Reactivity from 5 and 6. In the drybox, to a benzene solution of either **5** (10.0 mg, 0.008 mmol, 1.0 equiv.) or **6** (9.2 mg, 0.008 mmol, 1.0 equiv.) in a J. Young tube was added triphenylphosphine (6.9 mg, 0.080 mmol, 10 equiv.). The J. Young tube was sealed and heated to 100 ºC for two days in which the corresponding iminophosphine and parital conversion to **13** were confirmed by ^{1}H, ^{31}P, and ^{19}F NMR comparison to authentic samples. Complexes N-(4-methoxyphenyl)-1,1,1-triphenyl-λ^5-phosphanimine $Ph_3P(N(C_6H_4OMe))$ and N-(3,5-bis(trifluoromethyl)phenyl)-1,1,1-triphenyl-λ5-phosphanimine $Ph_3P(N(3,5\text{-}(CF_3)_2C_6H_3))$ were independently prepared according to literature procedures.[3,19]

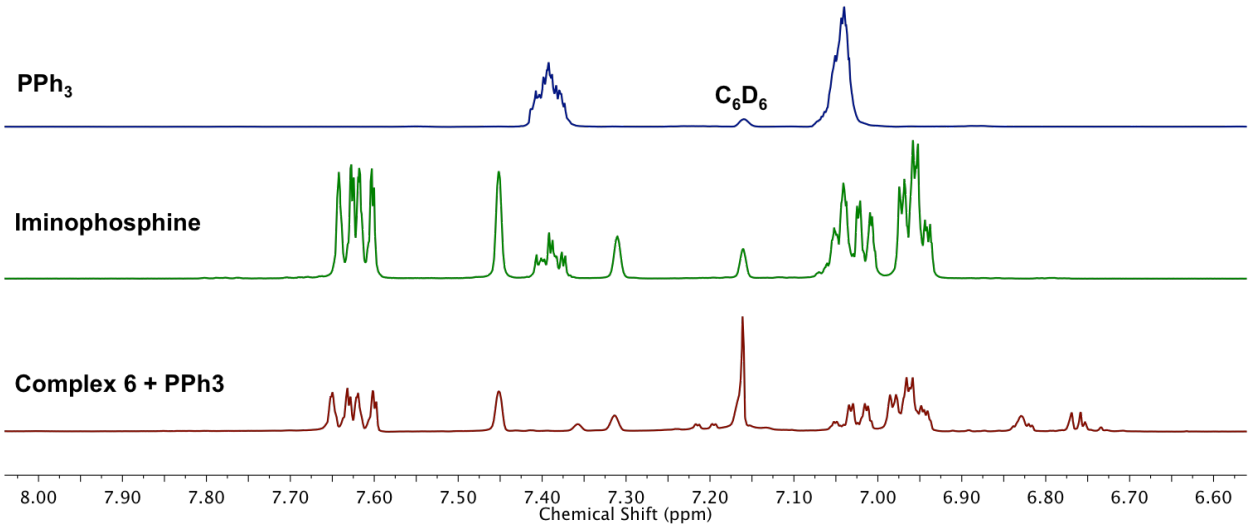
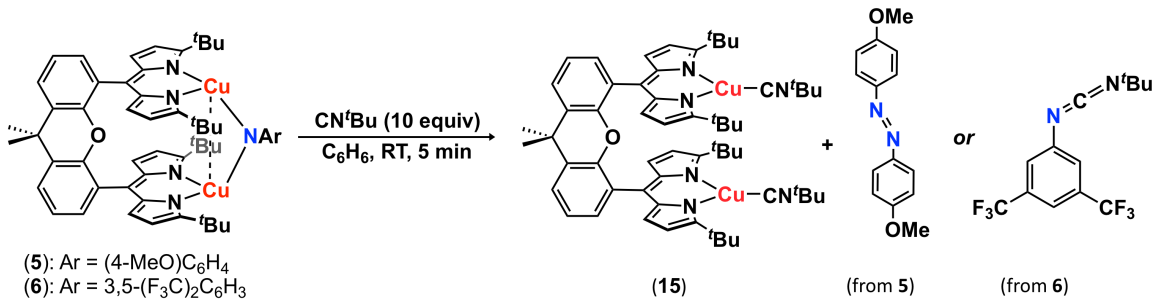


Figure S–56. Representative ^{1}H NMR spectra overlay of treatment of ($^{t\text{Bu}}$dmx)$Cu_2(\mu^2\text{–}N(3,5\text{-}(F_3C)_2C_6H_3))$ (**6**) with triphenylphosphine (*red*, bottom spectrum), iminophosphine prepared by treatment of aryl azide with triphenylphosphine (*green*, middle spectrum), and triphenylphosphine (*blue*, top).



***Tert*-butyl Isocyanide (CN^{t}Bu) Reactivity from 5 and 6**. In the drybox, to a benzene solution of either **5** (10.0 mg, 0.008 mmol) or **6** (9.2 mg, 0.008 mmol) in a J-Young tube was added neat *tert*-butyl isocyanide (6.9 mg, 0.080 mmol, 10 equiv.). A stark color change from purple to orange was observed upon inversion of the J-Young tube. ^{1}H-NMR spectroscopy revealed complete consumption of the starting material and conversion to **4**, accompanied by formation of either 1,2-bis(4-methoxyphenyl)diazene (from **5**) or *N*-(3,5-bis(trifluoromethyl)phenyl)-*N*-(*tert*-butyl)methanediimine (from **6**). Spectral data of both organic products are consistent with previously reported characterization data.

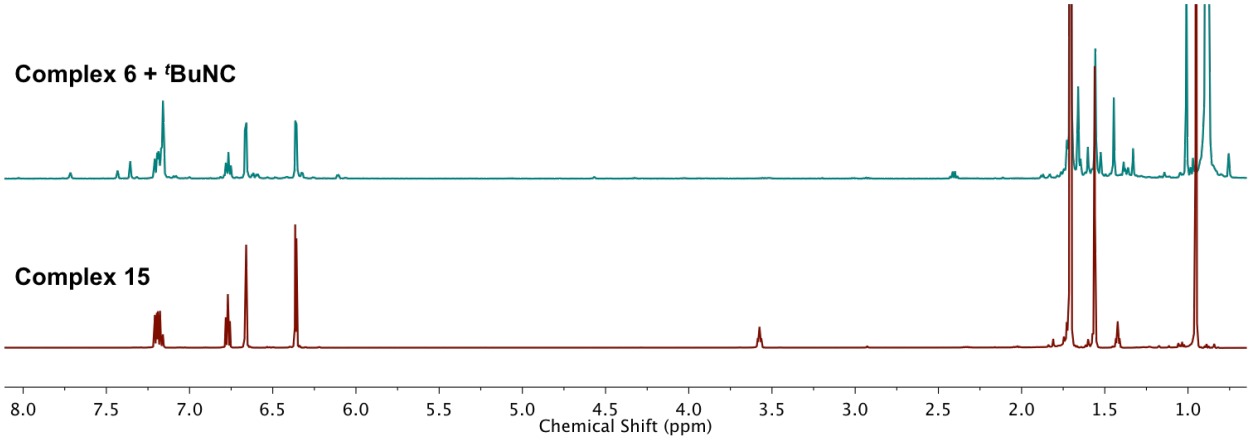


Figure S–57. Representative ^{1}H NMR spectra overlay of ($^{t\text{Bu}}$dmx)Cu_2(CN^{t}Bu)$_2$ (**15**) (*red*, bottom spectrum) and ($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(CF_3)_2C_6H_3$)) (**6**) upon addition of *tert*-butyl isocyanide (*cyan*, top spectrum).

Further Spectroscopic Characterization.

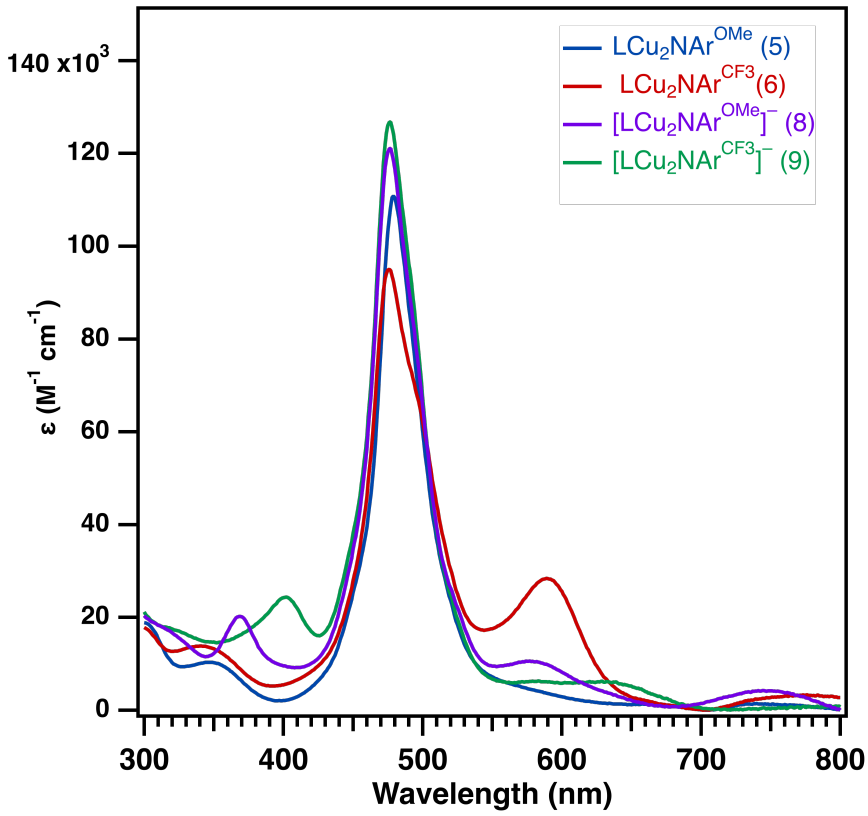


Figure S–58. Superimposed UV-Vis spectra of ($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**5**), ($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**6**), [K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (**8**), and [K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$))] (**9**).

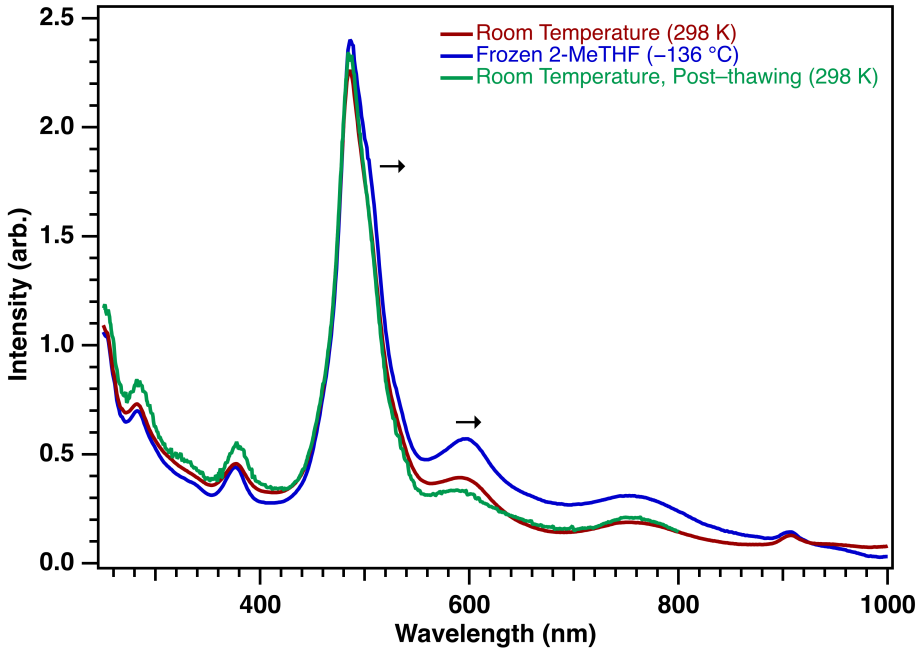


Figure S–59. Superimposed UV-Vis spectra of $[K(C_{222})][(^{tBu}dmx)Cu_2(N(C_6H_4OMe))]$ (**8**) in 2-methyltetrahydrofuran solution at room temperature (*maroon*), as a frozen glass (*blue*), and upon re-equilibration inwith room temperature (green). Insignificant shifts, denoted by arrows, are likely due to changes in accessible vibrational modes and not due to fundamentally distinct electronic structure upon cooling. Identical features for both room temperature measurements suggests against sample decomposition at low temperature.

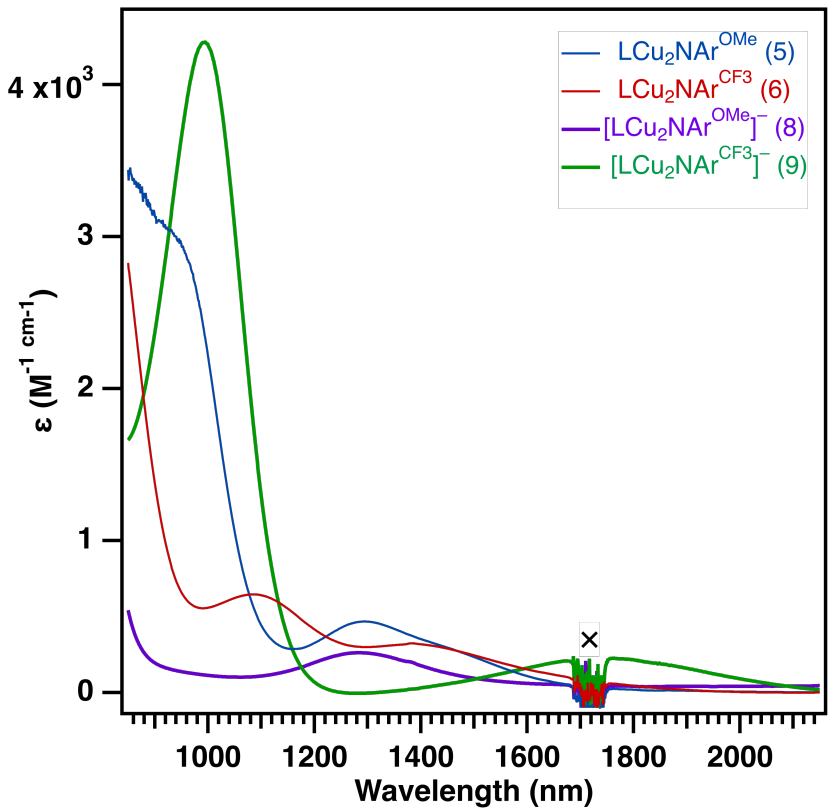


Figure S–60. Superimposed equimolar near-infrared spectra of ($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**5**), ($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**6**), [K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(N(4-MeOC$_6$H$_4$))] (**8**), and [K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$))] (**9**). Feature at *ca*. 1700 nm (**x**) is consequent of solvent (tetrahydrofuran) overtones.

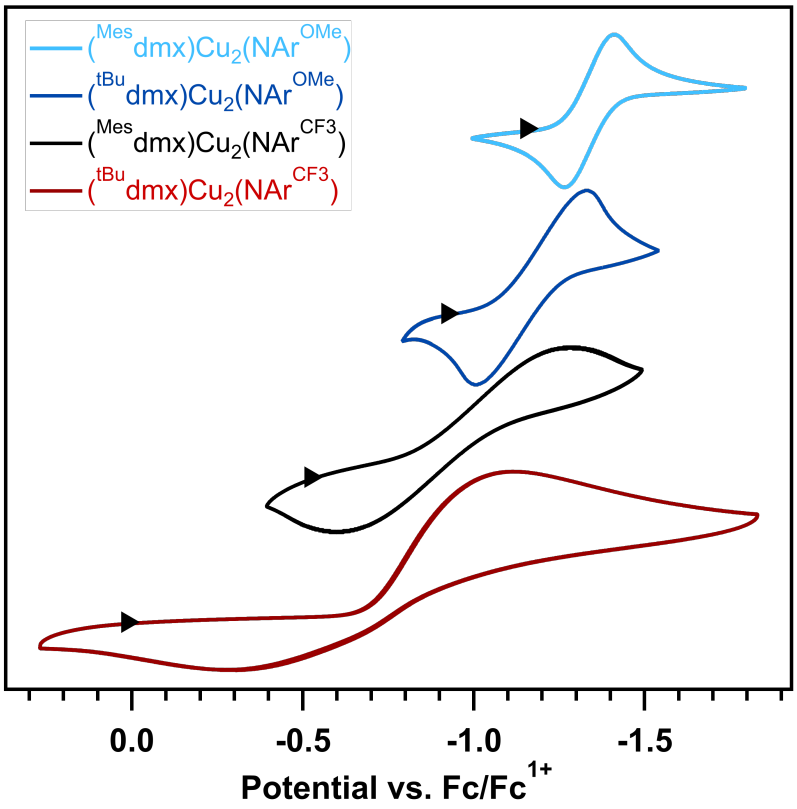


Figure S–61. Stacked cyclic voltammograms (CV) of (^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**2**, *light blue*), ($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**8**, *dark blue*), (^{Mes}dmx)Cu$_2$(μ^2–N(3,5-(CF$_3$)$_2$C$_6$H$_3$)) (**3**, black), and ($^{t\text{Bu}}$dmx)Cu$_2$(N(3,5-(CF$_3$)$_2$C$_6$H$_3$)) (**9**, *maroon*) at a scan rate of 50 mV s^{-1} . The data was recorded in tetrahydrofuran at a concentration of *ca.* 2 mM, with glassy carbon, Pt-wire, and Ag-wire as the working, counter, and reference electrodes, respectively. Saturated tetrabutylammonium hexafluorophosphate (TBAPF$_6$) solutions of 0.2 M in tetrahydrofuran were prepared before each experiment.

X-ray Absorption Spectroscopy (XAS) and TDDFT Plots

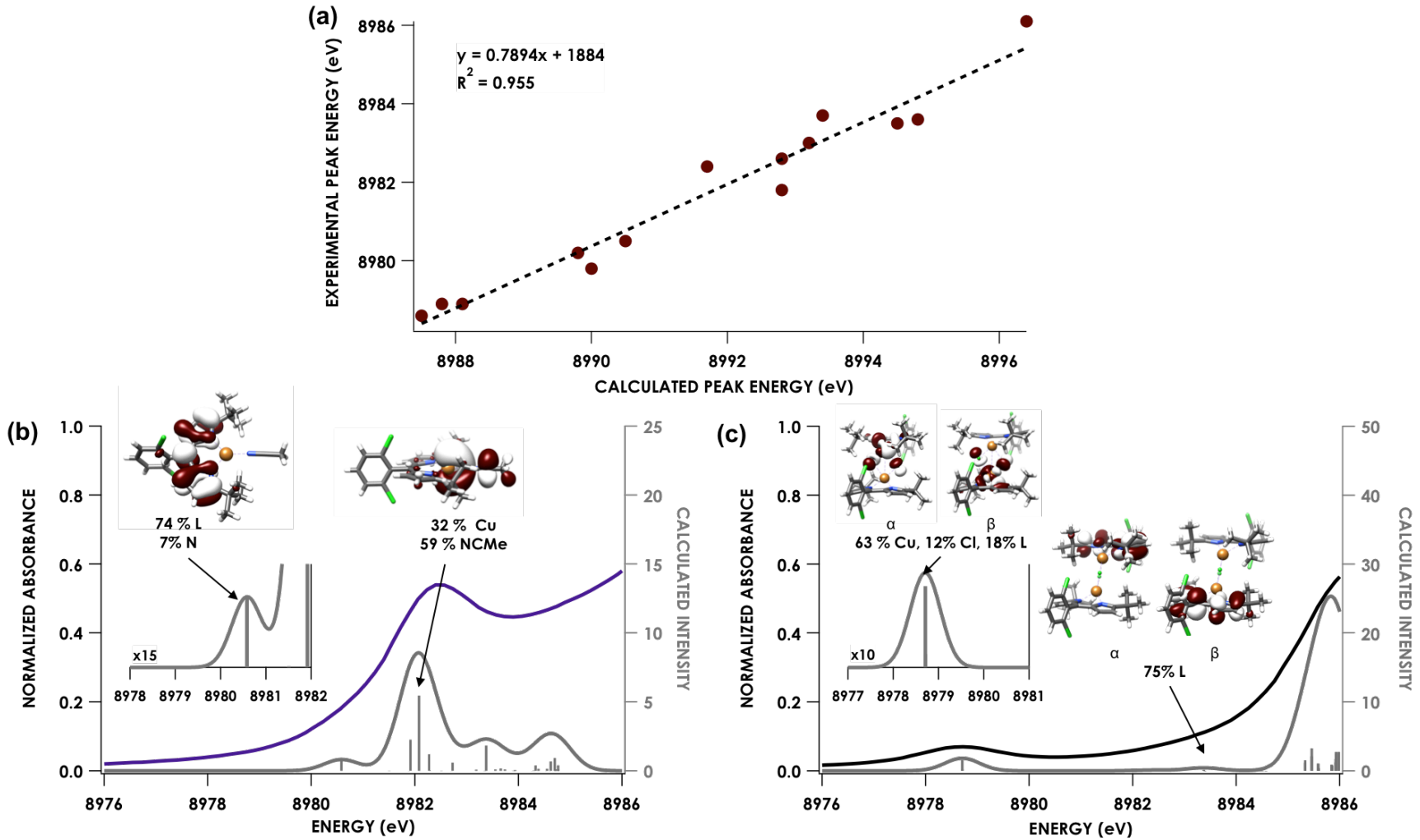


Figure S–62. (a) Correlation of experimental *vs*. TDDFT-calculated Cu K-edge XAS pre-edge peak energies, and comparison of experimental to calculated spectra (shifted according to correlation) of (b) ($^{t\text{Bu}}$L)Cu$^{\text{I}}$(NCMe) (**10**) and (c) [($^{t\text{Bu}}$L)Cu$^{\text{II}}$Cl]$_2$ (**11**).

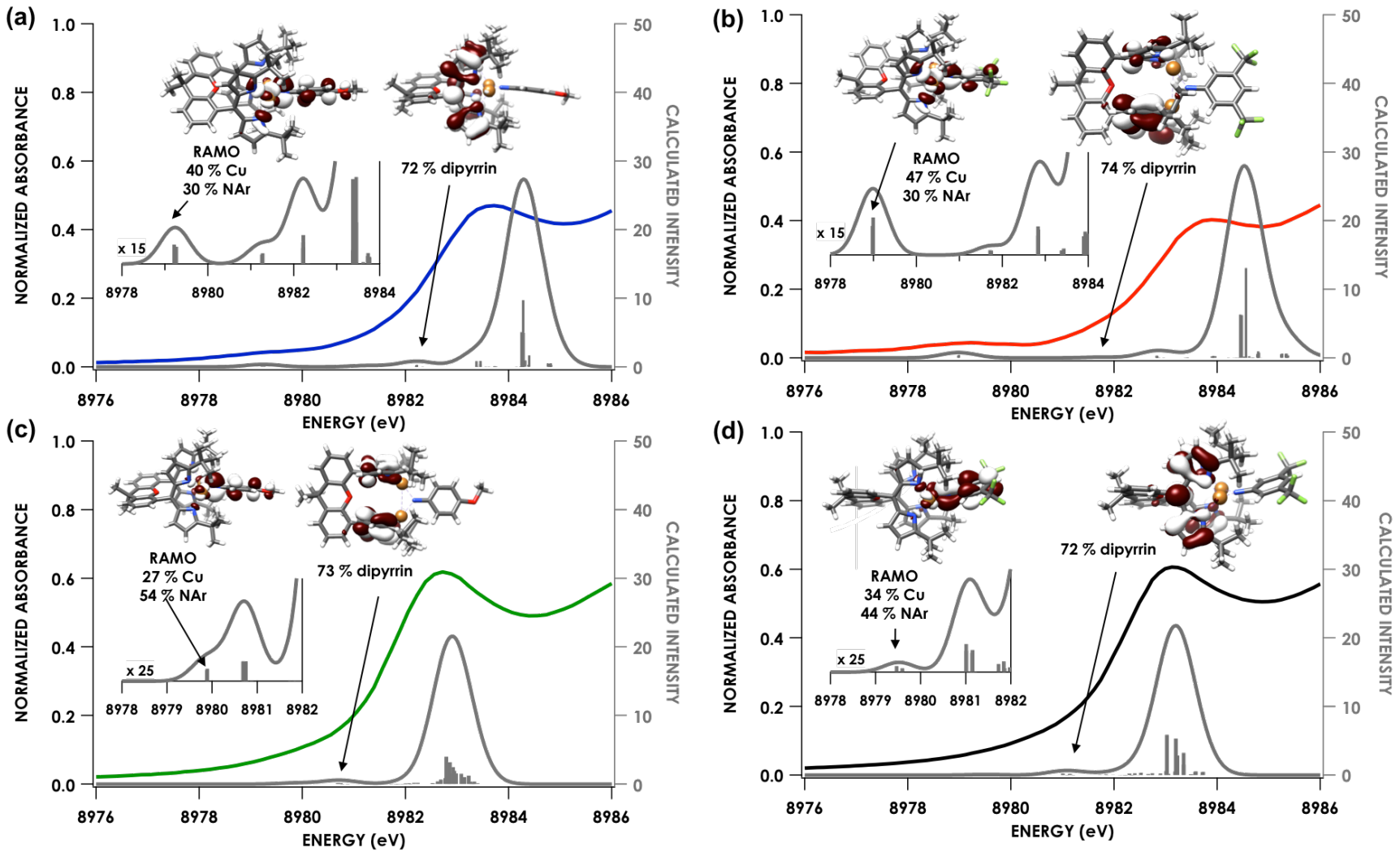


Figure S–63. Comparison of experimental Cu K-edge to calculated spectra (shifted according to correlation from Figure S–62 of (a) $^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**5**), (b) ($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(CF$_3$)$_2$C$_6$H$_3$)) (**6**), (c) [($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))]$^-$ (**8**), and (d) [($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))]$^-$ (**9**).

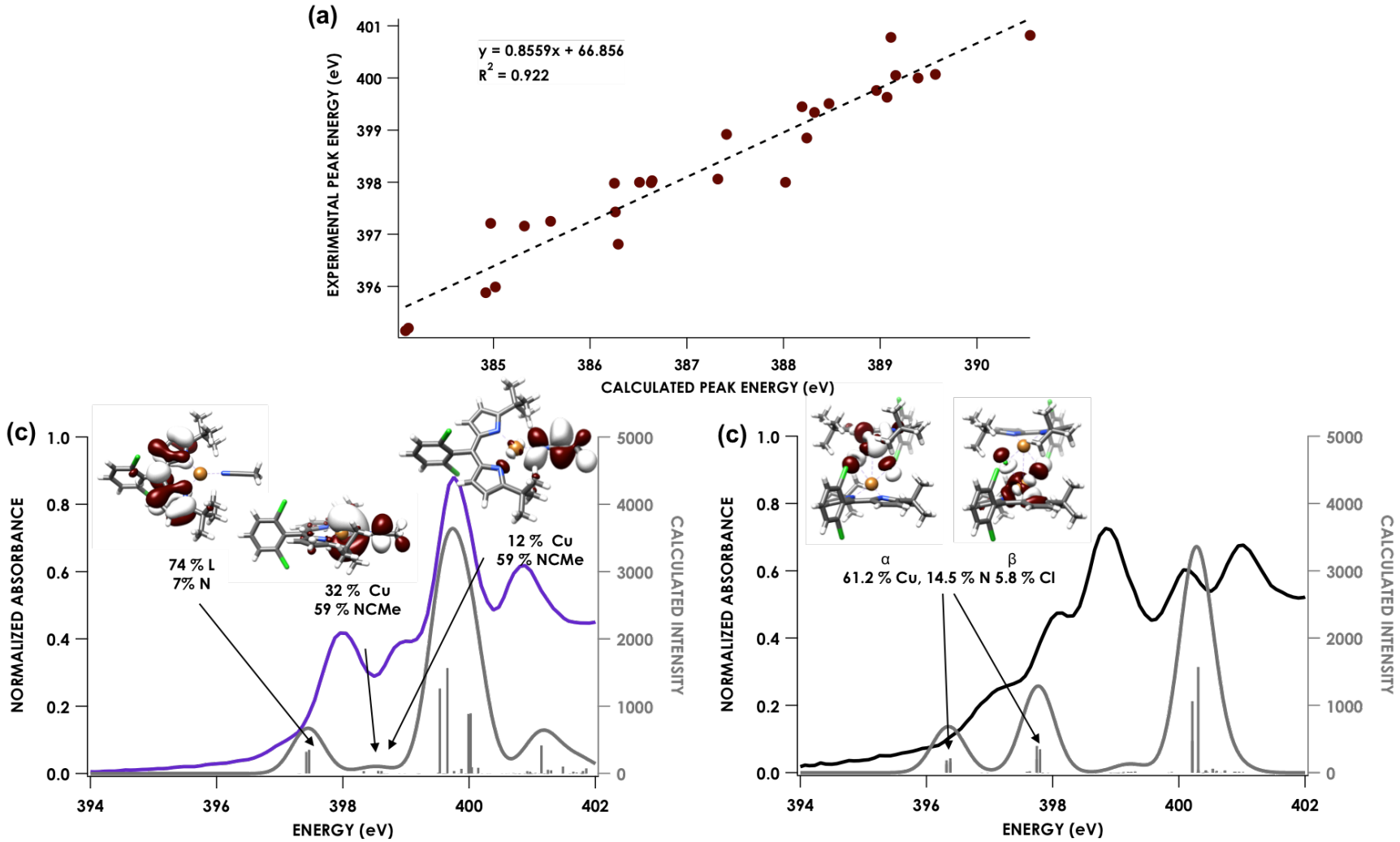


Figure S–64. (a) Correlation of experimental *vs*. TDDFT-calculated Cu N-edge XAS pre-edge peak energies, and (b) comparison of experimental to calculated spectra (shifted according to correlation) of (b) ($^{t\text{Bu}}$L)Cu$^{\text{I}}$(NCMe) (**10**) and (c) [($^{t\text{Bu}}$L)Cu$^{\text{II}}$Cl]$_2$ (**11**).

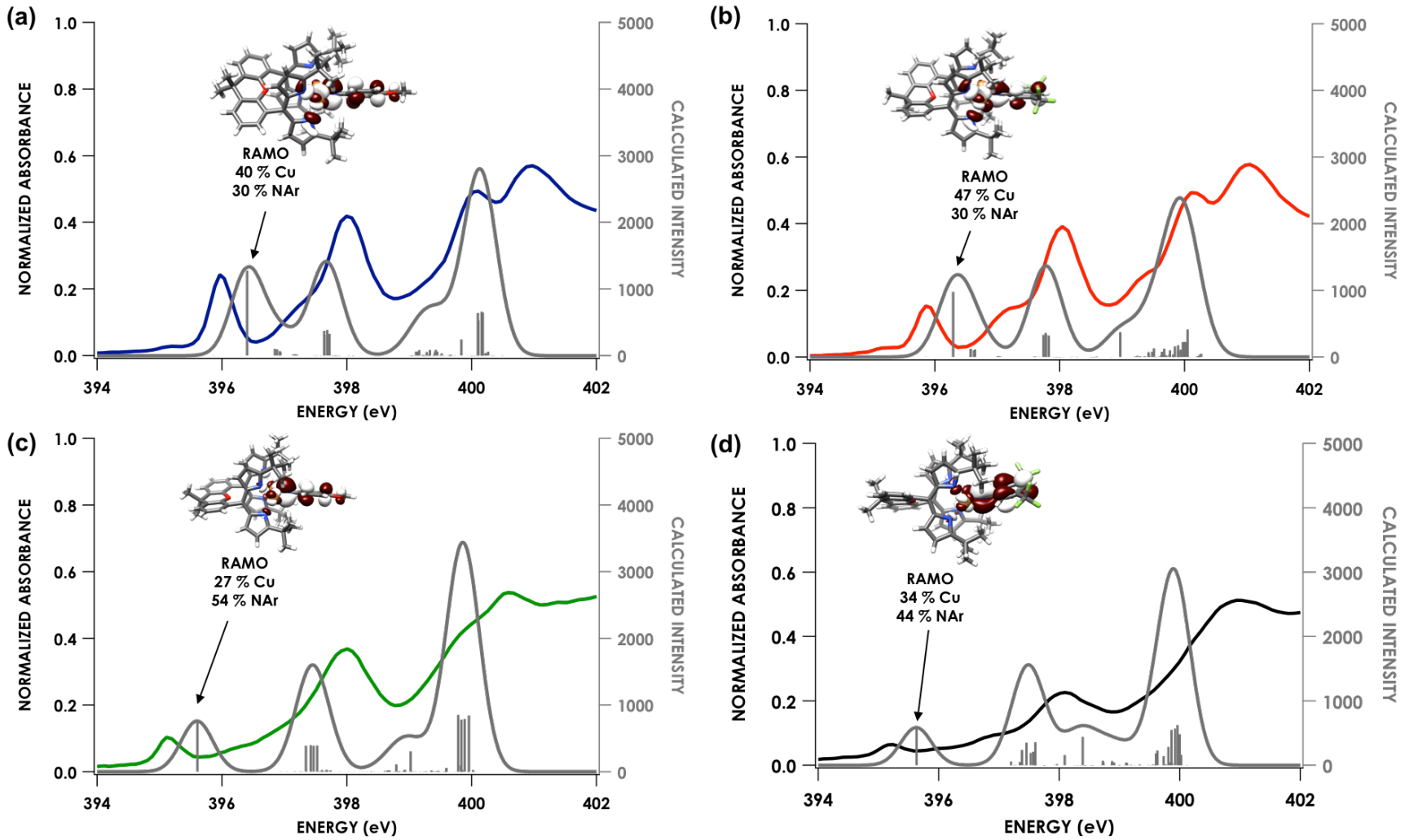


Figure S–65. Comparison of experimental N K-edge to calculated spectra (shifted according to correlation from Figure S–64 of (a) $^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**5**), (b) ($^{t\text{Bu}}$dmx)Cu$_2$(N(3,5-(CF$_3$)$_2$C$_6$H$_3$)) (**6**), (c) [($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))]$^-$ (**8**), and (d) [($^{t\text{Bu}}$dmx)Cu$_2$(N(3,5-(CF$_3$)$_2$C$_6$H$_3$))]$^-$ (**9**).

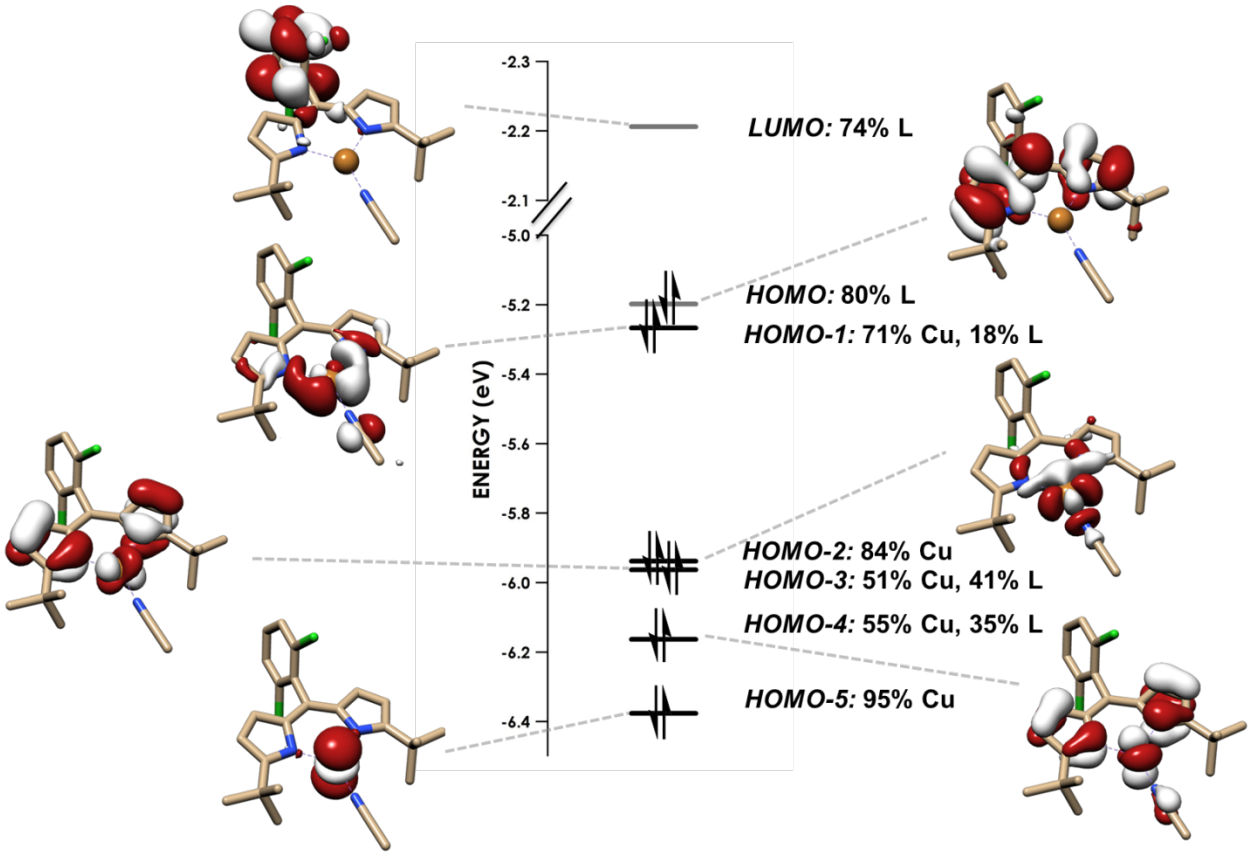


Figure S–66. Frontier MO diagrams of ($^{t\text{Bu}}$L)Cu$^{\text{I}}$NCMe (**10**) showing Cu-localized orbitals in black and the ligand-localized MOs in grey, plotted at an isolevel of 0.03 au. Orbitals shown are the β UKS MOs calculated at the B3LYP/def2-TZVP(-f)-ZORA level of theory.

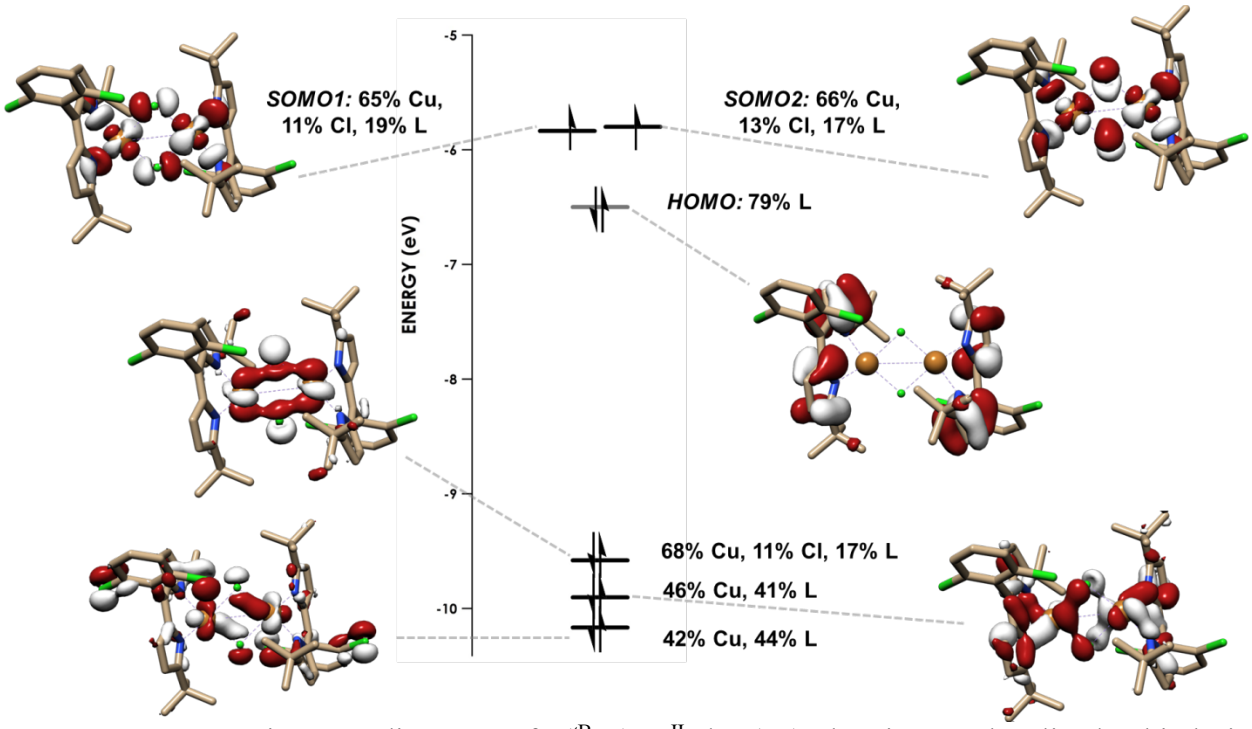


Figure S–67. Frontier MO diagrams of [($^{t\text{Bu}}$L)Cu$^{\text{II}}$Cl]$_2$ (**11**) showing Cu-localized orbitals in black and the ligand-localized MOs in grey, plotted at an isolevel of 0.03 au. Orbitals shown are the β UKS MOs calculated at the B3LYP/def2-TZVP(-f)-ZORA level of theory.

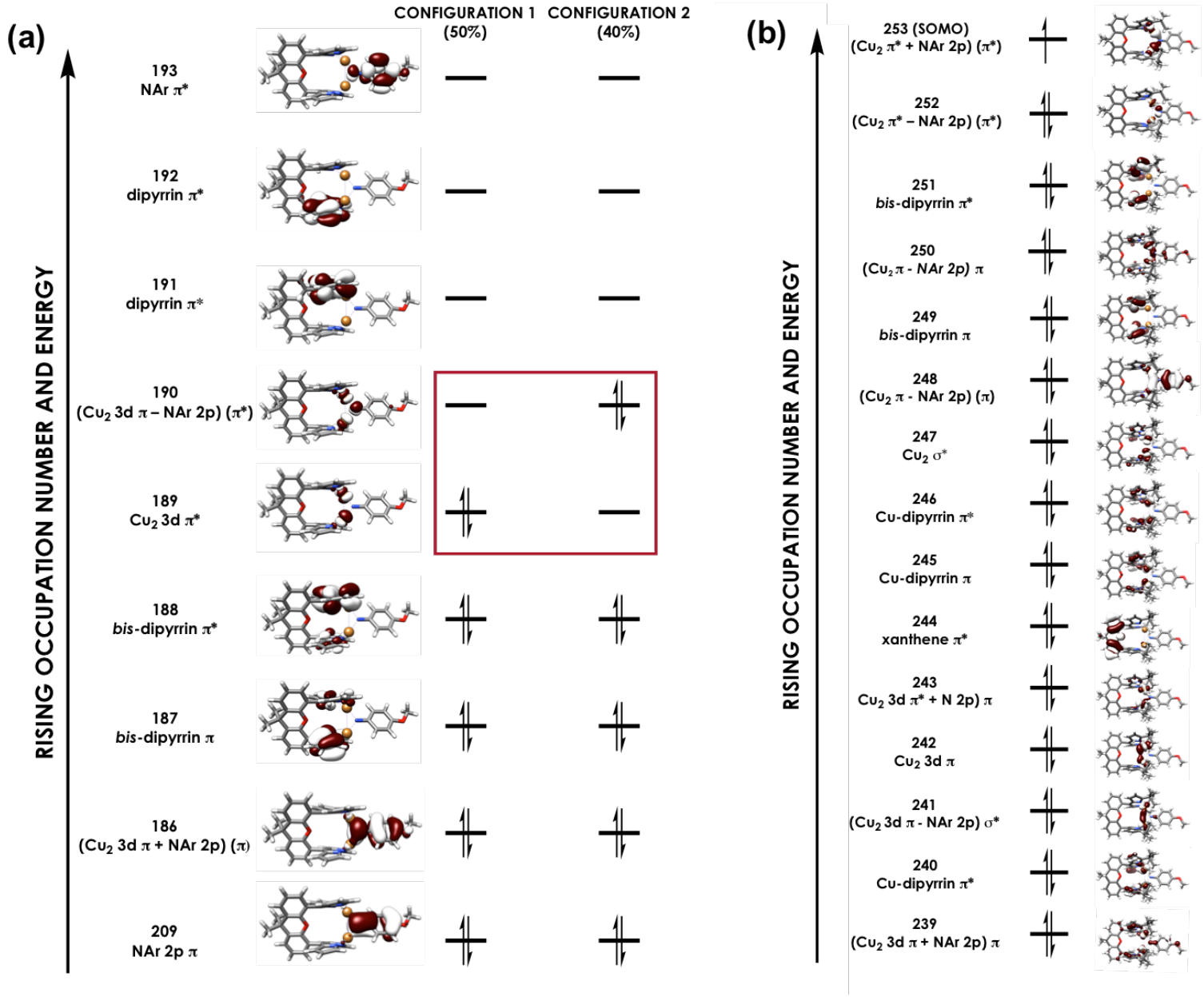

(a)
CONFIGURATION 1 (50%)
CONFIGURATION 2 (40%)
RISING OCCUPATION NUMBER AND ENERGY
193 NAr π*
192 dipyrrin π*
191 dipyrrin π*
190 (Cu2 3d π – NAr 2p) (π*)
189 Cu2 3d π*
188 bis-dipyrrin π*
187 bis-dipyrrin π
186 (Cu2 3d π + NAr 2p) (π)
209 NAr 2p π
(b)
RISING OCCUPATION NUMBER AND ENERGY
253 (SOMO) (Cu2 π* + NAr 2p) (π*)
252 (Cu2 π* – NAr 2p) (π*)
251 bis-dipyrrin π*
250 (Cu2 π - NAr 2p) π
249 bis-dipyrrin π
248 (Cu2 π - NAr 2p) (π)
247 Cu2 σ*
246 Cu-dipyrrin π*
245 Cu-dipyrrin π
244 xanthene π*
243 Cu2 3d π* + N 2p) π
242 Cu2 3d π
241 (Cu2 3d π - NAr 2p) σ*
240 Cu-dipyrrin π*
239 (Cu2 3d π + NAr 2p) π

Figure S–68. Qualitative frontier molecular orbital diagrams of $[(^{t\text{Bu}}\text{dmx})\text{Cu}_2(\mu^2\text{–N}(\text{C}_6\text{H}_4\text{OMe}))]^n$ (*n* = 0, **5**) (a-c) and (n = –1, **8**) (d). Diagram (a) depicts the two leading configurations making up the singlet ground state resulting from a CAS(10,9) calculation using the truncated model **5′**. These calculations employed the ZORA-def2-TZVP(-f) basis set on Cu and N with the ZORA-def2-SVP basis set on all other atoms. Occupation of MOs 213 and 214 differentiate the two configurations; these orbitals are printed beneath the diagram. Diagram (b) depicts the single configuration defining the doublet ground state of **8**. The MOs comprise QROs generated produced following an unrestricted B3LYP calculation employing the CP(PPP) basis set on Cu and def2-TZVP(-f) on all other atoms. Orbital plots are depicted at an isovalue of 0.03 au. All orbital labels are based on dominant interaction(s).

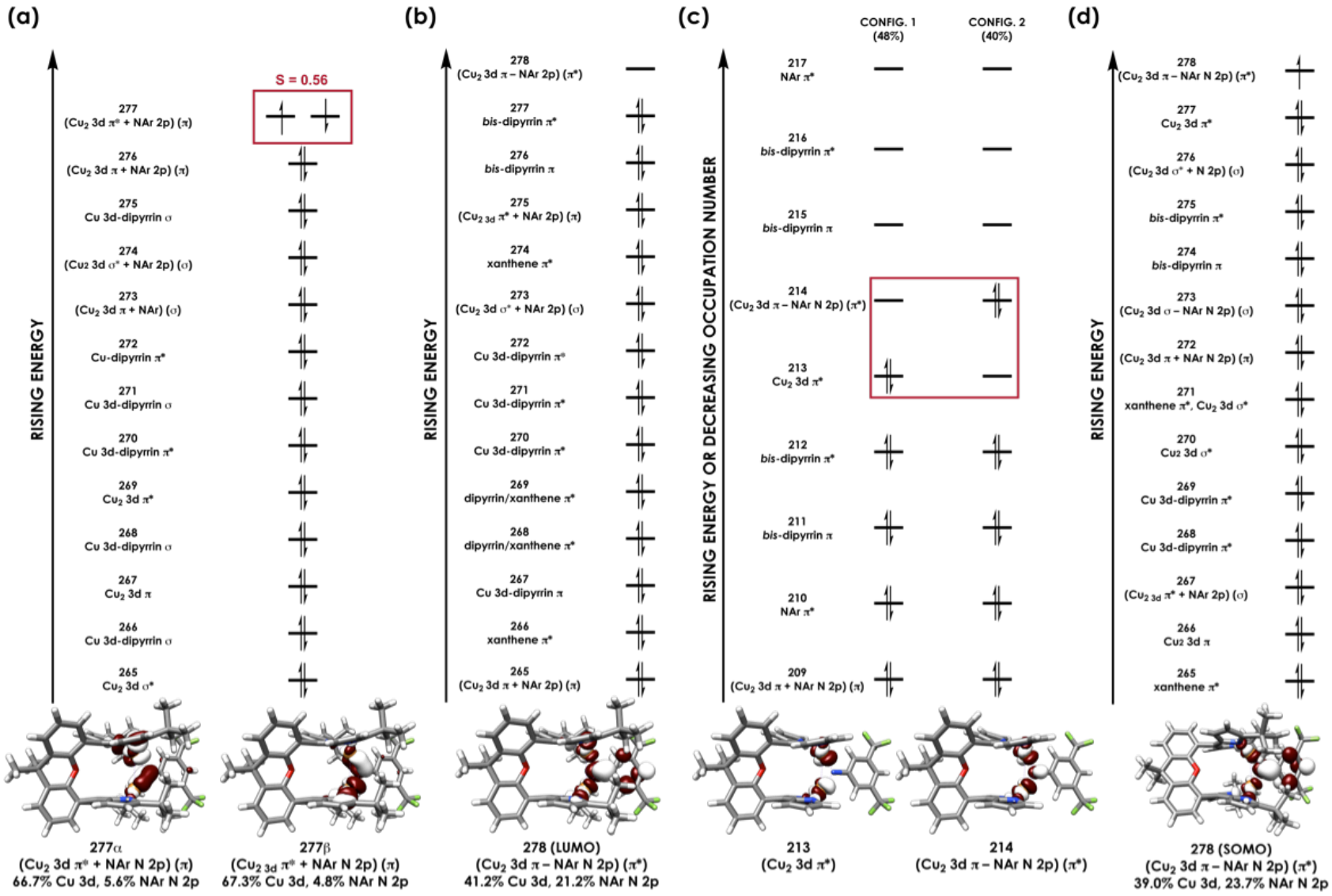

(a)
RISING ENERGY
S = 0.56
277 (Cu2 3d π* + NAr 2p) (π)
276 (Cu2 3d π + NAr 2p) (π)
275 Cu 3d-dipyrrin σ
274 (Cu2 3d σ* + NAr 2p) (σ)
273 (Cu2 3d π + NAr) (σ)
272 Cu-dipyrrin π*
271 Cu 3d-dipyrrin σ
270 Cu 3d-dipyrrin π*
269 Cu2 3d π*
268 Cu 3d-dipyrrin σ
267 Cu2 3d π
266 Cu 3d-dipyrrin σ
265 Cu2 3d σ*
277α
(Cu2 3d π* + NAr N 2p) (π)
66.7% Cu 3d, 5.6% NAr N 2p
277β
(Cu2 3d π* + NAr N 2p) (π)
67.3% Cu 3d, 4.8% NAr N 2p
(b)
RISING ENERGY
278 (Cu2 3d π – NAr 2p) (π*)
277 bis-dipyrrin π*
276 bis-dipyrrin π
275 (Cu2 3d π* + NAr 2p) (π)
274 xanthene π*
273 (Cu2 3d σ* + NAr 2p) (σ)
272 Cu 3d-dipyrrin π*
271 Cu 3d-dipyrrin π*
270 Cu 3d-dipyrrin π*
269 dipyrrin/xanthene π*
268 dipyrrin/xanthene π*
267 Cu 3d-dipyrrin π
266 xanthene π*
265 (Cu2 3d π + NAr 2p) (π)
278 (LUMO)
(Cu2 3d π – NAr N 2p) (π*)
41.2% Cu 3d, 21.2% NAr N 2p
(c)
RISING ENERGY OR DECREASING OCCUPATION NUMBER
CONFIG. 1 (48%)
CONFIG. 2 (40%)
217 NAr π*
216 bis-dipyrrin π*
215 bis-dipyrrin π
214 (Cu2 3d π – NAr N 2p) (π*)
213 Cu2 3d π*
212 bis-dipyrrin π*
211 bis-dipyrrin π
210 NAr π*
209 (Cu2 3d π + NAr N 2p) (π)
213
(Cu2 3d π*)
214
(Cu2 3d π – NAr N 2p) (π*)
(d)
RISING ENERGY
278 (Cu2 3d π – NAr N 2p) (π*)
277 Cu2 3d π*
276 (Cu2 3d σ* + N 2p) (σ)
275 bis-dipyrrin π*
274 bis-dipyrrin π
273 (Cu2 3d σ – NAr N 2p) (σ)
272 (Cu2 3d π + NAr N 2p) (π)
271 xanthene π*, Cu2 3d σ*
270 Cu2 3d σ*
269 Cu 3d-dipyrrin π*
268 Cu 3d-dipyrrin π*
267 (Cu2 3d π* + NAr 2p) (σ)
266 Cu2 3d π
265 xanthene π*
278 (SOMO)
(Cu2 3d π – NAr N 2p) (π*)
39.0% Cu 3d, 23.7% NAr N 2p

Figure S–69. Qualitative frontier molecular orbital diagrams of [($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(F_3C)_2C_6H_3$))]^n (n = 0, **6**) (a-c) and (n = –1, **9**) (d). Diagram (a) shows unrestricted corresponding orbitals (UCOs) resulting from a broken symmetry [BS(1,1)] calculation carried out using the B3LYP hybrid density functional, the CP(PPP) basis on Cu, and the ZORA-def2-TZVP(-f) basis set on all other atoms. MOs 277α and 277β are highlighted and plotted beneath, indicating antiferromagnetic coupling between electrons in spinorbitals involved in Cu–NAr π bonding. Diagram (b) depicts the frontier canonical orbitals following quasi-restricted orbital (QRO) transformation. This electronic structure allows from a Cu and N-based acceptor MO necessitated by the XAS observations; this orbital (278) is depicted beneath the diagram. Diagram (c) depicts the two leading configurations making up the singlet ground state resulting from a CAS(10,9) calculation using the truncated model **6′**. These calculations employed the ZORA-def2-TZVP(-f) basis set on Cu and N with the ZORA-def2-SVP basis set on all other atoms. Occupation of MOs 213 and 214 differentiate the two configurations; these orbitals are printed beneath the diagram. Diagram (d) depicts the single configuration defining the doublet ground state of **9**. The MOs comprise QROs generated produced following an unrestricted B3LYP calculation employing the CP(PPP) basis set on Cu and def2-TZVP(-f) on all other atoms. Orbital plots are depicted at an isovalue of 0.03 au. All orbital labels are based on dominant interaction(s).

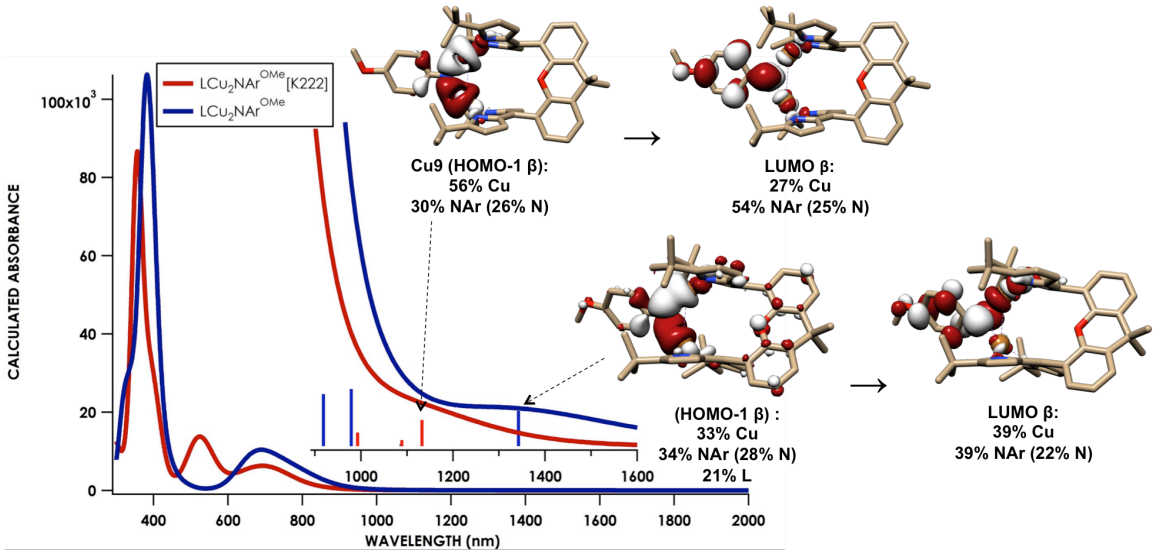


Figure S–70. TDDFT analysis of UV-Vis trace for $[(^{t\text{Bu}}\text{dmx})\text{Cu}_2(\mu^2\text{–N}(\text{C}_6\text{H}_4\text{OMe}))]^n$ (n = 0, **5**, *blue trace*) and (n = –1, **8**, *red trace*), demonstrating the absorption in the near-infrared region is representative of a metal-to-ligand charge transfer (MLCT) and not an intervalence charge transfer.

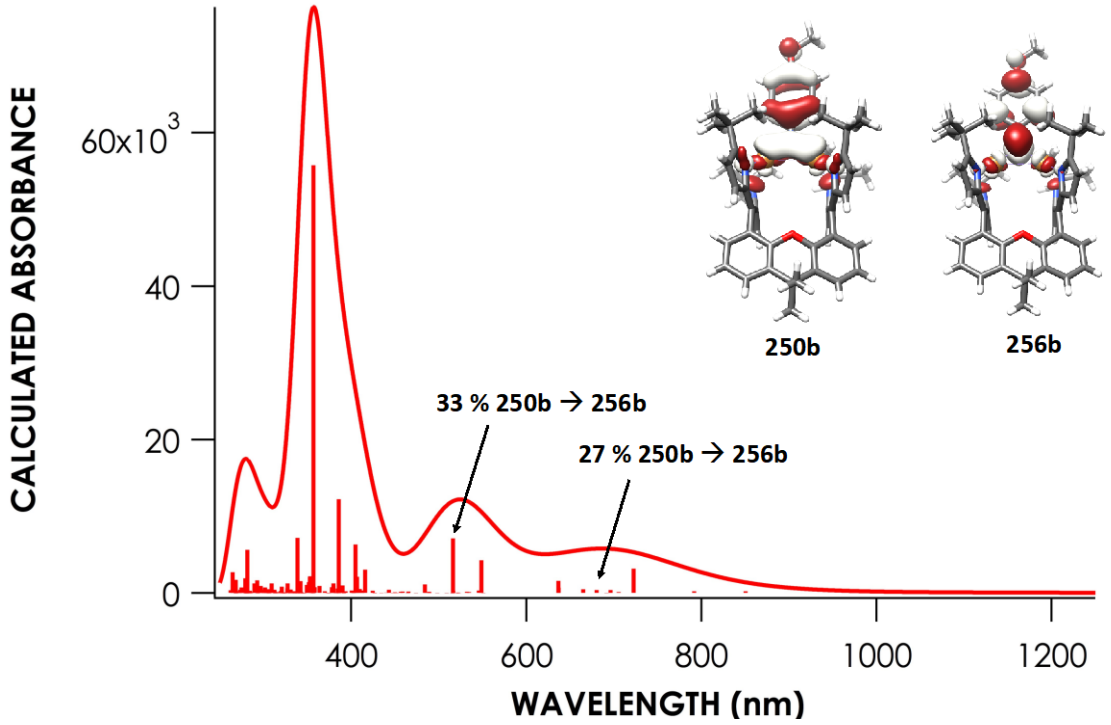


Figure S–71. Transitions modeled from TDDFT output of [($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))]$^{1-}$ (**8**), demonstrating a nitrenoid-dominant transition and not one assignable to a IVCT.

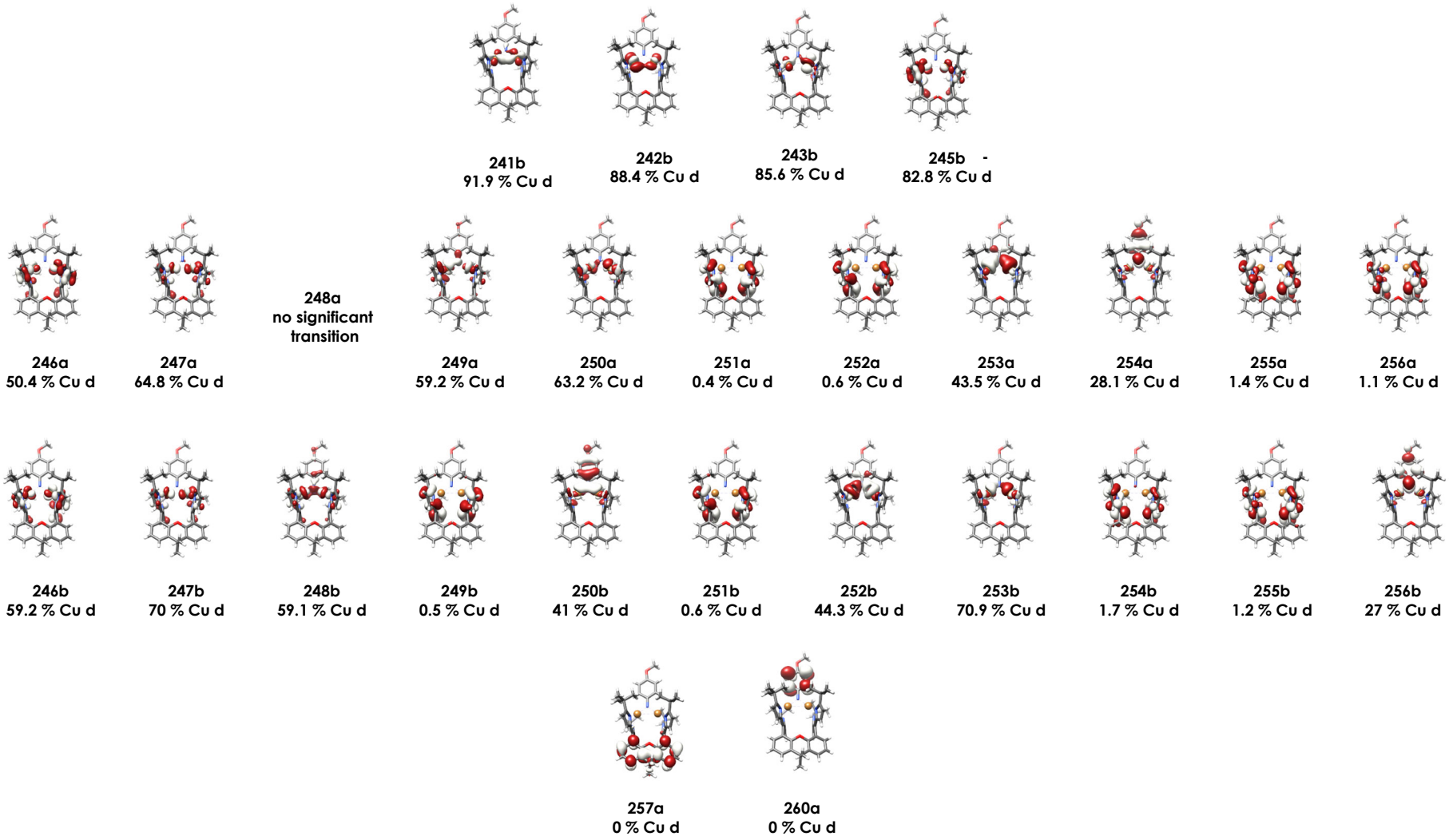


Figure S–72. Acceptor orbital Cu parentage by TDDFT for $[(^{t\text{Bu}}\text{dmx})\text{Cu}_2(\mu^2\text{–N}(\text{C}_6\text{H}_4\text{OMe}))]^{1-}$ (**8**).

State	Wavelength (nm)	Transition	Contribution to State	Donor Orbital d character	Acceptor Orbital d character	Transition Designation
1	1132.7	252b → 256b	0.863813	44	27	MLCT
2	1088.8	254a → 255a	0.969042	28	1.4	MLCT
3	992.7	254a → 256a	0.935631	44	27	MLCT
4	850.4	253b → 254b	0.931253	71	1.7	MLCT
5	791.7	253b → 255b	0.919432	71	1.2	MLCT
6	**722.5**	**252b → 254b**	**0.279212**	**44**	**1.7**	**MLCT**
		253b → 256b	**0.452706**	**71**	**27**	
7	705.5	252a → 255a	0.236148	0.6	1.4	L→L
		251b → 254b	0.230769	0.6	1.7	
8	691.5	251a → 255a	0.139377	0.4	1.4	L→L
		252a → 256a	0.196362	0.4	1.1	
		249b → 254b	0.137963	0.5	1.7	
		251b → 255b	0.194885	0.6	1.2	
9	696.2	253a → 255a	0.274547	43.5	1.4	MLCT
		252b → 254b	0.523353	44.3	1.7	
10	664.8	248b → 256b	0.622059	59.1	27	MLCT
		250b → 256b	**0.267144**	**41**	**27**	**IVCT**
11	680.1	252b → 255b	0.793892	44.3	1.2	MLCT
12	636.7	253a → 255a	0.512318	43.5	1.4	MLCT
		253a → 256a	0.101233	43.5	1.1	
		252b → 254b	0.121769	44.3	1.7	
		253b → 256b	0.143598	70.9	27	
13	**636.6**	**253a → 256a**	**0.680575**	**43.5**	**1.1**	**MLCT**
14	**548.5**	**250b → 254b**	**0.641519**	**41**	**1.7**	**MLCT**
15	534.5	247b → 256b	0.821308	70	27	MLCT
		249a → 255a	**0.121287**	**59**	**1.4**	**MLCT**
16	**516.2**	**248b → 256b**	**0.148748**	**59**	**27**	**MLCT**
		250b → 256b	**0.330277**	**41**	**27**	**IVCT**
17	532.2	250a → 255a	0.17749	63	1.4	MLCT
		250b → 255b	0.408718	41	1.2	
18	516.5	250a → 255a	0.524526	63	1.4	MLCT
		248b → 254b	0.117277	59	1.7	
19	520.6	249a → 255a	0.274124	59	1.4	MLCT
		248b → 254b	0.250591	59	1.7	
		250b → 254b	0.122908	41	1.7	
20	515.5	246b → 256b	0.335683	59	27	MLCT/LMCT
		251b → 256b	0.476303	0.6	27	

21	545.7	251a → 255a	0.111703	0.4	1.4	L→L
		251a → 256a	0.146406	0.4	1.1	
		252a → 255a	0.323991	0.6	1.4	
		251b → 254b	0.22173	0.6	1.7	
22	489.2	250a → 256a	0.196162	63	1.1	MLCT/ L→L
		251a → 255a	0.163869	0.4	1.4	
		252a → 256a	0.168567	0.6	1.1	
		250b → 255b	0.120438	63	1.1	
23	509.0	250a → 256a	0.191594	63	1.1	MLCT/L→L
		249b → 254b	0.174072	0.5	1.7	
		251b → 255b	0.122272	0.6	1.2	
24	522.1	251a → 255a	0.139133	0.4	1.4	L→L
		252a → 256a	0.175397	0.6	1.1	
		249b → 254b	0.19045	0.5	1.7	
		251b → 255b	0.232141	0.6	1.2	
25	522.7	250a → 256a	0.109769	63	1.1	L→L
		251a → 256a	0.22616	0.4	1.1	
		252a → 255a	0.106675	0.6	1.4	
		249b → 255b	0.204289	0.5	1.2	
26	498.3	249a → 256a	0.195412	59	1.1	MLCT
		250a → 256a	0.200894	63	1.1	
		248b → 255b	0.144679	59	1.2	
27	484.0	245b → 256b	0.134757	53	27	MLCT
		246b → 256b	0.111744	59	27	
		249b → 256b	0.274547	0.5	27	
28	484.9	243b → 256b	0.673105	86	27	MLCT
		249b → 256b	0.165499	0.5	27	
29	488.9	243b → 256b	0.113567	86	27	MLCT/LMCT
		246b → 256b	0.274643	59	27	
		251b → 256b	0.386845	0.6	27	
30	465.4	242b → 256b	0.681053	88	27	MLCT
		245b → 256b	0.101929	59	27	
31	456.5	249a → 255a	0.115682	59	1.4	MLCT/LMCT
		242b → 256b	0.142888	88	27	
		248b → 254b	0.134027	59	1.7	
		249b → 256b	0.372019	0.5	27	
32	451.8	246a → 255a	0.137962	50	1.4	MLCT
		245b → 254b	0.156189	53	1.7	
		245b → 255b	0.107942	53	1.2	
		246b → 254b	0.185657	59	1.7	

33	458.6	254a → 260a	0.83395	28	0	MLCT
		246a → 256a	0.146552	50	1.1	
34	447.5	246b → 254b	0.116321	59	1.7	MLCT
		246b → 255b	0.22361	59	1.2	
		249a → 255a	0.158007	59	1.4	
35	442.8	245b → 256b	0.213534	52	27	MLCT
		248b → 254b	0.170479	59	1.7	
36	449.8	249a → 256a	0.359964	59	1.1	MLCT
		248b → 255b	0.387814	59	1.2	
37	551.0	254a → 257a	0.992515	28	0	MLCT
38	424.6	241b → 256b	0.700793	92	27	MLCT
		249a → 256a	0.112468	59	1.1	
39	426.8	241b → 256b	0.172096	92	27	MLCT
		247b → 254b	0.411424	70	1.7	
40	426.9	247a → 256a	0.143877	65	1.1	MLCT

Table S–1. Assignment of transitions for $[(^{t\mathrm{Bu}}\mathrm{dmx})\mathrm{Cu}_2(\mu^2\text{–}\mathrm{N}(\mathrm{C}_6\mathrm{H}_4\mathrm{OMe}))]^{1-}$ (**8**), depicting no transition assignable to an IVCT.

Table S–2. X-ray diffraction experimental details.[a]

	(^{Mes}dmx)Cu$_2$(NCMe)$_2$ (**1**)	(^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**2**)	(^{Mes}dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**3**)	($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (**5**)	($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (**6**)	[K(C$_{222}$)][(^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (**7**)
CCDC Entry	1948008	1948009	1948010	1948011	1948012	1948013
Moiety Formula	$C_{79}H_{83}Cu_2N_7O_2$	$C_{84}H_{90}Cu_2N_5O_4$	$C_{77}H_{67}Cu_2F_6N_5O$	$C_{60}H_{71}Cu_2N_6O_3$	$C_{59}H_{62}Cu_2F_6N_6O$	$C_{94}H_{107}Cu_2KN_7O_8$
FW	1289.60	1361.69	1319.43	1038.17	1112.22	1629.04
λ (nm)	0.71073	0.71073	0.41328	0.71073	0.71073	1.54178
T **(K)**	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal System	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space Group (*Z*)	P 2$_1$/n (4)	$P\bar{1}$ (2)	C 2/c (4)	P 2/c (4)	Pna21 (16)	P 2$_1$/c (4)
a **(Å)**	17.5563(12)	12.304(3)	23.7718(17)	21.9597(5)	18.958(2)	17.7584(2)
b **(Å)**	19.7585(14)	16.241(4)	21.0479(14)	22.7867(5)	13.0693(16)	26.2650(3)
c **(Å)**	20.6328(14)	18.007(5)	17.5589(12)	21.3984(5)	43.638(5)	24.6763(3)
α (°)	90	92.531(4)	90	90	90	90
β (°)	111.704(2)	92.075(5)	113.5650(10)	92.534(2)	90	105.2606(12)
γ (°)	90	92.793(5)	90	90	90	90
Volume (Å^3)	6649.8(8)	3587.8(15)	8052.9(10)	10697.1(4)	10812(2)	11103.8(2)
Calc. ρ (mg/m^3)	1.288	1.260	1.088	1.289	1.367	0.974
μ (mm^{-1})	0.693	0.647	0.142	0.844	0.854	1.171
Crystal Size (mm)	0.10x0.11x0.24	0.09x0.16x0.21	0.07x0.10x0.11	0.22x0.27x0.39	0.09x0.23x0.34	0.12x0.13x0.34
Reflections	11828	12852	7108	18897	16866	19446
Completeness (to 2θ)	0.998	0.989	0.995	0.999	0.992	0.992
GOF on F^2	1.075	1.001	1.053	1.147	1.038	1.020
R1, *w*R2[a] [$I > 2\sigma(I)$]	0.0467, 0.0993	0.0679, 0.1607	0.0393, 0.0971	0.0988, 0.2228	0.0538, 0.1135	0.0639, 0.1715
(R1, *w*R2) [all data]	0.0723, 0.1105	0.1282, 0.1948	0.0536, 0.0971	0.1462, 0.2560	0.0865, 0.1329	0.0802, 0.1836

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

	[K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (**8**)	[K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$))] (**9**)	($^{t\text{Bu}}$L)Cu(NCMe) (**10**)	[($^{t\text{Bu}}$L)CuCl]$_2$ (**11**)	($^{\text{Mes}}$dmx)Cu$_2$(PMe$_3$)$_2$ (**12**)	($^{t\text{Bu}}$dmx)Cu$_2$(PPh$_3$) (**13**)
CCDC Entry	1948014	1948015	1948016	1948017	1948018	1948019
Moiety Formula	$C_{81}H_{117}Cu_2KN_7O_{10}$	$C_{75}H_{95}Cu_2F_6KN_7O_7$	$C_{26}H_{30}Cl_2CuN_4$	$C_{29}H_{31}Cl_3CuN_2$	$C_{79}H_{90}Cu_2N_4O_4P_2$	$C_{97}H_{100}Cu_2N_4OP_2$
FW	1510.48	1486.75	525.47	577.45	1316.56	1524.57
λ (nm)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
***T* (K)**	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space Group (*Z*)	P 2$_1$/n (4)	P 2$_1$/n (4)	C 2/c (4)	P 2$_1$/n (4)	$P\bar{1}$ (2)	C 2/c (4)
***a* (Å)**	17.164(3)	13.347(2)	36.448(4)	13.1817(13)	11.0169(6)	57.196(11)
***b* (Å)**	18.401(3)	41.261(6)	11.0154(11)	10.7516(19)	15.6053(7)	25.306(4)
***c* (Å)**	27.309(4)	13.763(2)	13.4471(12)	19.191(3)	21.4320(11)	26.078(3)
α (°)	90	90	90	90	80.283(4)	90
β (°)	104.668(4)	97.390(3)	105.928(3)	95.400(8)	89.945(4)	117.092(7)
γ (°)	90	90	90	90	74.102(4)	90
Volume (Å^3)	8344(2)	7516(2)	5191.6(9)	2707.7(7)	3488.9(3)	33604(10)
Calc. ρ (mg/m^3)	1.202	1.314	1.345	1.417	1.253	1.205
μ (mm^{-1})	0.617	0.692	1.067	1.124	0.704	0.594
Crystal Size (mm)	0.35x0.39x1.00	0.23x0.40x1.00	0.13x0.15x0.26	0.08x0.10x0.12	0.09x0.13x0.14	0.14x0.26x0.38
Reflections	14724	13315	4558	4789	12313	30048
Completeness (to 2θ)	1.000	0.999	0.987	0.996	0.998	0.989
GOF on F^2	1.043	1.012	1.117	1.034	1.007	1.052
R1, *w*R2[a] [*I* > 2σ(*I*)]	0.0370, 0.0969	0.0402, 0.0866	0.0691, 0.1072	0.0528, 0.1184	0.0554, 0.0914	0.0744, 0.1635
(R1, *w*R2) [all data]	0.0504, 0.1035	0.0561, 0.0932	0.1199, 0.1194	0.0769, 0.1310	0.1198, 0.1085	0.1338, 0.1931

	(^{Mes}dmx)Cu$_2$(CN^{t}Bu)$_2$ (**14**)	($^{t Bu}$dmx)Cu$_2$(CN^{t}Bu)$_2$ (**15**)	(^{Mes}dmx)Cu$_2$(dmap)$_2$ (**16**)	[($^{t Bu}$L)Cu]$_2$ (**18**)
	1948020	1948021	1948022	1948023
Moiety Formula	$C_{85}H_{94}Cu_2N_6O_3$	$C_{63}H_{82}Cu_2N_6O_2$	$C_{95}H_{111}Cu_2N_8O_4$	$C_{46}H_{50}Cl_4Cu_2N_4$
FW	1366.23	1082.42	1555.49	927.78
λ (nm)	0.71073	0.71073	0.71073	0.71073
T (K)	100(2)	100(2)	100(2)	100(2)
Crystal System	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group (Z)	$P\bar{1}$ (2)	P 2_1/n (4)	P 2_1/n (4)	P 2_1/n (4)
a (Å)	12.031(5)	16.3247(7)	13.3375(5)	11.189(9)
b (Å)	14.049(6)	18.2917(8)	25.1228(7)	17.657(12)
c (Å)	24.368(11)	20.5023(9)	25.4322(7)	22.207(15)
α (°)	99.925(7)	90	90	90
β (°)	99.557(8)	106.3000(10)	100.624(3)	95.88(2)
γ (°)	105.278(7)	90	90	90
Volume (Å^3)	3816(3)	5876.0(4)	8375.6(4)	4364(6)
Calc. ρ (mg/m^3)	1.189	1.224	1.234	1.412
μ (mm^{-1})	0.608	0.770	0.564	1.257
Crystal Size (mm)	0.12x0.19x0.42	0.12x0.15x0.20	0.05x0.15x0.48	0.29x0.37x0.49
Reflections	13626	10423	14837	7739
Completeness (to 2θ)	0.987	0.999	0.999	0.992
GOF on F^2	1.021	0.911	1.030	1.027
R1, wR2[a] [$I > 2\sigma(I)$]	0.0621, 0.1718	0.0342, 0.0658	0.0734, 0.1786	0.0354, 0.0828
(R1, wR2) [all data]	0.0927, 0.1921	0.0628, 0.0716	0.1323, 0.2128	0.0522, 0.0921

X-Ray Diffraction Techniques. All structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream-cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (λ = 0.71073 Å) source (**1**, **2**, **5–6**, **8–18**) or from a Cu Kα (λ = 1.54178 Å) source (**7**). The structure of **3** was collected using synchrotron radiation. Data was collected as a series of φ and/or ω scans. Data integration down to 0.84 Å resolution was carried out using SAINT V8.37 A[20] with reflection spot size optimization. Absorption corrections were made with the program SADABS.[21,22] Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[22] and SHELXL-2014[23] with the OLEX2 interface.[24] The program PLATON was employed to confirm the absence of higher symmetry space groups.[25] All non-H atoms, including the disorder fragments, were located in difference Fourier maps, and then refined anisotropically. The restraints on bond lengths and constraints of the atomic displacement parameters on each pair of disorder fragments (SADI/SAME and EADP instructions of SHELXL-2014)[23] as well as the restraints of the atomic displacement parameters (SIMU/RIGU instructions of SHELXL-2014) if necessary, have been applied for the disorder refinement.[26] All non-hydrogen atoms were refined anisotropically. Outlier reflections were omitted from refinement when appropriate. Hydrogen atoms on C atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the atoms they are linked to (1.5 times for methyl groups). Crystallographic refinement details, including disorder modeling and software employed, have been delineated within in each crystallographic information file (*.*cif*).

Molecular graphics were generated using POV-Ray v3.7.[27]

Specific structural refinement details are as followed:

(^{Mes}dmx)Cu$_2$(NCMe)$_2$ (1). The structure was solved in the monoclinic space group P 2_1/n with one molecule of copper-containing complex per asymmetric unit and four molecules per unit cell. One molecule of acetonitrile and one molecule of diethyl ether were located and refined at full occupancy. CCDC Identifier: 1948008.

(^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (2). The structure was solved in the triclinic space group $P\bar{1}$ with one molecule of copper-containing complex per asymmetric unit and two molecules per unit cell. Two molecules of diethyl ether were located and refined at full occupancy, one of which exhibited positional disorder and was modeled using similarity constraints and restraints. CCDC Identifier: 1948009.

(^{Mes}dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (3). The structure was solved in the monoclinic space group C2/c with one molecule of copper-containing complex per asymmetric unit and four molecules per unit cell. The solvent mask function in Olex2 was applied to correct for electron density contributing from a putative highly disordered diethyl ether molecule. CCDC Identifier: 1948010.

($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe)) (5). The structure was solved in the monoclinic space group P 2_1/n with two molecules of copper-containing complex per asymmetric unit and eight molecules per unit cell. Two molecules of acetonitrile were located and refined to full occupancy and 75 % occupancy. Two molecules of diethyl ether were located, one residing on a special position, and refined to full occupancy using similarity constraints and restraints. CCDC Identifier: 1948011.

($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$)) (6). The structure was solved in the orthorhombic space group P*na*2_1 with two molecules of copper-containing complex per asymmetric unit and sixteen molecules per unit cell. Two molecules of acetonitrile were located and refined with occupancies of unity The structure was refined as a Merohedral twin using the twin law [(-1.0, 0.0, 0.0), (0.0, -1.0, 0.0), (0.0, 0.0, -1.0)]. The trifluoromethyl substituents were rotationally disordered and modeled in parts using restraints and constraints. The *tert*-butyl substituents were rotationally disordered and modeled in parts using restraints and constraints. CCDC Identifier: 1948012.

[(K(C$_{222}$)][(^{Mes}dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (7). The structure was solved in the monoclinic space group P 2_1/n with one molecule of copper-containing complex with an outer-sphere cryptand-encapsulated potassium counterion per asymmetric unit and four molecules in the unit cell. A highly disordered, diffuse benzene/tetrahydrofuran channel was observed, and attempts at producing a chemically reasonable model required excessive application of similarity restraints

and constraints. A solvent mask was subsequently applied to remove unrefined electron density. Several reflections were co-incidental with the beamstop and were omitted from refinement.

In several crystal mounting attempts, we observed rapid crystal degradation upon allowing the crystal to stand in Paratone at room temperature over seconds. This degradation is denoted by a color change from brown-pink to deep red and a smearing of reflections in the diffraction pattern. The changes in diffraction pattern may be similarly attributed to the desolvation of the unit cell. The recorded data set represents the best data quality after employing an optimized mounting protocol to minimize exposure to room temperature, multiple data collection sets, and multiple crystallization attempts. CCDC Identifier: 1948013.

[(K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(C$_6$H$_4$OMe))] (8). The structure was solved in the monoclinic space group P 2_1/n with one molecule of copper-containing complex with an outer-sphere cryptand-encapsulated potassium counterion per asymmetric unit and four molecules per unit cell. One diethyl ether molecule was located and refined at full occupancy. A second diethyl ether molecule was refined with partial occupancy (75 % occupancy) with the oxygen atom disordered over two sites. Two sets of the *tert*-butyl substituents exhibited rotational disorder, addressed using similarity restraints and constraints. CCDC Identifier: 1948014.

[(K(C$_{222}$)][($^{t\text{Bu}}$dmx)Cu$_2$(μ^2–N(3,5-(F$_3$C)$_2$C$_6$H$_3$))] (9). The structure was solved in the monoclinic space group P 2_1/n with one molecule of copper-containing complex with an outer-sphere cryptand-encapsulated potassium counterion per asymmetric unit and four molecules per unit cell. One set of *tert*-butyl substituents exhibited part rotational disorder, addressed using similarity restraints and constraints. Rotational disorder for one trifluoromethyl substituent was modeled using similarity constraints and restraints. CCDC Identifier: 1948015.

($^{t\text{Bu}}$L)Cu(NCMe) (10). The structure was solved in the monoclinic space group C 2/c with one molecule of copper-containing complex per asymmetric unit and four molecules per unit cell. An acetonitrile molecule was modeled at full occupancy. CCDC Identifier: 1948016.

[($^{t\text{Bu}}$L)CuCl]$_2$ (11). The structure was solved in the monoclinic space group P 2_1/n with one molecule of copper-containing complex per asymmetric unit and four molecules per unit cell. A

benzene molecule was modeled with full occupancy. Several reflections were co-incidental with the beamstop and were omitted from refinement. CCDC Identifier: 1948017.

(^{Mes}dmx)Cu$_2$(PMe$_3$)$_2$ (12). The structure was solved in the triclinic space group $P\bar{1}$ with one molecule of copper-containing complex per asymmetric unit and two molecules per unit cell. A single disordered tetrahydrofuran molecule was located and refined at full occupancy with similarity restraints and constraints. Several reflections were co-incidental with the beamstop and were omitted from refinement. CCDC Identifier: 1948018.

($^{t\text{Bu}}$dmx)Cu$_2$(PPh$_3$)$_2$ (13). The structure was solved in the monoclinic space group C 2/c with two molecule of copper-containing complexes per asymmetric unit and eight molecules per unit cell. Four sets of the *tert*-butyl substituents exhibited rotational disorder, addressed using similarity restraints and constraints. One phenyl ring within the triphenylphosphine motif was disordered and modeled with similarity constraints and restraints. Three molecules of toluene were located and refined with partial occupancies using similarity restraints and constraints. A disordered benzene molecule was located and modeled using similarity restraints and constraints. Several reflections were co-incidental with the beamstop and were omitted from final refinement, resulting in a 'B'-level CheckCif alert. CCDC Identifier: 1948019.

(^{Mes}dmx)Cu$_2$(CN^{t}Bu)$_2$ (14). The structure was solved in the triclinic space group $P\bar{1}$ with one molecule of copper-containing complex per asymmetric unit and two molecules per unit cell. One set of the *tert*-butyl substituents within the isocyanide motif exhibited rotational disorder, which was addressed with similarity constraints. Two molecules of tetrahydrofuran (50 % occupancy, 25 % occupancy) were overlapping two molecules of diethyl ether (50 % occupancy, 25 % occupancy) and modeled with similarity constraints and restraints. Several reflections were co-incidental with the beamstop and were omitted from refinement. CCDC Identifier: 1948020.

($^{t\text{Bu}}$dmx)Cu$_2$(CN^{t}Bu)$_2$ (15). The structure was solved in the monoclinic space group P 2_1/n with one molecule of copper-containing complex per asymmetric unit and four molecules per unit cell. One set of the *tert*-butyl substituents within the isocyanide motif exhibited rotational disorder, which was addressed with similarity constraints. A disordered tetrahydrofuran molecule

was refined at full occupancy using similarity constraints and restraints. CCDC Identifier: 1948021.

(^{Mes}dmx)Cu$_2$(dmap)$_2$ (16). The structure was solved in the monoclinic space group P 2$_1$/n with one molecule of copper-containing complex per asymmetric unit and four molecules per unit cell. The dimethylxanthene backbone was disordered over two positions and refined appropriately. Molecules of overlapping diethyl ether and tetrahydrofuran were modeled using similarity constraints and restraints. CCDC Identifier: 1948022.

($^{t\text{Bu}}$L)$_2$Cu$_2$ (**18**). The structure was solved in the monoclinic space group P 2$_1$/n with one molecule of copper-containing complex per asymmetric unit. CCDC Identifier: 1948023.

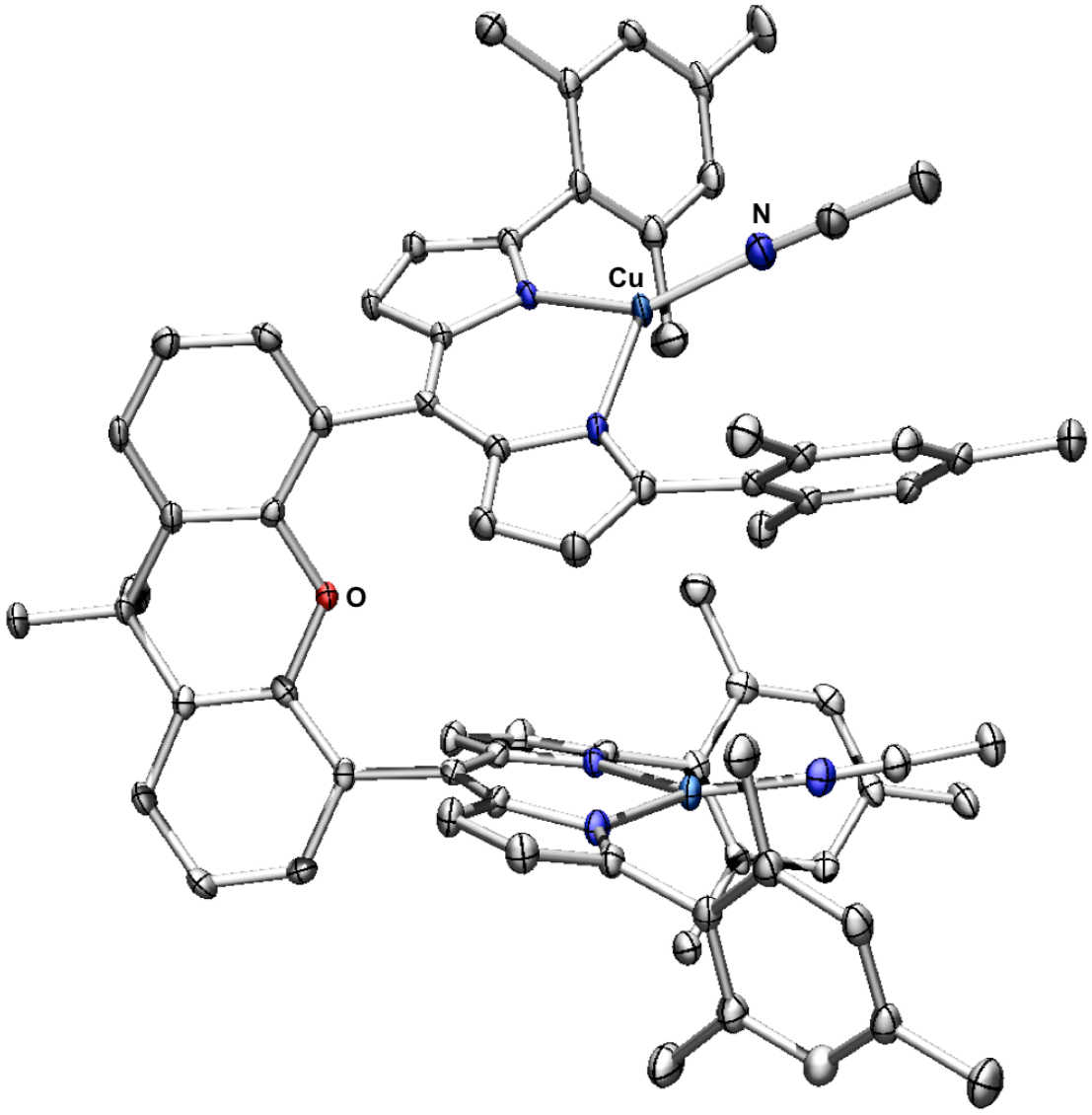


Figure S–73. Solid-state molecular structure of (^{Mes}dmx)Cu_2(NCMe)$_2$ (**1**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), O (red).

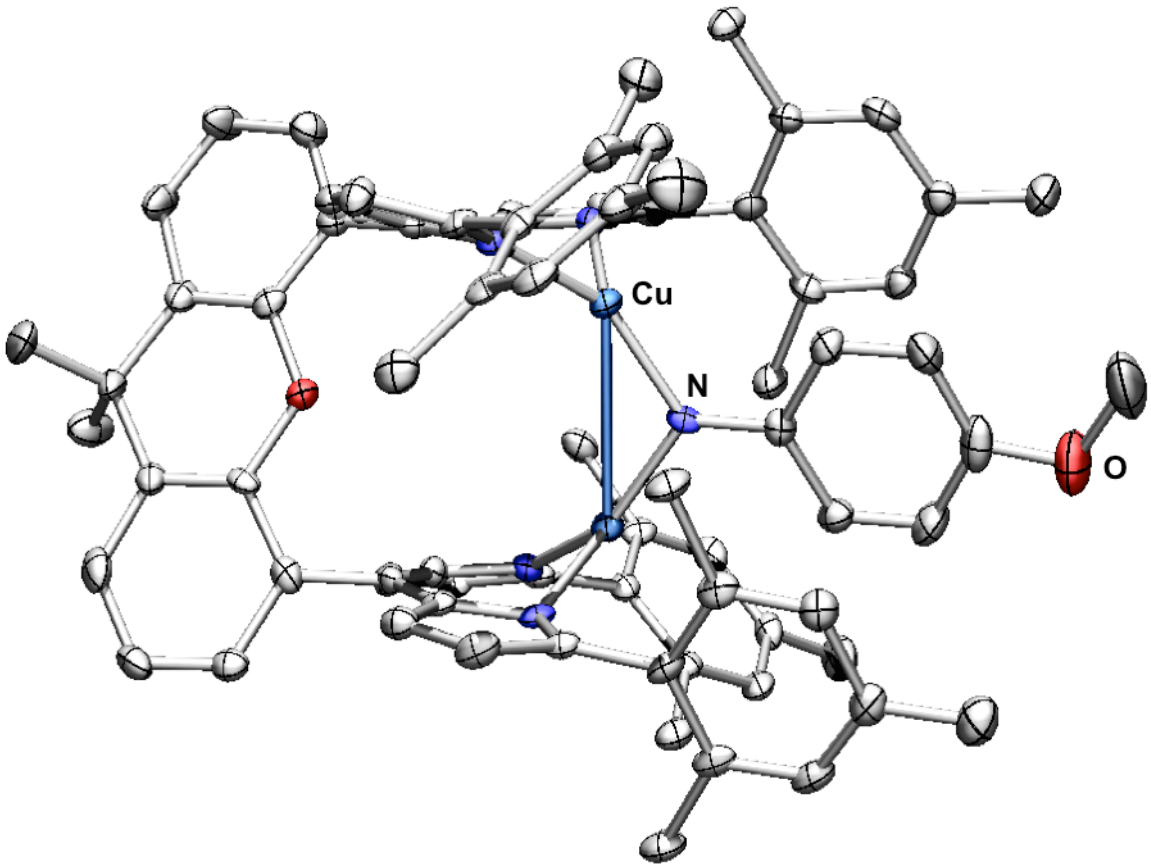


Figure S–74. Solid-state molecular structure of (^{Mes}dmx)Cu_2(μ^2–N(C_6H_4OMe)) (**2**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), O (red).

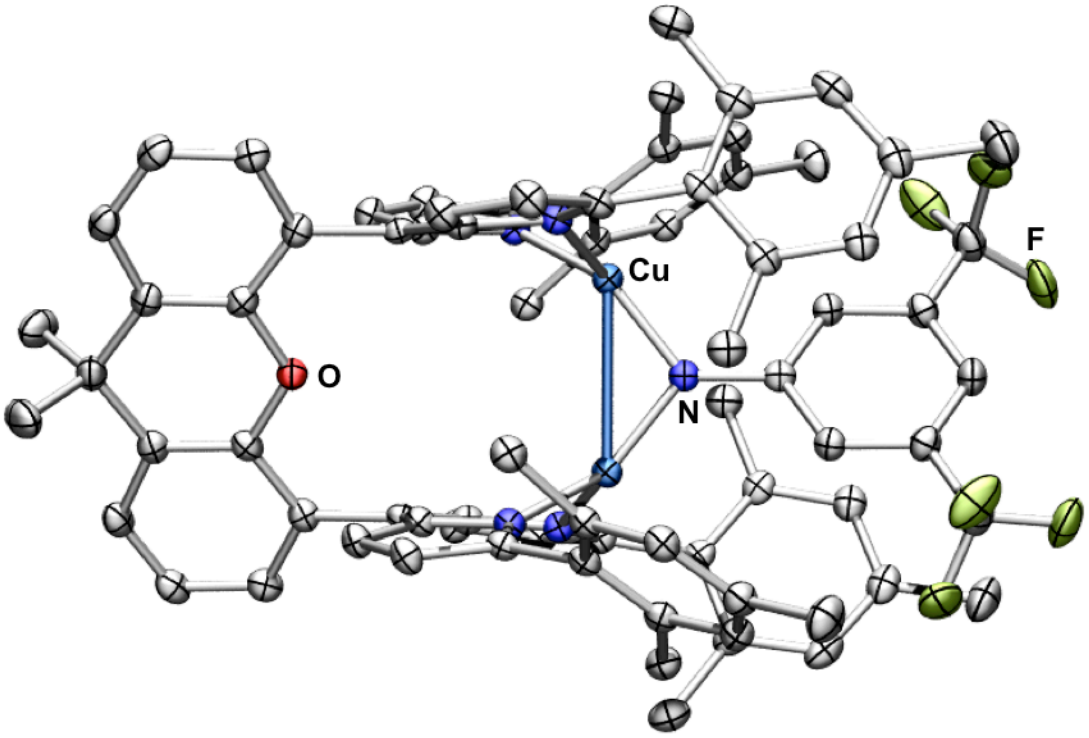


Figure S–75. Solid-state molecular structure of (^{Mes}dmx)Cu_2(μ^2–N(3,5-$(CF_3)_2C_6H_3$)) (**3**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms, solvent molecules, and rotational disorder of the trifluoromethyl units are omitted for clarity. Color scheme: Cu (cobalt blue), F (yellow-green), N (blue), O (red).

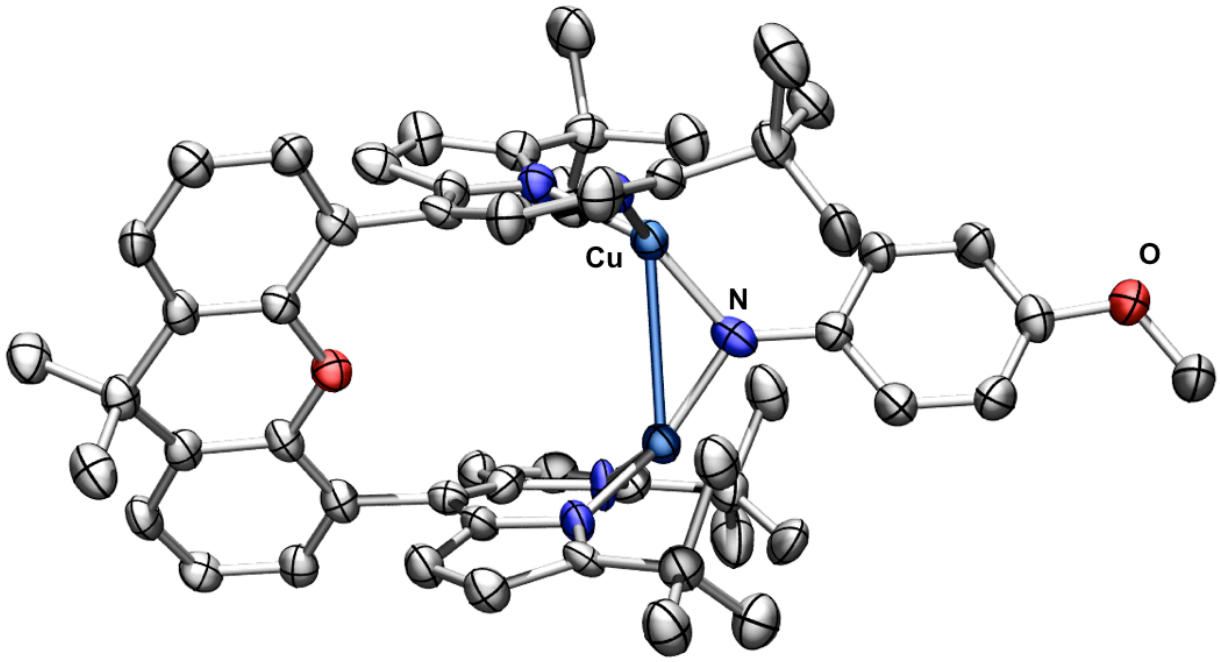


Figure S–76. Solid-state molecular structure of ($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(C_6H_4OMe)) (**5**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules in the unit cell are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), O (red).

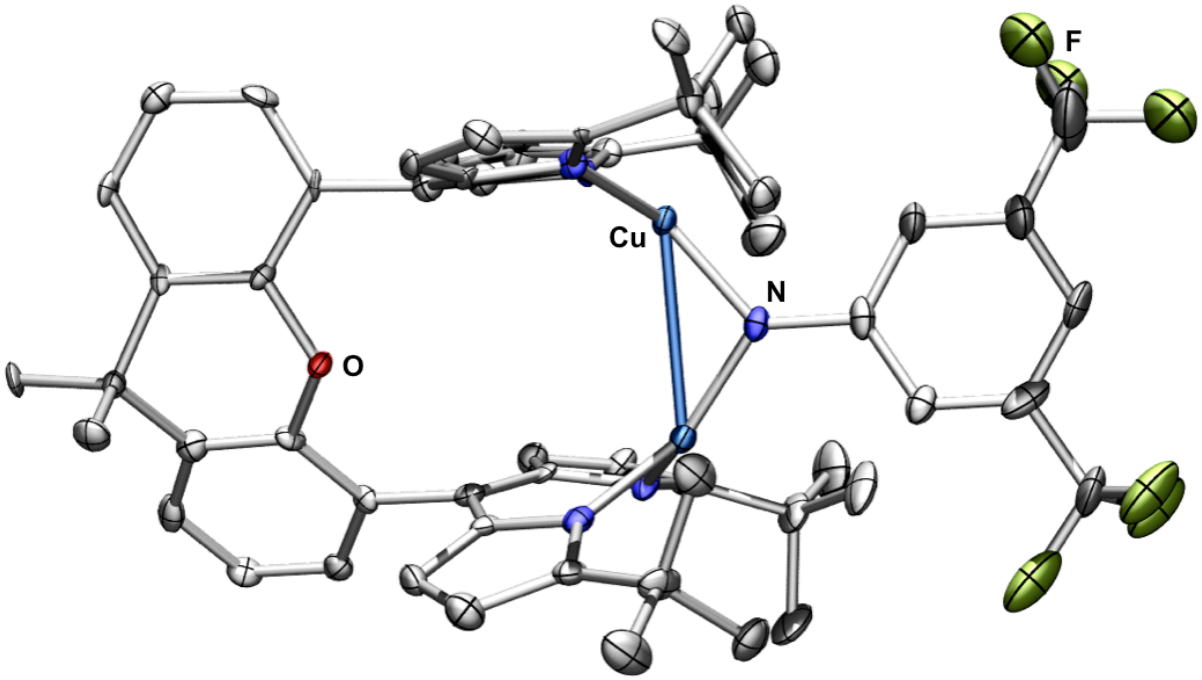


Figure S–77. Solid-state molecular structure of ($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(CF_3)_2C_6H_3$)) (**6**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms, disorder, and solvent molecules in the unit cell are omitted for clarity. Color scheme: Cu (cobalt blue), F (yellow-green), N (blue), O (red).

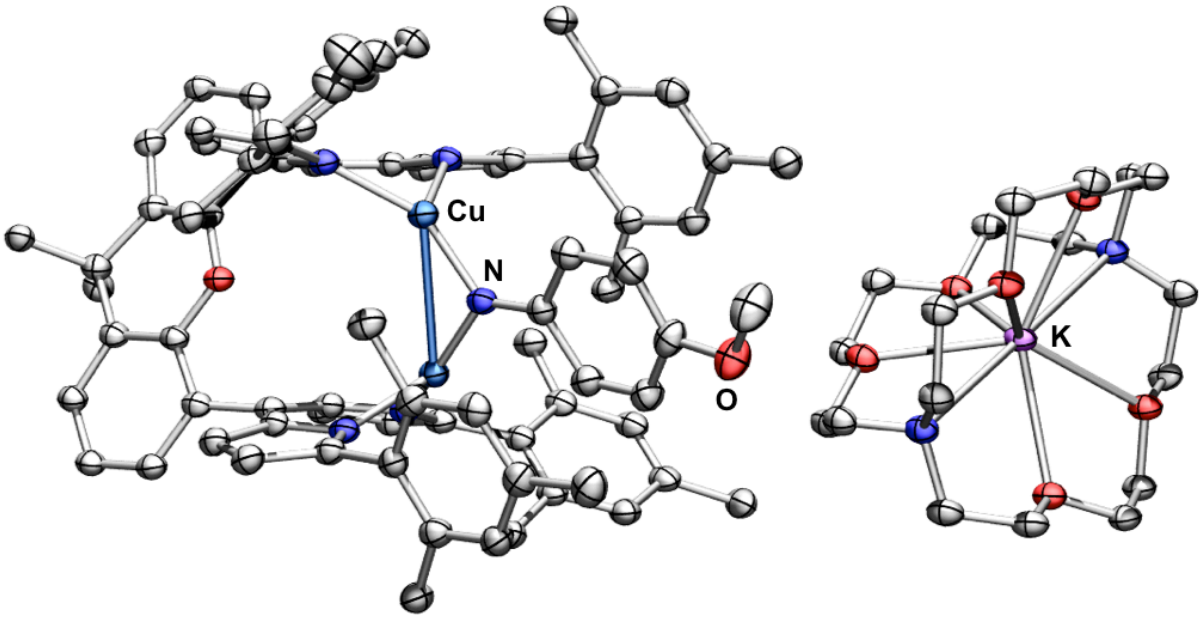


Figure S–78. Solid-state molecular structure of $[K(C_{222})][(^{tBu}dmx)Cu_2(\mu^2\text{–}N(C_6H_4OMe))]$ (**7**) with thermal ellipsoids at 35 % probability level. Hydrogen atoms and solvent molecules in the unit cell are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), K (purple) O (red).

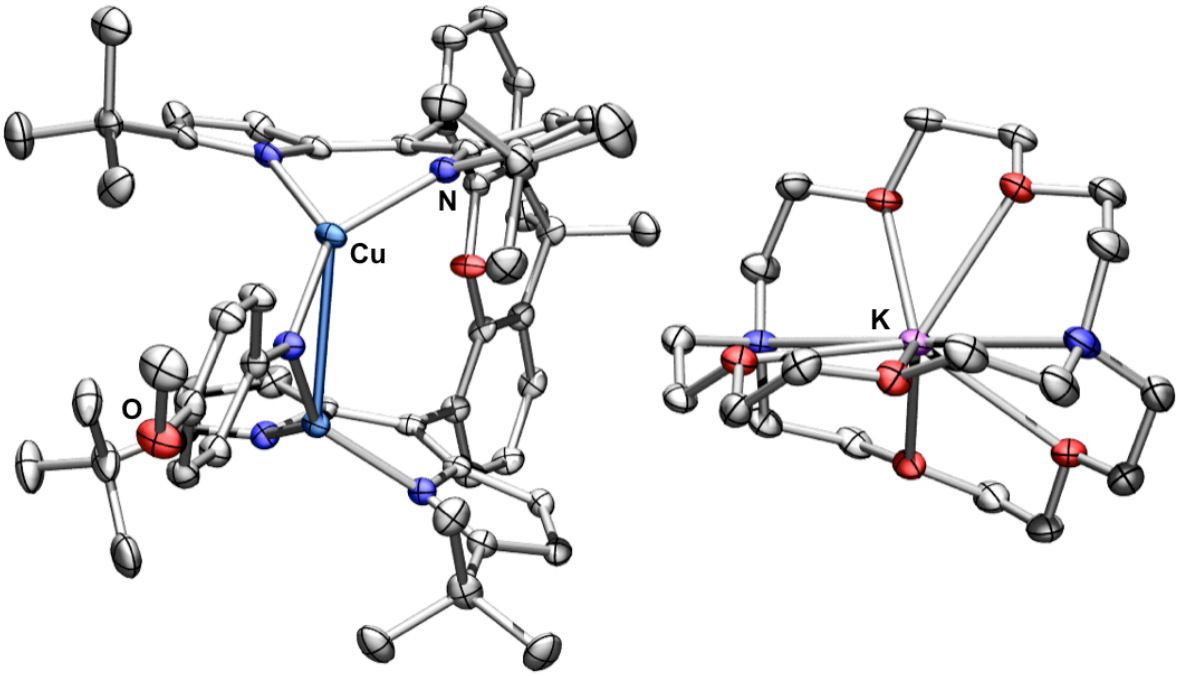


Figure S–79. Solid-state molecular structure of [K(C_{222})]($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**8**) with thermal ellipsoids at 50% probability level. Hydrogen atoms, disorder, and solvent molecules in the unit cell are omitted for clarity. Color scheme: Cu (cobalt blue), K (purple), N (blue), O (red).

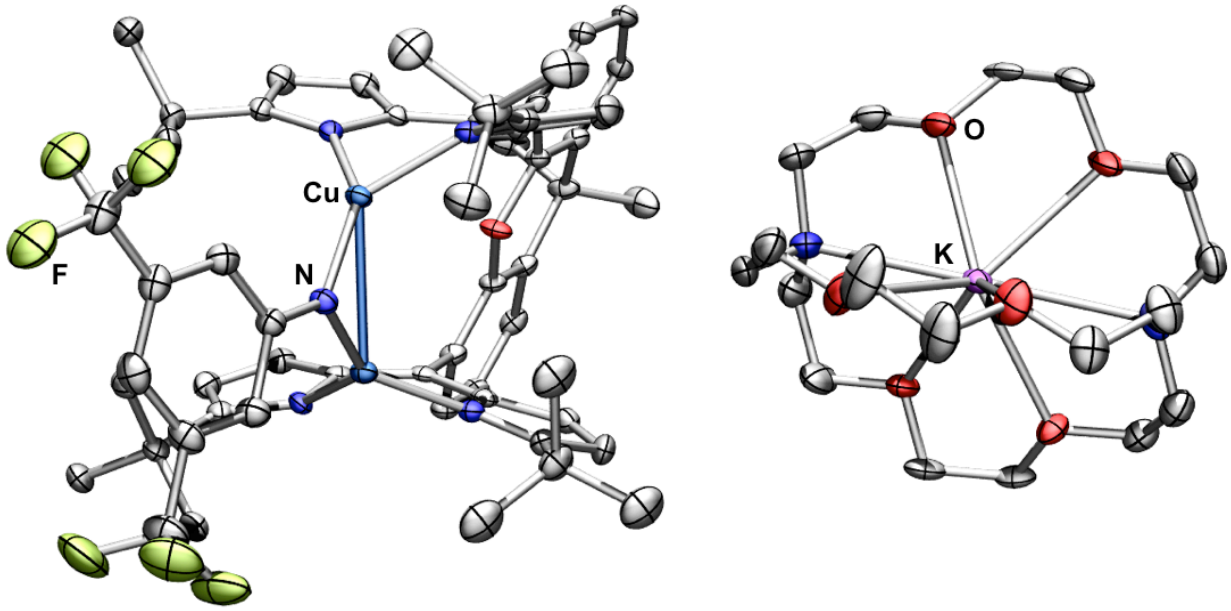


Figure S–80. Solid-state molecular structure of [K(C_{222})]($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(F_3C)_2C_6H_3$))] (**9**) with thermal ellipsoids at 50% probability level. Hydrogen atoms, disorder, and solvent molecules in the unit cell are omitted for clarity. Color scheme: Cu (cobalt blue), F (yellow-green), K (purple), N (blue), O (red).

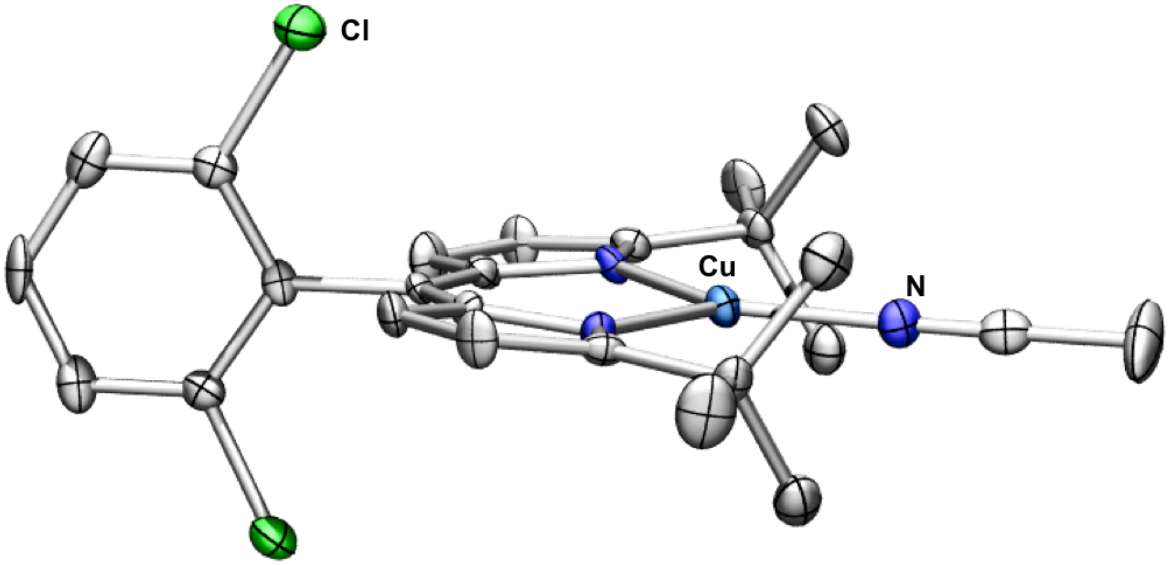


Figure S–81. Solid-state molecular structure of ($^{t\text{Bu}}$L)Cu(NCMe) (**10**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), Cl (green), N (blue).

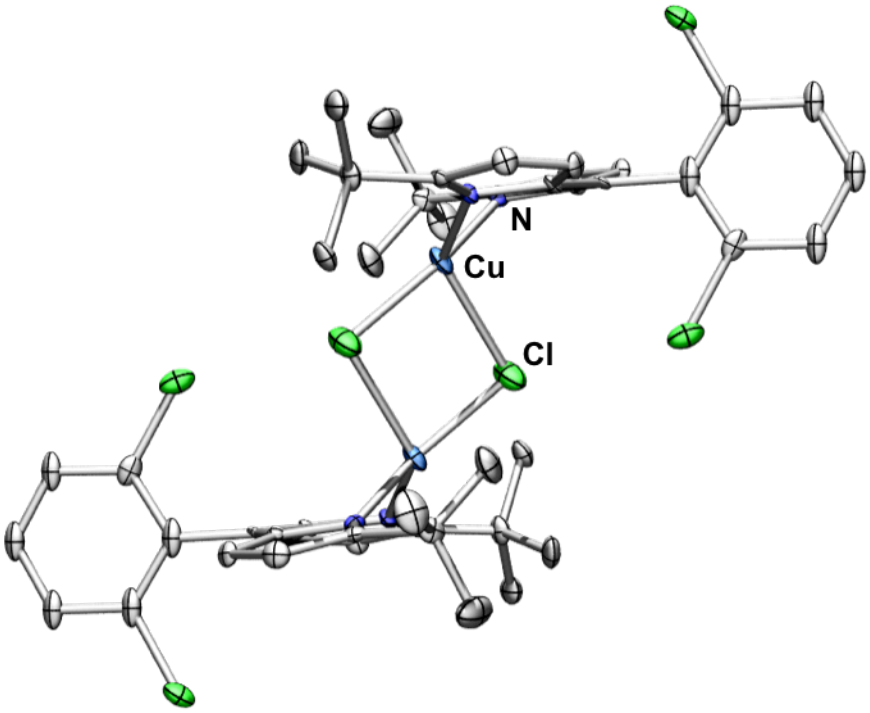


Figure S–82. Solid-state molecular structure of [($^{t\text{Bu}}$L)CuCl]$_2$ (**11**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), Cl (green), N (blue).

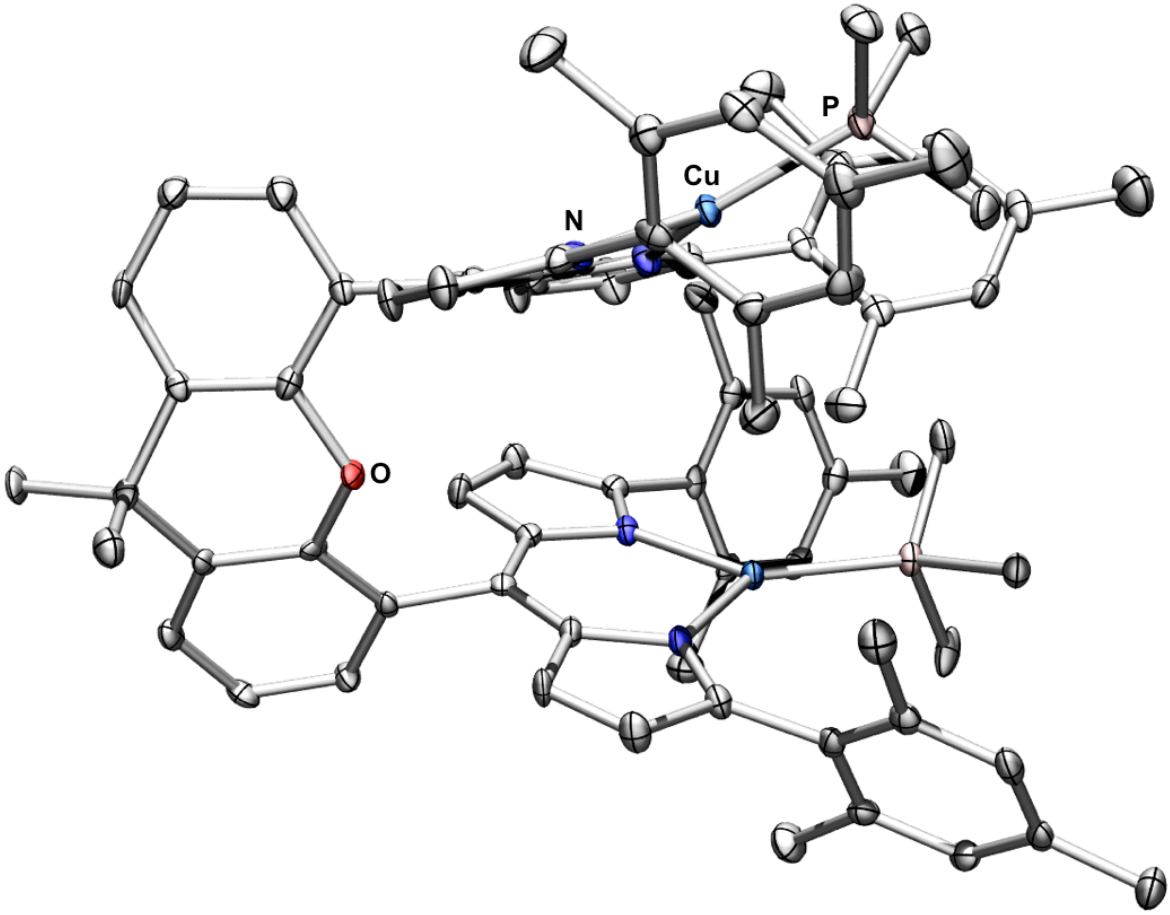


Figure S–83. Solid-state molecular structure of (^{Mes}dmx)$Cu_2(PMe_3)_2$ (**12**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), O (red), P (pink).

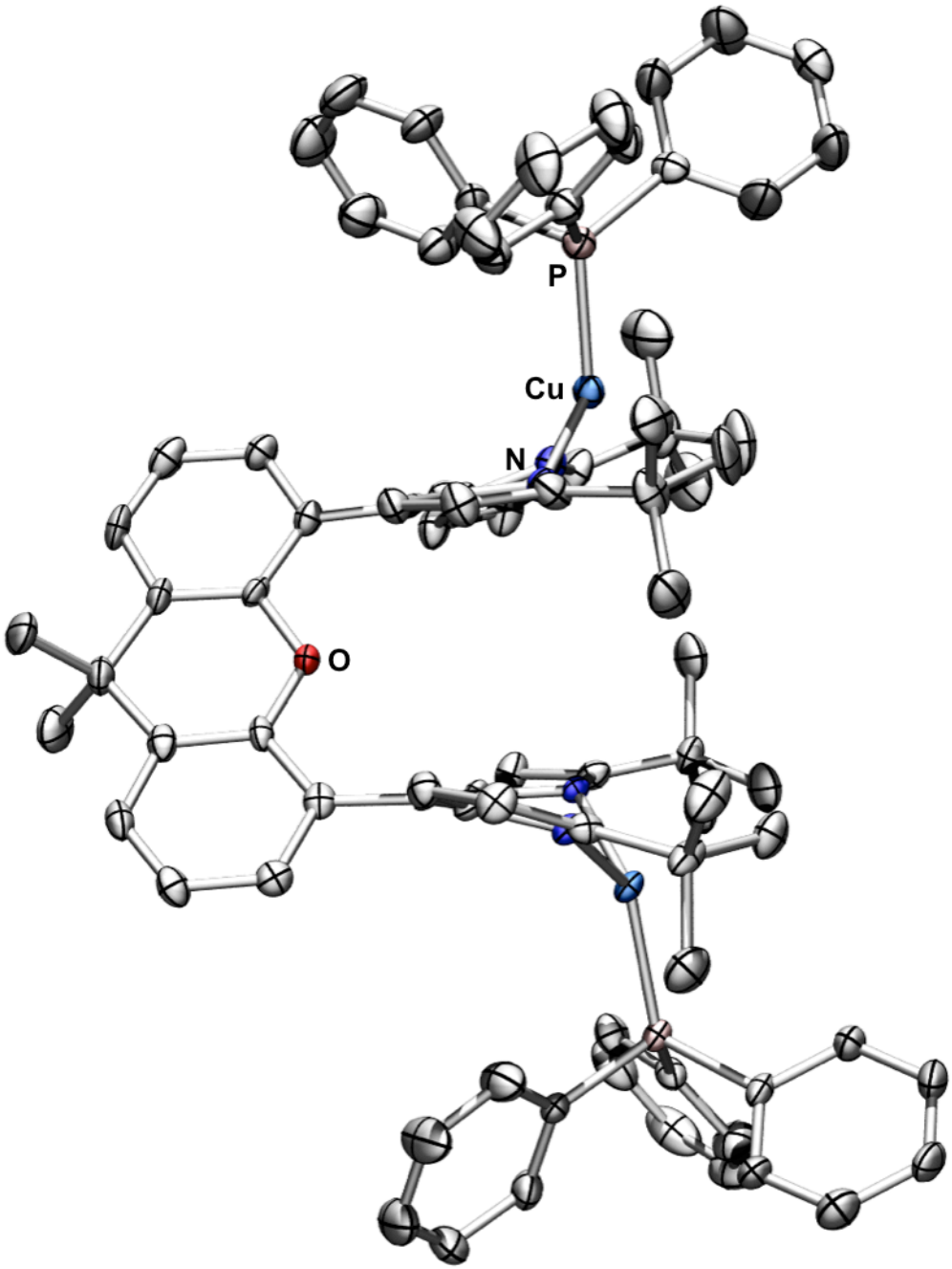


Figure S–84. Solid-state molecular structure of ($^{t\text{Bu}}$dmx)$Cu_2(PPh_3)_2$ (**13**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), O (red), P (pink).

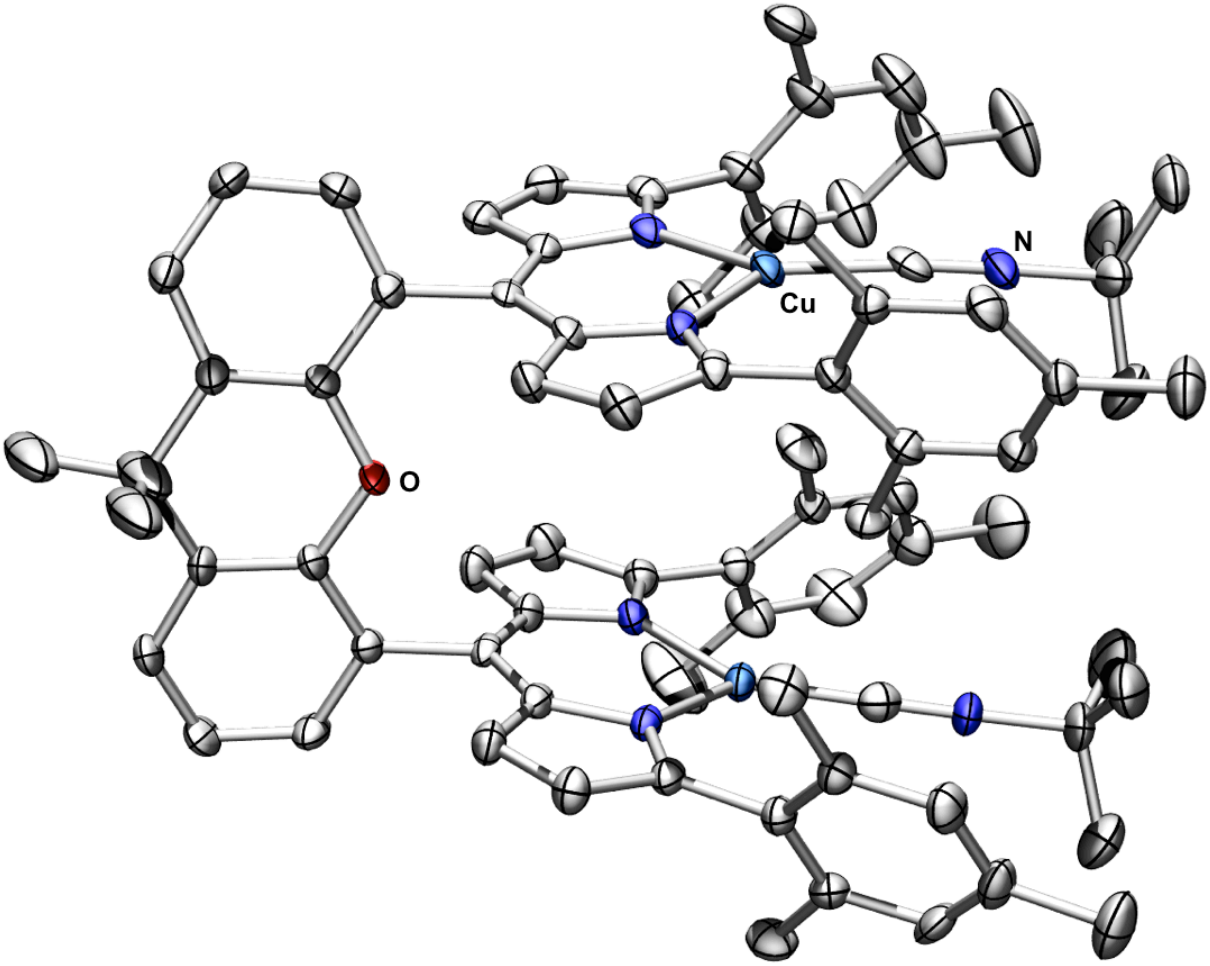


Figure S–85. Solid-state molecular structure of (^{Mes}dmx)Cu_2(CN^tBu)$_2$ (**14**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), O (red).

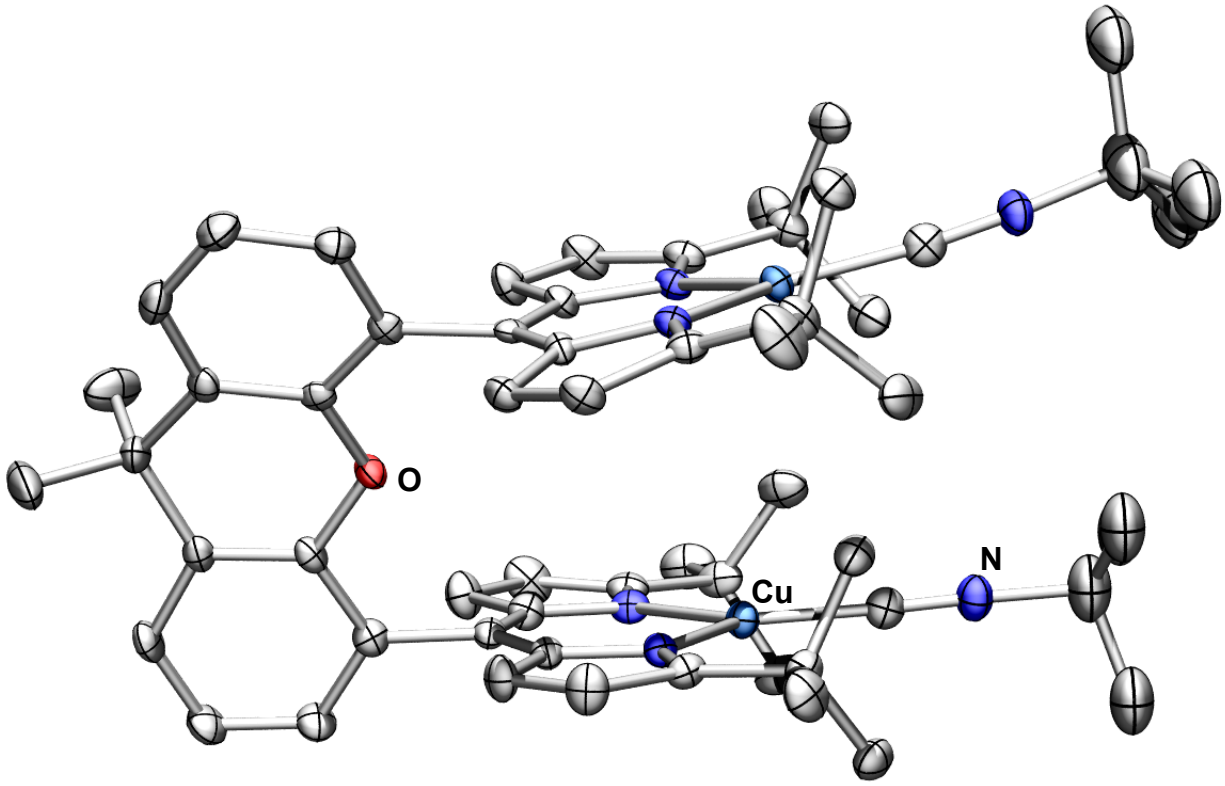


Figure S–86. Solid-state molecular structure of ($^{t\text{Bu}}$dmx)Cu_2(CN^{t}Bu)$_2$ (**15**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), O (red).

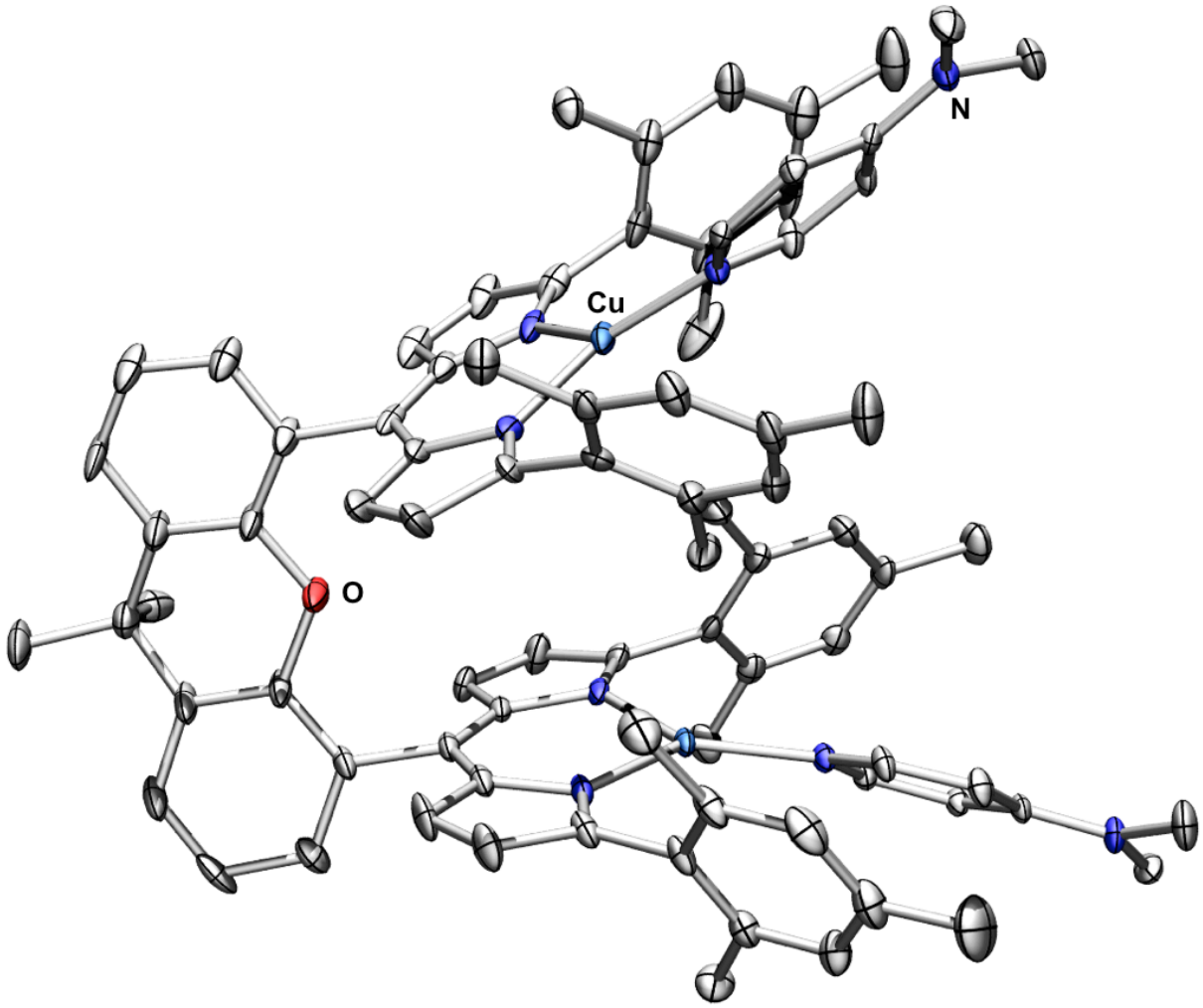


Figure S–87. Solid-state molecular structure of (^{Mes}dmx)Cu_2(CN^tBu)$_2$ (**16**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), N (blue), O (red).

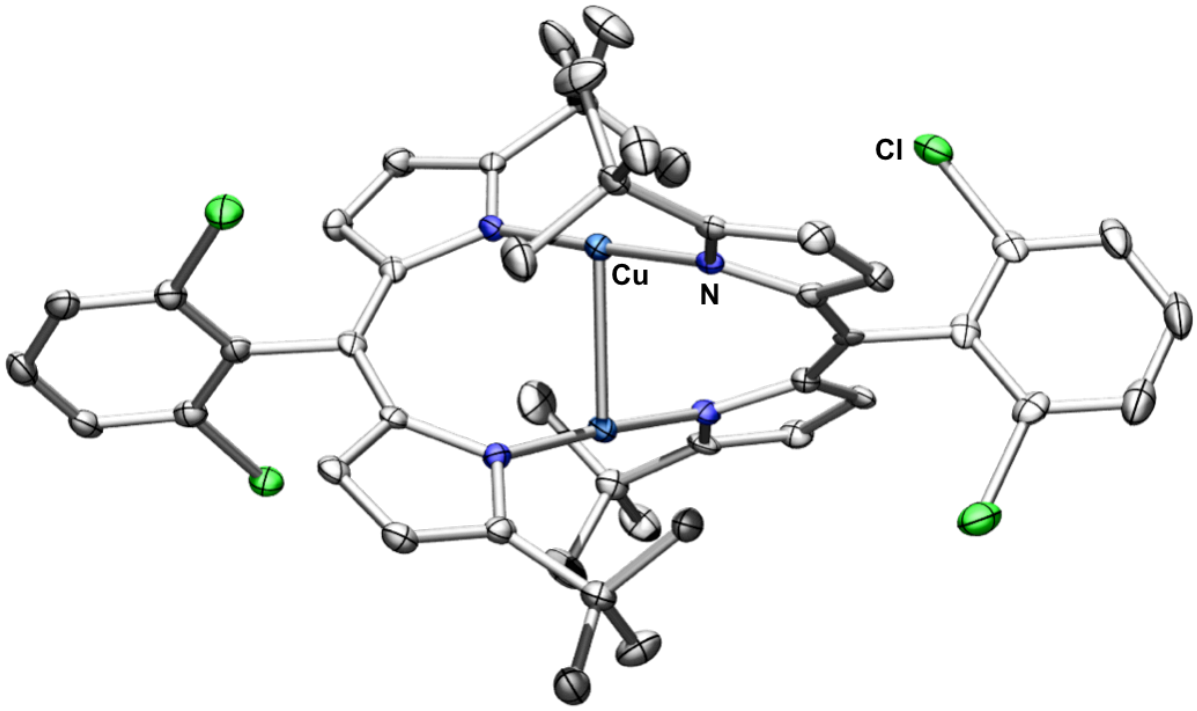


Figure S–88. Solid-state molecular structure of [(^{tBu}L)Cu]$_2$ (**18**) with thermal ellipsoids at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color scheme: Cu (cobalt blue), Cl (green), N (blue).

Table S–3. Selected Bond Parameters for (^{Mes}dmx)$Cu_2(NCMe)_2$ (**1**).

$Cu1–N_{dipyrrin}$	1.938(3) Å	$Cu2–N_{dipyrrin}$	1.931(3) Å
$Cu1–N_{dipyrrin}$	1.991(3) Å	$Cu2–N_{dipyrrin}$	2.002(3) Å
$Cu1–N_{acetonitrile}$	1.869(3) Å	$Cu2–N_{acetonitrile}$	1.869(3) Å

Table S–4. Selected Bond Parameters for (^{Mes}dmx)$Cu_2(\mu^2–N(C_6H_4OMe))$ (**2**).

$Cu1–N_{dipyrrin}$	1.949(4) Å	$Cu2–N_{dipyrrin}$	1.925(4) Å
$Cu1–N_{dipyrrin}$	1.930(4) Å	$Cu2–N_{dipyrrin}$	1.962(3) Å
$Cu1–N_{Ar}$	1.822(4) Å	$Cu2–N_{Ar}$	1.802(3) Å
Cu1–Cu2	2.822(1) Å	$N_{Ar}–C_{ipso}$	1.375(6) Å

Table S–5. Selected Bond Parameters for (^{Mes}dmx)$Cu_2(\mu^2–N(3,5\text{-}(F_3C)_2C_6H_3))$ (**3**).[†]

$Cu–N_{dipyrrin}$	1.923(2) Å
$Cu–N_{dipyrrin}$	1.937(2) Å
$Cu–N_{Ar}$	1.814(4) Å
Cu–Cu	2.844(1) Å
$N_{Ar}–C_{ipso}$	1.406(4) Å

[†]Cu1 and Cu2 are symmetry-equivalent.

Table S–6. Selected Bond Parameters for (^{tBu}dmx)$Cu_2(\mu^2–N(C_6H_4OMe))$ (**5**).[†]

$Cu1–N_{dipyrrin}$	1.977(6), 1.935(7) Å	$Cu2–N_{dipyrrin}$	1.942(7), 1.976(7) Å
$Cu1–N_{dipyrrin}$	1.929(7), 1.956(7) Å	$Cu2–N_{dipyrrin}$	1.968(7), 1.950(6) Å
$Cu1–N_{Ar}$	1.821(7), 1.807(7) Å	$Cu2–N_{Ar}$	1.822(7), 1.813(7) Å
Cu1–Cu2	2.856(1), 2.837(1) Å	$N_{Ar}–C_{ipso}$	1.390(10), 1.383(10) Å

[†]Two inequivalent copper-containing molecules are present in the asymmetric unit.

Table S–7. Selected Bond Parameters for ($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(F_3C)_2C_6H_3$)) (**6**).[†]

Cu1–$N_{dipyrrin}$	1.932(7), 1.929(7) Å	Cu2–$N_{dipyrrin}$	1.927(8), 1.963(7) Å
Cu1–$N_{dipyrrin}$	1.931(7), 1.934(8) Å	Cu2–$N_{dipyrrin}$	1.931(8), 1.957(8) Å
Cu1–N_{Ar}	1.812(7), 1.818(7) Å	Cu2–N_{Ar}	1.830(8), 1.827(8) Å
Cu1–Cu2	2.884(2), 2.875(2) Å	N_{Ar}–C_{ipso}	1.392(12), 1.386(12) Å

[†]Two inequivalent copper-containing molecules are present in the asymmetric unit.

Table S–8. Selected Bond Parameters for [K(C_{222})][($^{\text{Mes}}$dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**7**).

Cu1–$N_{dipyrrin}$	1.958(2) Å	Cu2–$N_{dipyrrin}$	1.972(3) Å
Cu1–$N_{dipyrrin}$	2.058(3) Å	Cu2–$N_{dipyrrin}$	2.039(3) Å
Cu1–N_{Ar}	1.852(3) Å	Cu2–N_{Ar}	1.848(3) Å
Cu1–Cu2	2.9031(7) Å	N_{Ar}–C_{ipso}	1.318(5) Å
C_{ipso}–C_{ortho}	1.428(5) Å	C_{ipso}–C_{ortho}	1.438(5) Å

Table S–9. Selected Bond Parameters for [K(C_{222})][($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(C_6H_4OMe))] (**8**).

Cu1–$N_{dipyrrin}$	2.028(2) Å	Cu2–$N_{dipyrrin}$	2.068(2) Å
Cu1–$N_{dipyrrin}$	2.005(2) Å	Cu2–$N_{dipyrrin}$	1.985(2) Å
Cu1–N_{Ar}	1.860(2) Å	Cu2–N_{Ar}	1.869(2) Å
Cu1–Cu2	2.9558(7) Å	N_{Ar}–C_{ipso}	1.351(3) Å
C_{ipso}–C_{ortho}	1.438(4) Å	C_{ipso}–C_{ortho}	1.417(3) Å

Table S–10. Selected Bond Parameters for [K(C_{222})][($^{t\text{Bu}}$dmx)Cu_2(μ^2–N(3,5-$(F_3C)_2C_6H_3$))] (**9**).

Cu1–$N_{dipyrrin}$	2.006(2) Å	Cu2–$N_{dipyrrin}$	1.973(2) Å
Cu1–$N_{dipyrrin}$	1.999(2) Å	Cu2–$N_{dipyrrin}$	2.043(2) Å
Cu1–N_{Ar}	1.853(2) Å	Cu2–N_{Ar}	1.860(2) Å
Cu1–Cu2	2.8401(5) Å	N_{Ar}–C_{ipso}	1.342(3) Å
C_{ipso}–C_{ortho}	1.435(4) Å	C_{ipso}–C_{ortho}	1.420(4) Å

Table S–11. Selected Bond Parameters for ($^{t\text{Bu}}$L)Cu(NCMe) (**10**).

Cu–$N_{dipyrrin}$	1.968(4) Å
Cu–$N_{dipyrrin}$	1.965(4) Å
Cu–N_{Ar}	1.881(4) Å

Table S–12. Selected Bond Parameters for [($^{t\text{Bu}}$L)CuCl]$_2$ (**11**).†

Cu–$N_{dipyrrin}$	1.920(3) Å
Cu–$N_{dipyrrin}$	1.971(3) Å
Cu–Cl	2.222(2) Å

†Cu1 and Cu2 within the dimer are symmetry-equivalent.

Table S–13. Selected Bond Parameters for ($^{\text{Mes}}$dmx)Cu$_2$(PMe$_3$)$_2$ (**12**).

Cu1–$N_{dipyrrin}$	1.984(3) Å	Cu2–$N_{dipyrrin}$	1.985(4) Å
Cu1–$N_{dipyrrin}$	1.979(4) Å	Cu2–$N_{dipyrrin}$	1.981(3) Å
Cu1–P	2.160(2) Å	Cu2–P	2.169(2) Å

Table S–14. Selected Bond Parameters for ($^{t\text{Bu}}$dmx)Cu$_2$(PPh$_3$)$_2$ (**13**).†

Cu1–$N_{dipyrrin}$	1.943(6), 2.004(5) Å	Cu2–$N_{dipyrrin}$	1.998(4), 1.953(4) Å
Cu1–$N_{dipyrrin}$	1.992(4), 1.949(4) Å	Cu2–$N_{dipyrrin}$	1.963(5), 1.988(4) Å
Cu1–P	2.149(2), 2.151(2) Å	Cu2–P	2.156(2), 2.153(2) Å

†Two inequivalent copper-containing molecules are present in the asymmetric unit.

Table S–15. Selected Bond Parameters for ($^{\text{Mes}}$dmx)Cu$_2$(CN^{t}Bu)$_2$ (**14**).

Cu1–$N_{dipyrrin}$	1.965(4) Å	Cu2–$N_{dipyrrin}$	1.954(4) Å
Cu1–$N_{dipyrrin}$	1.955(3) Å	Cu2–$N_{dipyrrin}$	1.959(3) Å
Cu1–CN^{t}Bu	1.819(5) Å	Cu2– CN^{t}Bu	1.820(4) Å

Table S–16. Selected Bond Parameters for ($^{t\text{Bu}}$dmx)Cu_2(CN^tBu)$_2$ (**15**).

Cu1–$N_{dipyrrin}$	1.978(2) Å	Cu2–$N_{dipyrrin}$	1.967(2) Å
Cu1–$N_{dipyrrin}$	1.960(2) Å	Cu2–$N_{dipyrrin}$	1.968(2) Å
Cu1–CN^tBu	1.833(3) Å	Cu2– CN^tBu	1.837(3) Å

Table S–17. Selected Bond Parameters for ($^{t\text{Bu}}$dmx)Cu_2(dmap)$_2$ (**16**).

Cu1–$N_{dipyrrin}$	1.983(4) Å	Cu2–$N_{dipyrrin}$	1.981(5) Å
Cu1–$N_{dipyrrin}$	2.005(4) Å	Cu2–$N_{dipyrrin}$	1.968(2) Å
Cu1–N_{DMAP}	1.955(4) Å	Cu2–N_{DMAP}	1.948(4) Å

Table S–18. Selected Bond Parameters for [$^{t\text{Bu}}$LCu]$_2$ (**18**).

Cu1–$N_{dipyrrin}$	1.862(2) Å	Cu2–$N_{dipyrrin}$	1.859(2) Å
Cu1–$N_{dipyrrin}$	1.867(2) Å	Cu2–$N_{dipyrrin}$	1.862(2) Å
Cu1–Cu2		2.443(2) Å	

DFT Calculations.

Density Functional Theory (DFT) calculations were performed with version 4.002 of the ORCA software package.[28] Cu K-edge, N K-edge XAS spectra were calculated using TDDFT. All spectra were calculated from crystallographic coordinates. Single-point energies were calculated by using the B3LYP functional.[29] The CP(PPP) basis set was used for Cu with a special integration accuracy (ORCA Grid7).[30] The scalar relativistically recontracted ZORA-def2-TZVP(-f) basis set[31] with ORCA Grid4 was used for all other atoms. Calculations included the zeroth-order regular approximation (ZORA)[32] for relativistic effects as implemented by van Wüllen.[33] Solvation was modeled with CPCM in an infinite dielectric.[34] A broken symmetry surface was used to optimize the neutral imidos [(BS) (1,1)] structures that converged as antiferromagnetically-coupled configurations. Here, the broken symmetry notation BS(*m,n*) denotes a system with (*m+n)* unpaired electrons and a net spin of $\frac{(m+n)}{2}$ if antiferromagnetically coupled. In particular, one fragment bears *m* α-spin electrons while the second fragment bears *n* β-spin electrons.

Multireference character in the ground state of **5** and **6** was investigated using SORCI calculations. SORCI was performed on a complete active space (CAS) for a truncated models of **5** and **6** comprising 10 electrons and 9 orbitals [CAS(10,9)]. A total of 5 singlet and 5 triplet states were calculated. Sufficiency of the active space was evaluated by ensuring that it captured ca. 90% of chosen state references without requiring holes or particles outside the active orbitals. The ZORA-def2-TZVP(-f) basis set[31] was used on Cu and N, and ZORA-def2-SVP was used on all other atoms. The ZORA relativistic correction[32] was used in all SORCI calculations. As described elsewhere,[35] individual selection was used to ease the computational burden. The size of the first-order interacting space was reduced with a threshold: $T_{sel} = 10^{-6}$ E_h. A further approximation involved reducing the reference space through another selection: all initial references that contributed less than a second threshold ($T_{pre} = 10^{-5}$) to the zeroth-order states were rejected from the reference space. Starting orbitals were taken from unrestricted Kohn–Sham orbitals generated via B3LYP calculations using the aforementioned basis sets that were subsequently transformed to quasi-restricted orbitals (QROs).[36] These orbitals were then used in a CASSCF calculation, whereupon the resulting orbitals were used in the SORCI procedure.

EXAMPLE ORCA INPUT FILES

Geometry Optimization Calculation:

```
!UKS BP86 ZORA-def2-TZVP(-f) def2/J CPCM ZORA
!NormalPrint TightSCF Grid4 NoFinalGrid Opt PAL8 NumFreq

%scf Directresetfreq 1
    DIIS MaxEq 15
        end
    Shift Shift 0.5
         Erroff 0.1
          end
    MaxIter 500
    end

%maxcore 4000

* xyz Charge SpinMultiplicity
Coordinates
*
```

Single Point and TD-DFT XAS Calculations:

```
!WB97X RIJCOSX ZORA-def2-TZVP(-f) def2/J ZORA CPCM UKS PAL4
!NormalPrint TightSCF Grid4 NoFinalGrid UNO UCO

%basis newgto 3d Metal Atom "CP(PPP)"
          end

%tddft   NRoots 100
       MaxDim 1000
       OrbWin[0] = LowestEnergyDonorOrbital, HighestEnergyDonorOrbital, -1, -1
       OrbWin[1] = LowestEnergyDonorOrbital, HighestEnergyDonorOrbital, -1, -1
       DoQuad true
       end

%method SpecialGridAtoms Metal Atomic Number
      SpecialGridIntAcc 7
      end

%MaxCore 4000

%SCF
    MaxIter 500
    end
```

* xyz ***Charge SpinMultiplicity***
Coordinates
*

DFT-ROCIS XAS Calculation:

!B3LYP RIJCOSX ZORA-def2-TZVP(-f) def2/J ZORA CPCM ROKS PAL4
!NormalPrint TightSCF Grid4 NoFinalGrid UNO UCO MOREAD NOITER

%moinp "***TD-DFT FILENAME.qro***"

%basis newgto ***3d Metal Atom*** "CP(PPP)" end
end

%rocis NRoots 100
MaxDim 500
SOC false
DoRI true
DoQuad true
DoHigherMult false
DoLowerMult false
PrintLevel 3
Orbwin ***LowestEnergyDonorOrbital, HighestEnergyDonorOrbital***,0,500
DoDFTCIS true
DFTCIS_c = 0.21, 0.49, 0.29
end

%method SpecialGridAtoms ***Metal Atomic Number***
SpecialGridIntAcc 7
end

%MaxCore 4000

* xyz ***Charge SpinMultiplicity***
Coordinates

INPUT COORDINATES FOR ORCA CALCULATIONS

($^{t\text{Bu}}$L)Cu^{I}(NCMe)
Charge = 0, Spin Multiplicity = 1

Cu	0.00000	0.00000	0.00000
Cl	3.84033	3.46400	-1.48748
Cl	2.99207	2.39616	3.75947
N	1.85221	-0.37004	0.55401
N	0.00000	1.96619	0.00000
N	-1.37184	-1.23150	-0.38056
C	2.71763	0.72222	0.75992
C	2.61554	-1.48035	0.64484
C	3.97114	-1.13952	0.88587
H	4.69871	-1.74445	0.97496
C	3.43196	3.02992	1.16354
C	2.35447	2.06156	0.78107
C	1.12164	2.65034	0.48093
C	-0.94603	2.91260	-0.19784
C	5.35877	4.94770	1.86630
H	5.98931	5.61503	2.10806
C	-2.12339	-2.02783	-0.63271
C	4.72823	4.21424	2.84584
H	4.94604	4.35378	3.75943
C	3.78271	3.28164	2.49935
C	4.03338	0.21600	0.96468
H	4.81289	0.73186	1.12904
C	0.81634	4.02243	0.60236
H	1.39543	4.70513	0.92323
C	-2.31374	2.58794	-0.76006
C	5.07837	4.71428	0.53225
H	5.52736	5.20215	-0.14732
C	2.05880	-2.88144	0.51397
C	4.14054	3.76362	0.20367
C	-0.46341	4.18638	0.17376
H	-0.94412	5.00668	0.13171
C	-3.06798	3.88046	-1.09942
H	-3.20055	4.40545	-0.28195
H	-3.93897	3.65718	-1.48815
H	-2.54699	4.40441	-1.74271
C	-3.12371	1.79984	0.28516
H	-2.67073	0.95024	0.47701
H	-4.02073	1.62079	-0.06466
H	-3.19371	2.32741	1.10787
C	-2.17447	1.75968	-2.05428
H	-1.69648	2.28409	-2.72875

H	-3.06533	1.52951	-2.39110
H	-1.67345	0.94047	-1.86491
C	3.15562	-3.91439	0.79594
H	3.89380	-3.78597	0.16391
H	2.78923	-4.81717	0.69313
H	3.48518	-3.79832	1.71166
C	0.91902	-3.10379	1.52595
H	1.27220	-3.03206	2.43767
H	0.53527	-3.99799	1.39588
H	0.22373	-2.42777	1.38923
C	1.53169	-3.12373	-0.91532
H	0.87364	-2.43545	-1.14116
H	1.10811	-4.00656	-0.96185
H	2.27693	-3.08339	-1.55049
C	-3.08022	-3.08182	-0.96914
H	-2.59648	-3.91543	-1.15420
H	-3.59194	-2.81805	-1.76151
H	-3.69225	-3.22108	-0.21587

$[(^{t\text{Bu}}\text{L})\text{LCu}^{II}\text{Cl}]_2$, BS(1,1)
Charge = 0, Spin Multiplicity = 3

Cu	0.00000	0.00000	0.00000
Cl	3.73630	0.75563	2.28251
Cl	-0.88132	-2.02663	0.23579
Cl	3.54702	4.15336	-1.91675
N	-0.00000	1.92105	0.00000
C	3.73609	2.49541	0.21622
C	2.53868	0.67641	-0.94402
N	1.44002	-0.10015	-1.34511
C	2.45248	1.84647	-0.19347
C	4.39737	2.07509	1.36789
C	-0.90885	2.81739	0.43268
C	3.70129	0.15860	-1.57390
H	4.59036	0.47321	-1.46206
C	3.30500	-0.87418	-2.37078
H	3.86475	-1.40548	-2.92607
C	1.26276	2.47809	0.20402
C	-3.13580	3.49563	1.32583
H	-2.94433	4.43600	1.13038
H	-2.83146	3.28316	2.23263
H	-4.10043	3.33654	1.26010
C	-0.24629	3.98084	0.88891
H	-0.65836	4.76839	1.22447
C	1.89522	-1.00886	-2.22082
C	1.04188	-1.99101	-3.00891
C	1.10609	-3.37215	-2.32921
H	0.75196	-3.30440	-1.41740
H	2.03676	-3.67705	-2.29535
H	0.57118	-4.01338	-2.83979
C	-0.38946	-1.51071	-3.15757
H	-0.39453	-0.62255	-3.57027
H	-0.81116	-1.46236	-2.27465
H	-0.88718	-2.13759	-3.72236
C	-2.40092	2.60371	0.31950
C	4.31984	3.53791	-0.49559
C	1.10917	3.75921	0.75803
H	1.80550	4.35980	0.99790
C	5.52631	4.12497	-0.07877
H	5.92421	4.82113	-0.58822
C	1.62931	-2.13212	-4.42310
H	2.53272	-2.50691	-4.36546
H	1.66833	-1.25036	-4.85015
H	1.06218	-2.72829	-4.95475
C	5.57079	2.66217	1.81515

H	5.98514	2.36803	2.61744
C	-2.82910	2.96581	-1.09370
H	-2.34418	2.40481	-1.73554
H	-2.62474	3.90852	-1.26411
H	-3.79181	2.81549	-1.19112
C	6.12161	3.67864	1.07743
H	6.93011	4.08037	1.37010
C	-2.80413	1.15960	0.59765
H	-2.46331	0.88990	1.47669
H	-2.42692	0.57596	-0.09196
H	-3.78200	1.08603	0.58989
Cu	-0.63876	-2.01077	2.66183
Cl	-4.37506	-2.76639	0.37933
Cl	0.24256	0.01587	2.42605
Cl	-4.18577	-6.16413	4.57859
N	-0.63876	-3.93181	2.66184
C	-4.37484	-4.50618	2.44561
C	-3.17743	-2.68717	3.60585
N	-2.07878	-1.91062	4.00695
C	-3.09124	-3.85722	2.85530
C	-5.03612	-4.08585	1.29395
C	0.27010	-4.82815	2.22915
C	-4.34005	-2.16936	4.23573
H	-5.22911	-2.48398	4.12390
C	-3.94376	-1.13659	5.03262
H	-4.50351	-0.60529	5.58791
C	-1.90152	-4.48886	2.45781
C	2.49704	-5.50640	1.33601
H	2.30557	-6.44676	1.53146
H	2.19270	-5.29392	0.42921
H	3.46168	-5.34731	1.40174
C	-0.39246	-5.99159	1.77292
H	0.01961	-6.77916	1.43737
C	-2.53398	-1.00191	4.88266
C	-1.68063	-0.01975	5.67074
C	-1.74484	1.36138	4.99104
H	-1.39072	1.29364	4.07923
H	-2.67552	1.66628	4.95718
H	-1.20994	2.00261	5.50163
C	-0.24930	-0.50006	5.81941
H	-0.24423	-1.38822	6.23211
H	0.17240	-0.54841	4.93649
H	0.24843	0.12682	6.38420
C	1.76217	-4.61448	2.34234
C	-4.95860	-5.54868	3.15743
C	-1.74793	-5.76997	1.90381

H	-2.44426	-6.37057	1.66394
C	-6.16507	-6.13573	2.74060
H	-6.56296	-6.83189	3.25005
C	-2.26806	0.12135	7.08494
H	-3.17148	0.49616	7.02730
H	-2.30709	-0.76041	7.51199
H	-1.70094	0.71754	7.61659
C	-6.20955	-4.67294	0.84668
H	-6.62389	-4.37880	0.04440
C	2.19035	-4.97657	3.75553
H	1.70543	-4.41558	4.39737
H	1.98598	-5.91928	3.92595
H	3.15305	-4.82626	3.85296
C	-6.76037	-5.68941	1.58441
H	-7.56887	-6.09114	1.29174
C	2.16538	-3.17037	2.06419
H	1.82455	-2.90067	1.18515
H	1.78816	-2.58671	2.75380
H	3.14325	-3.09680	2.07195

($^{t\text{Bu}}$dmx)Cu_2NAr^{CF3}, BS(1,1)
Charge = 0, Spin Multiplicity = 1

Cu	0.00000	0.00000	0.00000
Cu	-0.00000	0.00000	2.88312
F	1.66193	-5.27107	4.13211
F	-0.29519	-4.92069	4.87406
F	0.16865	-6.67472	3.72175
F	-2.02020	-6.07218	-0.86925
F	-1.23383	-4.48595	-2.01886
F	0.00452	-6.11484	-1.35161
O	-0.31231	4.68554	1.35624
N	-1.38891	0.96483	3.80796
N	-1.13298	1.32465	-0.83354
N	-0.12244	-1.11415	1.44581
N	1.64517	0.73628	-0.78998
N	1.41195	1.15808	3.50816
C	1.14494	2.52205	3.53368
C	0.37561	5.30336	0.33231
C	2.74639	1.01024	3.66272
C	-0.66661	2.62337	-0.88382
C	-2.60663	2.87250	4.03387
H	-2.86132	3.78686	4.02155
C	0.51873	6.67361	0.30553
C	-0.28054	5.34763	2.57886
C	1.75573	2.12523	-0.55514
C	-0.20041	4.55314	3.71269
C	-3.41467	1.80586	4.35408
H	-4.32614	1.84039	4.61316
C	0.34046	-5.37757	3.80553
C	1.70101	5.06440	-1.63463
H	2.06607	4.52539	-2.32611
C	-0.20955	-2.50150	1.42961
C	0.94951	4.46539	-0.63474
C	1.92882	6.41027	-1.64641
H	2.49636	6.79239	-2.30433
C	-0.29453	7.47470	1.29678
C	0.66736	3.00873	-0.63751
C	2.37277	3.21367	3.66706
H	2.48616	4.15511	3.70162
C	3.43218	-0.34666	3.72159
C	-2.39004	1.33195	-1.32616
C	-0.12967	7.33337	3.88571
H	-0.09317	8.28039	3.95437
C	3.11980	2.45300	-0.51760
H	3.48195	3.31205	-0.33535

C	-1.32859	2.35584	3.72510
C	-1.69113	3.46962	-1.38711
H	-1.64148	4.41097	-1.50214
C	-2.53024	-0.92744	-2.31986
H	-2.45825	-0.56863	-3.22840
H	-3.05095	-1.75790	-2.33768
H	-1.63566	-1.11035	-1.96723
C	-0.13524	5.18509	4.94229
H	-0.11100	4.66622	5.73767
C	-3.28800	-1.63568	3.35517
H	-4.05035	-1.26478	2.86544
H	-3.48595	-2.55824	3.62088
H	-2.49430	-1.62550	2.77883
C	1.32020	7.22155	-0.68502
H	1.45826	8.15987	-0.71085
C	-2.75699	2.66674	-1.67878
H	-3.58995	2.94739	-2.04363
C	-0.10410	6.56010	5.02809
H	-0.06681	6.97902	5.88100
C	-3.01965	-0.78566	4.61165
C	0.18943	8.93077	1.41146
H	1.11759	8.94417	1.72848
H	-0.38015	9.41637	2.04695
H	0.14107	9.36193	0.53168
C	-4.61000	0.40923	-2.03706
H	-5.01736	1.16283	-1.55783
H	-5.18937	-0.37736	-1.95895
H	-4.50349	0.64495	-2.98197
C	-1.77107	7.49774	0.81212
H	-1.82226	7.94164	-0.06078
H	-2.31886	7.99102	1.45916
H	-2.10459	6.58085	0.73174
C	-3.23274	0.09834	-1.42351
C	2.72810	-1.20946	4.72306
H	2.90392	-0.87320	5.62681
H	3.06027	-2.13127	4.64707
H	1.76460	-1.19647	4.55043
C	3.41306	-0.98161	2.31090
H	2.49419	-1.00881	1.97320
H	3.77128	-1.89479	2.35839
H	3.96715	-0.44663	1.70349
C	0.07710	-3.23804	2.59406
H	0.31145	-2.78937	3.39663
C	2.88826	0.28570	-0.97437
C	-3.49194	-0.49384	-0.04770
H	-2.63759	-0.69594	0.38897

H	-4.01305	-1.31932	-0.13925
H	-3.99230	0.15097	0.49583
C	-0.31533	-5.30849	1.40099
H	-0.33290	-6.25608	1.37376
C	3.17210	-0.94444	-3.08037
H	2.27122	-0.69129	-3.36849
H	3.42332	-1.79211	-3.50047
H	3.80660	-0.24574	-3.34593
C	4.58152	-1.55384	-1.17490
H	5.21987	-0.83456	-1.36409
H	4.81788	-2.34751	-1.70318
H	4.61432	-1.77748	-0.22210
C	4.88717	-0.16619	4.14128
H	5.34995	0.39559	3.48367
H	5.32364	-1.04321	4.18719
H	4.92329	0.26491	5.02105
C	3.36732	2.28361	3.73243
H	4.29673	2.45705	3.81177
C	-0.20991	6.73327	2.63378
C	-2.62884	0.64931	4.22308
C	-0.12780	3.06709	3.60096
C	-1.89615	-1.38965	5.43228
H	-2.13614	-2.30412	5.69398
H	-1.74940	-0.84785	6.23498
H	-1.07544	-1.40928	4.89837
C	3.82571	1.33072	-0.78551
H	4.77177	1.25531	-0.83771
C	3.19724	-1.10422	-1.53793
C	-4.30166	-0.74749	5.44826
H	-5.02254	-0.34025	4.92394
H	-4.14798	-0.22066	6.25842
H	-4.55518	-1.66190	5.69633
C	-0.62479	-4.55585	0.26789
C	-0.59017	-3.20421	0.28481
H	-0.82814	-2.72554	-0.49905
C	2.17899	-2.12855	-1.12204
H	2.21551	-2.24961	-0.15059
H	2.37148	-2.98069	-1.56459
H	1.28154	-1.81991	-1.37804
C	0.01971	-4.63548	2.56994
C	-0.96492	-5.30703	-0.95443

$[(^{t\text{Bu}}\text{dmx})\text{Cu}_2\text{NAr}^{\text{CF3}}]^-$
Charge = -1, Spin Multiplicity = 2

Cu	0.00000	0.00000	2.83971
Cu	0.00000	0.00000	0.00000
F	-5.34838	-3.44389	4.11917
F	-3.65506	-2.61858	5.12278
F	-3.63678	-4.66293	4.48856
O	3.80620	2.63615	1.51717
N	0.38572	1.74262	3.67849
N	-0.21525	1.73605	-0.98810
N	-0.97314	-0.68833	1.41613
N	1.86631	-0.23776	-0.67354
N	1.61682	-0.88380	3.72110
C	2.78652	-0.12804	3.58442
C	4.12782	3.40493	0.42378
C	3.23984	3.28687	-0.65970
C	5.82950	3.36360	2.65936
C	1.71536	2.12607	3.82849
C	2.66752	0.91346	-0.71443
C	0.84127	2.63365	-0.78935
C	5.25976	4.21677	0.37522
C	6.59703	3.26081	3.82152
H	7.42834	3.71986	3.87249
C	2.01126	-2.15549	3.89654
C	3.46078	4.09269	-1.76916
H	2.86467	4.04684	-2.50746
C	2.68414	-1.26988	-0.91531
C	-1.27260	2.46165	-1.36699
C	-0.36547	2.79474	4.05090
C	3.42685	-2.26049	3.81817
H	3.93772	-3.05628	3.90030
C	1.76149	3.46593	4.30163
H	2.54042	3.98059	4.47398
C	0.36528	3.95393	-1.00782
H	0.86000	4.75797	-0.90997
C	-0.95316	3.83919	-1.38750
H	-1.53770	4.55029	-1.61982
C	1.02104	-3.26968	4.19474
C	0.46300	3.87400	4.46136
H	0.17336	4.71846	4.78506
C	6.33562	4.14118	1.45203
C	4.15563	1.91472	3.71068
C	4.01202	0.53871	-0.97307
H	4.76060	1.11895	-1.03494
C	-0.02696	-2.77656	5.20108

H	0.41762	-2.50170	6.02885
H	-0.65988	-3.49945	5.39508
H	-0.51081	-2.01307	4.82172
C	1.75753	-4.46919	4.80495
H	2.40065	-4.82246	4.15478
H	1.11013	-5.16735	5.03601
H	2.23513	-4.18435	5.61189
C	4.01792	-0.82334	-1.11439
H	4.77098	-1.36756	-1.31024
C	-3.26387	-3.41458	0.44178
C	-2.40607	-2.32935	0.32621
H	-2.10311	-2.07068	-0.53511
C	-2.59662	-1.96182	2.69307
H	-2.41935	-1.44321	3.46806
C	2.72510	-3.35686	-2.27116
H	2.23580	-2.94744	-3.01446
H	2.54509	-4.32051	-2.25292
H	3.68443	-3.20685	-2.38816
C	-2.57123	1.80946	-1.81155
C	0.33700	-3.73668	2.90556
H	-0.00847	-2.96048	2.41889
H	-0.40354	-4.33925	3.12851
H	0.98800	-4.21078	2.34459
C	2.97289	-3.45392	0.21433
H	3.94165	-3.43542	0.07381
H	2.66516	-4.38385	0.25264
H	2.75451	-3.00284	1.05609
C	-1.87335	2.77797	3.96628
C	7.52213	3.36153	0.85873
H	8.23515	3.29635	1.52681
H	7.85835	3.83024	0.06672
H	7.22865	2.46168	0.60709
C	-3.43681	2.81097	-2.56745
H	-3.68068	3.54857	-1.96963
H	-4.25009	2.36658	-2.88507
H	-2.93735	3.16363	-3.33275
C	-4.00752	-3.43156	4.11821
C	4.95759	1.84313	4.84446
H	4.66783	1.33388	5.59123
C	2.17940	2.22403	-0.65976
C	4.53840	4.96502	-1.81427
H	4.65814	5.53288	-2.56658
C	6.17800	2.50887	4.90119
H	6.72131	2.44543	5.67750
C	3.91471	-1.00089	3.59933
H	4.82361	-0.75595	3.48168

C	-1.97223	-1.59692	1.45781
C	5.43540	5.00529	-0.76643
H	6.19007	5.58202	-0.82209
C	2.81434	1.26677	3.66473
C	2.26967	-2.73002	-0.95490
C	4.62532	2.66898	2.62005
C	0.76527	-2.91233	-0.82602
H	0.46275	-2.53067	0.02405
H	0.54796	-3.86775	-0.85045
H	0.31497	-2.45698	-1.56879
C	-2.24830	0.62480	-2.74107
H	-1.75065	0.94702	-3.52004
H	-3.08217	0.20451	-3.03797
H	-1.70889	-0.03388	-2.25555
C	-3.44330	-3.04213	2.79225
C	-3.77197	-3.80482	1.67335
H	-4.32898	-4.57095	1.75104
C	-3.62854	-4.16678	-0.76444
C	-3.35864	1.30444	-0.59814
H	-2.80215	0.68705	-0.07986
H	-4.16396	0.83761	-0.90353
H	-3.61476	2.06348	-0.03513
C	6.79087	5.54921	1.87676
H	6.03331	6.03395	2.26589
H	7.12149	6.03541	1.09291
H	7.50752	5.47428	2.54072
C	-2.37117	3.51101	2.70219
H	-2.16771	4.46651	2.77555
H	-3.34028	3.39052	2.61460
C	-2.51125	3.60370	5.22927
H	-2.27853	3.15019	6.06636
H	-3.48372	3.64011	5.13654
C	-2.62370	1.44334	3.99070
H	-2.52982	0.99982	3.12255
H	-3.57427	1.60753	4.17232
F	-4.31095	-3.43787	-1.62699
F	-4.39017	-5.24270	-0.51728
F	-2.57617	-4.63868	-1.42406
H	-2.15548	4.09467	5.52695
H	-1.88277	3.47991	2.00040
H	-1.97300	0.72811	4.30534

($^{t\text{Bu}}$dmx)Cu_2NAr^{OMe}, BS(1,1)
Charge = 0, Spin Multiplicity = 1

Cu	0.00000	0.00000	0.00000
Cu	0.00000	0.00000	2.85652
O	2.45785	3.82012	1.49281
O	-3.11449	-5.89497	1.30765
N	1.77268	-0.31985	-0.81362
N	-0.21319	1.75652	-0.81611
N	1.62755	0.61114	3.72047
N	-0.56569	-0.96501	1.43810
N	-1.08732	1.42595	3.60028
C	3.28397	3.15735	-0.59172
C	2.76517	0.02505	4.06746
C	2.23024	2.10174	-0.64044
C	3.32438	4.08418	0.47510
C	2.64760	0.77144	-0.61724
C	4.18190	3.30637	-1.62151
H	4.16578	2.70123	-2.35302
C	1.83678	2.00658	3.71340
C	1.35654	4.38962	3.47065
C	2.97471	5.94543	2.52277
C	5.07481	5.25997	-0.56043
H	5.68505	5.98816	-0.57457
C	3.76319	1.01430	4.33608
H	4.65785	0.86073	4.62045
C	4.19246	6.18613	1.62989
C	4.19469	5.15808	0.46997
C	1.64985	6.55707	4.44586
H	1.39556	7.21204	5.08579
C	2.50656	-1.40020	-1.01739
C	1.02386	5.31252	4.45675
H	0.38328	5.09642	5.12357
C	1.97799	-2.76140	-1.40893
C	2.62457	6.85095	3.52799
H	3.07373	7.68899	3.57755
C	2.93734	-1.48731	4.16084
C	-0.53179	2.72876	3.50236
C	3.96939	0.27100	-0.67378
H	4.76910	0.77007	-0.54997
C	3.87830	-1.07409	-0.94588
H	4.60562	-1.67300	-1.06214
C	-2.67348	2.08398	-1.35653
C	0.58357	3.86969	-1.23630
H	1.16966	4.61118	-1.32283
C	-3.37292	0.46647	3.97640

C	2.14335	-3.70644	-0.24423
H	3.07565	-3.69317	0.05790
H	1.90262	-4.61494	-0.52189
H	1.55910	-3.42485	0.49153
C	4.19763	7.59801	1.07050
H	3.39714	7.73650	0.52280
H	4.99862	7.72600	0.51776
H	4.20528	8.24263	1.80816
C	-1.59461	-4.39078	2.45761
H	-1.40109	-5.02163	3.14145
C	-0.78801	3.83680	-1.48863
H	-1.31224	4.53464	-1.70500
C	-2.73748	-3.78032	0.41686
H	-3.34067	-3.99451	-0.28289
C	5.43903	5.97259	2.48587
H	5.49197	6.67512	3.16730
H	6.23707	6.00776	1.91729
H	5.38763	5.09586	2.92264
C	-2.85998	0.57589	-1.19613
H	-2.23006	0.10364	-1.77771
H	-3.77709	0.33240	-1.44380
H	-2.69574	0.32235	-0.26458
C	0.51912	-2.72842	-1.83167
H	-0.02327	-2.35638	-1.10561
H	0.21433	-3.63906	-2.03142
H	0.42093	-2.17113	-2.63079
C	2.84305	-2.05574	2.74788
H	1.92958	-1.94247	2.41174
H	3.07102	-3.00913	2.76336
H	3.46913	-1.57948	2.16233
C	4.29237	-1.83338	4.73275
H	4.99326	-1.50893	4.12839
H	4.36700	-2.80548	4.82990
H	4.39595	-1.40733	5.60874
C	-2.66244	-0.71361	4.64878
H	-2.03610	-1.12140	4.01561
H	-3.32769	-1.37971	4.92661
H	-2.17242	-0.39419	5.43543
C	-3.54406	2.82989	-0.37362
H	-3.27680	2.59830	0.54210
H	-4.48214	2.57931	-0.51243
H	-3.43912	3.79382	-0.50862
C	-0.99002	-3.14862	2.45871
H	-0.41307	-2.92726	3.17881
C	-3.02160	-6.81986	2.38484
H	-2.08951	-7.10223	2.49193

H	-3.57815	-7.60351	2.19219
H	-3.33127	-6.39361	3.21067
C	-3.13642	2.45009	-2.82082
H	-3.16953	3.42375	-2.91840
H	-4.02607	2.07449	-2.98462
H	-2.49920	2.07808	-3.46523
C	-4.52358	0.93898	4.83319
H	-4.18974	1.18387	5.72270
H	-5.18585	0.22044	4.91947
H	-4.94253	1.72167	4.41567
C	0.90715	2.56205	-0.82637
C	-1.25289	2.52422	-1.22855
C	2.26701	4.73790	2.48752
C	3.16456	2.22869	4.10396
H	3.58284	3.07863	4.19086
C	-1.19438	-2.19881	1.44362
C	0.83473	2.96324	3.50449
C	5.11397	4.33430	-1.59762
H	5.77045	4.40432	-2.28099
C	-2.09253	-2.55941	0.43488
H	-2.26588	-1.94166	-0.26394
C	-1.58810	3.66915	3.46202
H	-1.50532	4.60810	3.34153
C	-2.48607	-4.70324	1.44718
C	-2.74969	2.96809	3.63502
H	-3.62345	3.33551	3.67013
C	-2.41994	1.61477	3.75382
C	2.78846	-3.28056	-2.61165
H	2.63974	-2.69552	-3.38502
H	2.50097	-4.19117	-2.83359
H	3.74240	-3.28693	-2.38632
C	-3.94010	0.00698	2.62608
H	-4.46528	0.73139	2.22895
H	-4.51638	-0.77570	2.76191
H	-3.20364	-0.23195	2.02721
C	1.85033	-2.05967	5.05629
H	1.98839	-1.74938	5.97676
H	1.89108	-3.03880	5.03484
H	0.97277	-1.76086	4.73803

$[(^{t\text{Bu}}\text{dmx})\text{Cu}_2\text{NAr}^{\text{OMe}}]^-$
Charge = -1, Spin Multiplicity = 2

Cu	0.00000	-0.00000	0.00000
Cu	-0.00000	-0.00000	2.94363
O	3.59990	5.66262	1.44343
O	-3.15065	-3.47562	1.60849
N	0.33041	-1.85825	-0.74000
N	-1.71851	0.11061	-1.02296
N	-1.69449	-0.07684	3.97123
N	0.71953	0.88403	1.46739
N	0.64739	-1.79598	3.73052
C	-2.55140	-1.01485	-0.97952
C	-3.12272	-3.40521	-0.74049
C	-2.44712	1.10971	-1.53391
C	-0.76285	-2.71984	-0.56078
C	-0.34192	-2.79204	3.64013
C	-3.77451	0.20276	4.85647
H	-4.52782	0.62617	5.25187
C	2.93157	4.45552	1.54144
C	-3.84646	-0.64525	-1.43708
H	-4.61071	-1.20871	-1.48281
C	-2.61326	-3.74526	3.87403
C	1.48409	2.00272	1.50676
C	-2.35065	-1.30898	4.00193
C	-3.36502	-4.18331	2.77918
C	-1.72040	-2.54595	3.77346
C	-2.09754	-2.30944	-0.68846
C	-3.57902	-3.85939	-1.97389
H	-3.25292	-3.45830	-2.77290
C	-3.78329	0.67836	-1.79947
H	-4.48927	1.20398	-2.15665
C	1.62768	-3.86438	3.78217
H	2.30353	-4.53054	3.83400
C	1.69532	2.75010	2.69329
H	1.35107	2.41077	3.51065
C	2.38446	3.96067	2.71665
H	2.47942	4.44400	3.52974
C	0.27803	-4.06765	3.64064
H	-0.15967	-4.90560	3.55865
C	-2.77621	-4.40228	5.09348
H	-2.27028	-4.12825	5.85013
C	2.10400	2.55109	0.33369
H	2.02484	2.08032	-0.48829
C	1.08408	-4.00537	-0.72556
H	1.68351	-4.73979	-0.76744

C	-4.98216	-5.47138	-0.88722
H	-5.61573	-6.17521	-0.94827
C	-4.50568	-4.89195	-2.05104
H	-4.81085	-5.19901	-2.89729
C	-3.67752	-5.45686	5.20469
H	-3.79215	-5.89558	6.03867
C	-0.27176	-4.06264	-0.51029
H	-0.78599	-4.84570	-0.35789
C	3.13526	-1.75674	4.16945
C	-1.85091	2.47158	-1.82601
C	-2.18389	2.28184	4.67221
C	3.76638	6.38982	2.65521
H	4.24753	7.22439	2.47233
H	4.27928	5.84938	3.29167
H	2.88667	6.59572	3.03527
C	-0.92050	2.38529	5.54908
H	-1.12418	2.06682	6.45478
H	-0.62662	3.31914	5.58955
H	-0.20883	1.83524	5.16216
C	-5.13542	-7.20744	1.53771
H	-5.66531	-7.46790	0.75487
H	-5.53429	-7.59293	2.34377
H	-4.21982	-7.53891	1.43592
C	4.32179	-2.62951	3.73518
H	4.28798	-3.48669	4.20903
H	5.16055	-2.17170	3.94990
H	4.27394	-2.78913	2.76914
C	-3.32941	3.04763	5.35589
H	-4.13049	3.00823	4.79160
H	-3.06655	3.98272	5.48592
H	-3.52153	2.63866	6.22469
C	-3.62462	-3.99916	0.41687
C	-2.54933	0.82113	4.49237
C	-4.55383	-5.04738	0.37311
C	-5.11565	-5.66535	1.65998
C	-3.66259	-1.12956	4.52575
H	-4.32948	-1.79901	4.62769
C	-4.26500	-5.24470	2.85867
C	1.81328	-2.44018	3.83584
C	-4.40503	-5.86540	4.10428
H	-5.01581	-6.58586	4.19585
C	1.41634	-2.62823	-0.87480
C	2.80932	3.73613	0.35808
H	3.21301	4.06223	-0.43727
C	-1.91947	2.91379	3.28476
H	-1.20038	2.42402	2.83354

H	-1.65390	3.85147	3.39711
H	-2.73533	2.86683	2.74379
C	-6.54424	-5.13814	1.86152
H	-6.52084	-4.16418	1.97186
H	-6.93471	-5.55020	2.66182
H	-7.08980	-5.36543	1.07935
C	3.22867	-1.57134	5.69695
H	2.52000	-0.96368	5.99630
H	4.10296	-1.19166	5.92655
H	3.12299	-2.44023	6.13805
C	3.23054	-0.37436	3.52280
H	3.18590	-0.46605	2.54800
H	4.08017	0.04461	3.77371
H	2.48741	0.18282	3.83373
C	2.77122	-2.04029	-1.23587
C	-1.36520	3.11514	-0.47099
H	-2.14299	3.33529	0.08428
H	-0.85913	3.93157	-0.65885
H	-0.79345	2.47874	0.00734
C	-0.60791	2.28463	-2.72010
H	0.04762	1.72402	-2.25427
H	-0.20873	3.15789	-2.91211
H	-0.87088	1.85188	-3.55811
C	-2.85412	3.38836	-2.46594
H	-3.14760	3.00455	-3.31820
H	-2.44088	4.26369	-2.62526
H	-3.62536	3.49339	-1.87078
C	3.75220	-3.07727	-1.64959
H	3.87968	-3.71676	-0.91816
H	4.60692	-2.65100	-1.86394
H	3.41500	-3.54799	-2.44129
C	2.56669	-1.00168	-2.41980
H	2.21991	-1.46930	-3.20803
H	3.42508	-0.58184	-2.64075
H	1.92788	-0.31144	-2.14271
C	3.28319	-1.20103	-0.04769
H	2.60757	-0.53398	0.19590
H	4.11364	-0.74710	-0.30150
H	3.45155	-1.78644	0.71894

Respective Contributions. K.M.C. and T.A.B. conceived the experimental design, executed syntheses, characterized new complexes, and assessed nitrene transfer reactivity from the dinuclear copper complexes. J.T.L., I.M.D., and K.M.L. performed XANES measurements, EPR simulations, and computational studies. D.A.I. assessed nitrene transfer reactivity from mononuclear copper complexes. S.L.Z. assisted K.M.C. in crystallographic refinement. All authors contributed of the construction of this manuscript.

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checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1

Bond precision: C-C = 0.0046 A Wavelength=0.71073

Cell: a=17.5563(12) b=19.7585(14) c=20.6328(14)
alpha=90 beta=111.704(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	6649.8(8)	6649.8(8)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C73 H70 Cu2 N6 O, C4 H10 O, C2 H3 N	?
Sum formula	C79 H83 Cu2 N7 O2	C79 H83 Cu2 N7 O2
Mr	1289.63	1289.60
Dx,g cm-3	1.288	1.288
Z	4	4
Mu (mm-1)	0.693	0.693
F000	2720.0	2720.0
F000’	2723.34	
h,k,lmax	20,23,24	20,23,24
Nref	11852	11828
Tmin,Tmax	0.913,0.936	0.701,0.746
Tmin’	0.845	

Correction method= # Reported T Limits: Tmin=0.701 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.111

R(reflections)= 0.0467(9145) wR2(reflections)= 0.1105(11828)

S = 1.075 Npar= 830

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT232_ALERT_2_C	Hirshfeld Test Diff (M-X) Cu1 --N3 .	6.5	s.u.
PLAT232_ALERT_2_C	Hirshfeld Test Diff (M-X) Cu2 --N6 .	6.0	s.u.
PLAT244_ALERT_4_C	Low 'Solvent' Ueq as Compared to Neighbors of	C1S	Check
PLAT910_ALERT_3_C	Missing # of FCF Reflection(s) Below Theta(Min).	6	Note
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.597	20	Report
PLAT975_ALERT_2_C	Check Calcd Resid. Dens. 1.09A From O1S	0.52	eA-3

Alert level G

PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	12.58	Why ?
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	13	Note
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (I) .	0.99	Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu2 (I) .	0.99	Info
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please	Do !
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	58%	Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	1	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	4	Info

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
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8 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

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Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

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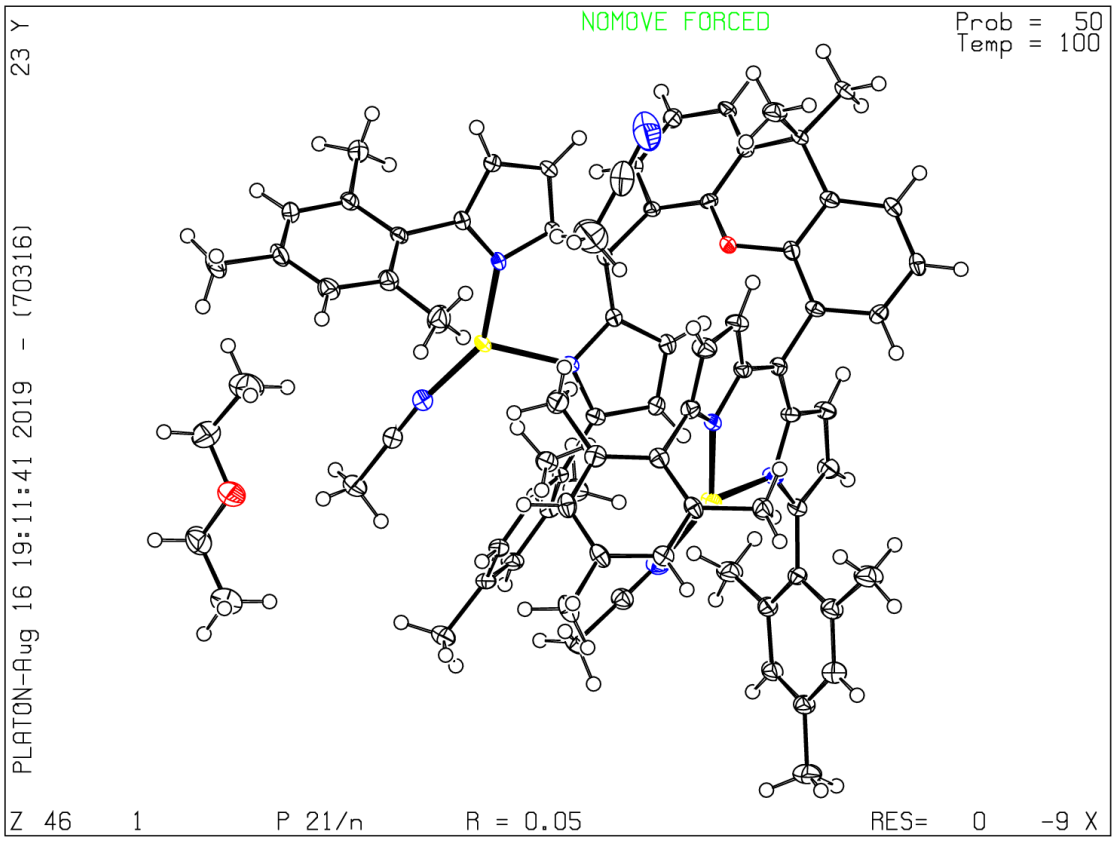
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 1 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 2

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 2

Bond precision: C-C = 0.0074 A Wavelength=0.71073

Cell: a=12.304(3) b=16.241(4) c=18.007(5)
alpha=92.531(4) beta=92.075(5) gamma=92.793(5)
Temperature: 100 K

	Calculated	Reported
Volume	3587.9(16)	3587.8(15)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C76 H71 Cu2 N5 O2, 2(C4 H10 O)	?
Sum formula	C84 H91 Cu2 N5 O4	C84 H91 Cu2 N5 O4
Mr	1361.72	1361.69
Dx,g cm-3	1.260	1.260
Z	2	2
Mu (mm-1)	0.647	0.647
F000	1440.0	1440.0
F000’	1441.73	
h,k,lmax	14,19,21	14,19,21
Nref	13149	12852
Tmin,Tmax	0.883,0.943	0.466,0.745
Tmin’	0.873	

Correction method= # Reported T Limits: Tmin=0.466 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.977 Theta(max)= 25.355

R(reflections)= 0.0679(7846) wR2(reflections)= 0.1948(12852)

S = 1.001 Npar= 893

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	3.3	Ratio
PLAT341_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00737	Ang.
PLAT905_ALERT_3_C	Negative K value in the Analysis of Variance ...	-0.301	Report
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	149	Report

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Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	15	Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	5	Report
PLAT072_ALERT_2_G	SHELXL First Parameter in WGHT Unusually Large	0.11	Report
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records	5	Report
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records	2	Report
PLAT178_ALERT_4_G	The CIF-Embedded .res File Contains SIMU Records	1	Report
PLAT187_ALERT_4_G	The CIF-Embedded .res File Contains RIGU Records	1	Report
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 3)	100%	Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 4)	100%	Note
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 3	9.74	Check
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 4	5.26	Check
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	35	Note
PLAT790_ALERT_4_G	Centre of Gravity not Within Unit Cell: Resd. # C4 H10 O	3	Note
PLAT790_ALERT_4_G	Centre of Gravity not Within Unit Cell: Resd. # C4 H10 O	4	Note
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (II) .	2.03	Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu2 (II) .	2.06	Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	66	Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !	
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	148	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	2	Info

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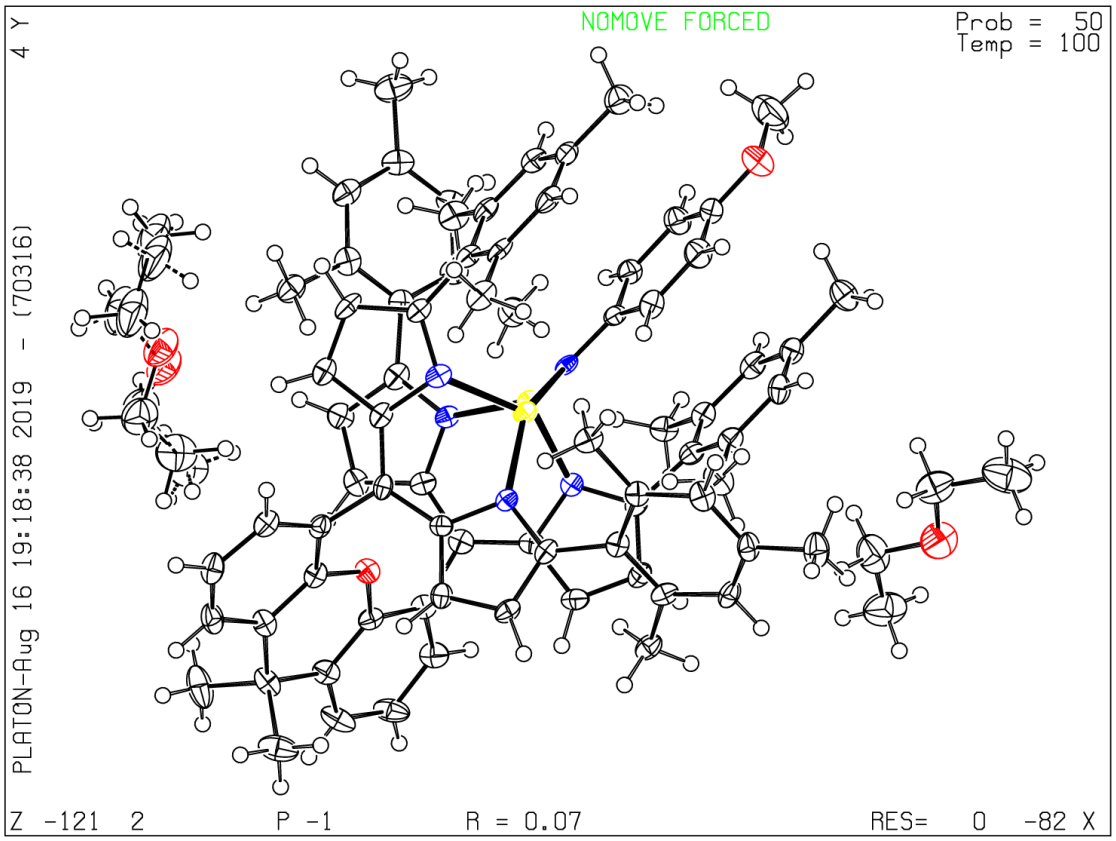
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 2 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 3

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 3

Bond precision: C-C = 0.0036 A Wavelength=0.41328

Cell: a=23.7718(17) b=21.0479(14) c=17.5589(12)
alpha=90 beta=113.565(1) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	8052.9(10)	8052.9(10)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C77 H67 Cu2 F6 N5 O [+ solvent]	?
Sum formula	C77 H67 Cu2 F6 N5 O [+ solvent]	C77 H67 Cu2 F6 N5 O
Mr	1319.46	1319.43
Dx,g cm-3	1.088	1.088
Z	4	4
Mu (mm-1)	0.142	0.142
F000	2736.0	2736.0
F000’	2737.56	
h,k,lmax	28,25,20	28,25,20
Nref	7140	7108
Tmin,Tmax	0.985,0.990	0.612,0.744
Tmin’	0.985	

Correction method= # Reported T Limits: Tmin=0.612 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 14.258

R(reflections)= 0.0393(5465) wR2(reflections)= 0.1034(7108)

S = 1.050 Npar= 430

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT905_ALERT_3_C	Negative K value in the Analysis of Variance ...	-1.333	Report
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.596	33	Report

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Alert level G

ABSMU01_ALERT_1_G	Calculation of _exptl_absorpt_correction_mu not performed for this radiation type.		
PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	7	Note
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	5.96	Why ?
PLAT092_ALERT_4_G	Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka	0.41328	Ang.
PLAT128_ALERT_4_G	Alternate Setting for Input Space Group C2/c	I2/a	Note
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records	3	Report
PLAT176_ALERT_4_G	The CIF-Embedded .res File Contains SADI Records	2	Report
PLAT230_ALERT_2_G	Hirshfeld Test Diff for F1' --C40 .	21.5	s.u.
PLAT230_ALERT_2_G	Hirshfeld Test Diff for F2' --C40 .	30.0	s.u.
PLAT230_ALERT_2_G	Hirshfeld Test Diff for F3' --C40 .	23.0	s.u.
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C40	Check
PLAT301_ALERT_3_G	Main Residue Disorder .....(Resd 1)	7%	Note
PLAT606_ALERT_4_G	VERY LARGE Solvent Accessible VOID(S) in Structure	!	Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (II) .	2.08	Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	30	Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !	
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	56%	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	7	Info

---

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18 **ALERT level G** = General information/check it is not something unexpected

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5 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

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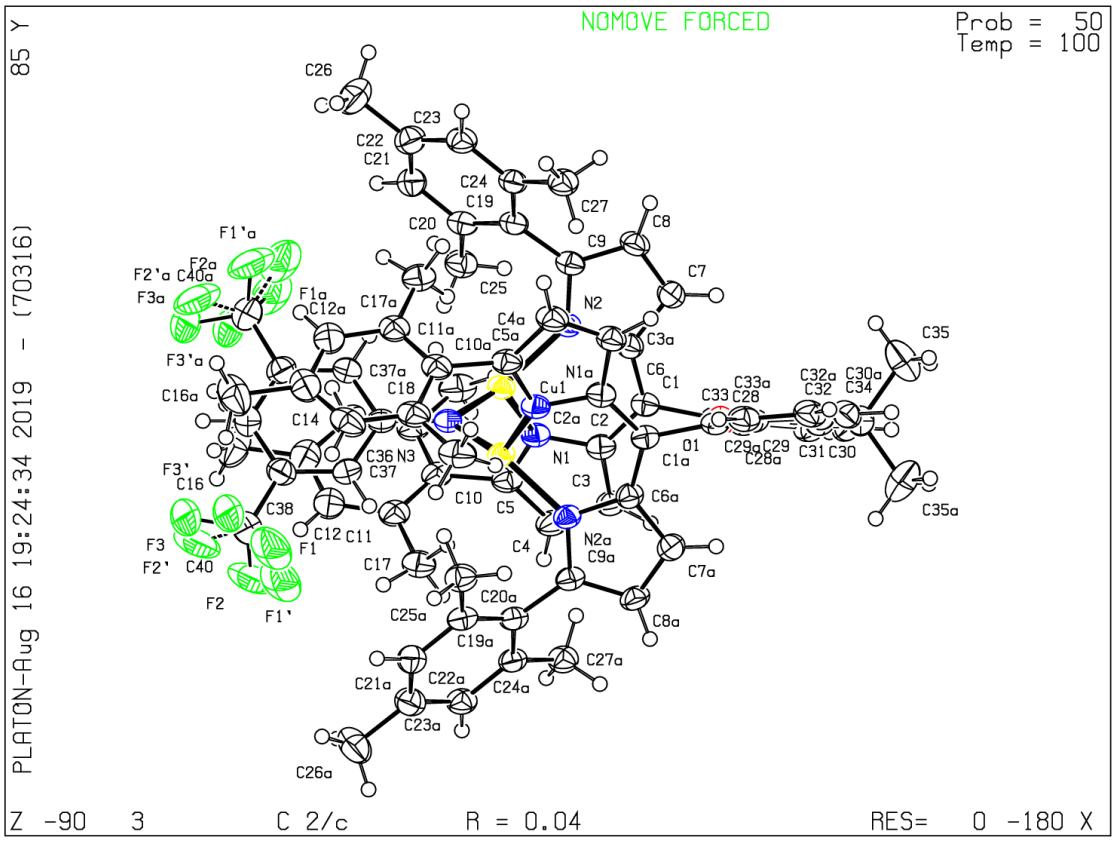
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 3 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 5

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 5

Bond precision: C-C = 0.0118 A Wavelength=0.71073

Cell: a=21.9597(5) b=22.7867(5) c=21.3984(5)
alpha=90 beta=92.534(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	10697.1(4)	10697.1(4)
Space group	P 2/c	P 2/c
Hall group	-P 2yc	-P 2yc
Moiety formula	8(C56 H63 Cu2 N5 O2), 4(C4 H10 O), 7(C2 H3 N)	?
Sum formula	C478 H565 Cu16 N47 O20	C59.75 H70.62 Cu2 N5.88 O2.50
Mr	8305.57	1038.17
Dx,g cm-3	1.289	1.289
Z	1	8
Mu (mm-1)	0.844	0.844
F000	4386.0	4386.0
F000'	4392.35	
h,k,lmax	26,27,25	26,27,25
Nref	18916	18897
Tmin,Tmax	0.765,0.834	0.589,0.745
Tmin'	0.722	

Correction method= # Reported T Limits: Tmin=0.589 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.027

R(reflections)= 0.0988(12782) wR2(reflections)= 0.2560(18897)

S = 1.147 Npar= 1328

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT041_ALERT_1_C	Calc. and Reported SumFormula Strings Differ	Please	Check
PLAT084_ALERT_3_C	High wR2 Value (i.e. > 0.25)	0.26	Report
PLAT094_ALERT_2_C	Ratio of Maximum / Minimum Residual Density	2.55	Report
PLAT243_ALERT_4_C	High 'Solvent' Ueq as Compared to Neighbors of	C5S	Check
PLAT244_ALERT_4_C	Low 'Solvent' Ueq as Compared to Neighbors of	C1S	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including O2S	0.159	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including N1S	0.132	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including N2S	0.134	Check
PLAT341_ALERT_3_C	Low Bond Precision on C-C Bonds	0.01182	Ang.
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	6.254	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.595	16	Report
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.03A From Cu3	2.05	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.01A From Cu4	2.01	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 0.84A From N9	1.91	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.05A From Cu1	1.84	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.09A From Cu3	1.80	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.00A From Cu2	1.70	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.71A From Cu2	1.67	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.05A From Cu4	1.66	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.08A From Cu2	1.65	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 1.09A From N6	1.64	eA-3
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 0.85A From N5	1.56	eA-3
PLAT977_ALERT_2_C	Check Negative Difference Density on H12B	-0.44	eA-3
PLAT978_ALERT_2_C	Number C-C Bonds with Positive Residual Density.	0	Info

---

Alert level G

CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.

CELLZ01_ALERT_1_G ALERT: check formula stoichiometry or atom site occupancies.

From the CIF: _cell_formula_units_Z 8

From the CIF: _chemical_formula_sum C59.75 H70.62 Cu2 N5.88 O2.50

TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	478.00	478.00	0.00
H	564.96	565.00	-0.04
Cu	16.00	16.00	0.00
N	47.04	47.00	0.04
O	20.00	20.00	0.00

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	14	Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	8	Report
PLAT045_ALERT_1_G	Calculated and Reported Z Differ by a Factor ...	0.13	Check
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	111.67	Why ?
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records	2	Report
PLAT176_ALERT_4_G	The CIF-Embedded .res File Contains SADI Records	2	Report
PLAT178_ALERT_4_G	The CIF-Embedded .res File Contains SIMU Records	1	Report
PLAT187_ALERT_4_G	The CIF-Embedded .res File Contains RIGU Records	2	Report
PLAT300_ALERT_4_G	Atom Site Occupancy of O2S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C11S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C12S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C13S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C14S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H11G Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H11H Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H11I Constrained at	0.5	Check

```
PLAT300_ALERT_4_G Atom Site Occupancy of H12A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H12B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H13A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H13B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14C       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of N2S        Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C3S        Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C4S        Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SA       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SB       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SC       Constrained at       0.75 Check
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  6  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  4          7.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... Resd  6          4.50 Check
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O2S           132.6 Degree
PLAT411_ALERT_2_G Short Inter H...H Contact  H12A     ..H53      .       1.69 Ang.
                                               1-x,1-y,1-z  =      3_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H11A     ..H12B     .       2.01 Ang.
                                             x,1-y,-1/2+z  =      4_565 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H11C     ..H12A     .       1.81 Ang.
                                               1-x,1-y,1-z  =      3_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H14B     ..H53      .       1.83 Ang.
                                               x,1-y,1/2+z  =      4_566 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H4SA     ..H2SB     .       2.10 Ang.
                                                      x,y,z  =      1_555 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H4SB     ..H11A     .       2.01 Ang.
                                               x,1-y,1/2+z  =      4_566 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........         11 Note
PLAT722_ALERT_1_G Angle   Calc      108.00, Rep      109.50 Dev...       1.50 Degree
            H14A    -C14S    -H14C       1.555  1.555  1.555     #  538 Check
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         21 Check
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1       (II)      .       1.98 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Cu2       (II)      .       1.99 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Cu3       (II)      .       1.97 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Cu4       (II)      .       2.04 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............        88 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .    Please Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still       47% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         4 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         1 Note
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 24 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 54 ALERT level G = General information/check it is not something unexpected

  6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 28 ALERT type 2 Indicator that the structure model may be wrong or deficient
  7 ALERT type 3 Indicator that the structure quality may be low
 33 ALERT type 4 Improvement, methodology, query or suggestion
  4 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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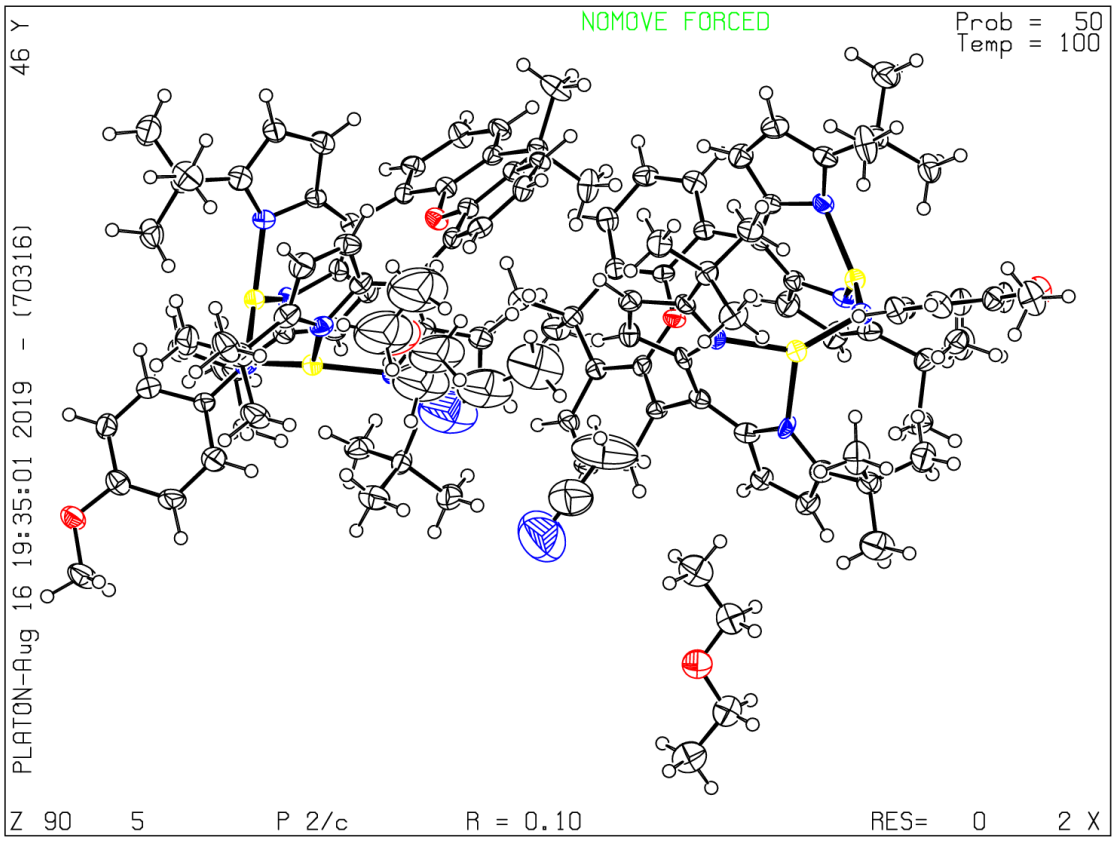
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 5 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 6

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 6

Bond precision: C-C = 0.0137 A Wavelength=0.71073

Cell: a=18.958(2) b=13.0693(16) c=43.638(5)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	10812(2)	10812(2)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	C57 H59 Cu2 F6 N5 O, C2 H3 N	?
Sum formula	C59 H62 Cu2 F6 N6 O	C59 H62 Cu2 F6 N6 O
Mr	1112.25	1112.22
Dx,g cm-3	1.367	1.367
Z	8	8
Mu (mm-1)	0.854	0.854
F000	4624.0	4624.0
F000'	4631.00	
h,k,lmax	22,15,52	22,15,51
Nref	19298[9788]	16866
Tmin,Tmax	0.784,0.928	0.650,0.801
Tmin'	0.745	

Correction method= # Reported T Limits: Tmin=0.650 Tmax=0.801
AbsCorr = MULTI-SCAN

Data completeness= 1.72/0.87 Theta(max)= 25.109

R(reflections)= 0.0538(12888) wR2(reflections)= 0.1329(16866)

S = 1.038 Npar= 1397

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
STRVA01_ALERT_4_C          Flack test results are ambiguous.
          From the CIF: _refine_ls_abs_structure_Flack    0.656
          From the CIF: _refine_ls_abs_structure_Flack_su    0.019
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ........       6.95 Note
PLAT213_ALERT_2_C Atom F2B            has ADP max/min Ratio .....        3.5 prolat
PLAT213_ALERT_2_C Atom F2B'           has ADP max/min Ratio .....        3.5 prolat
PLAT213_ALERT_2_C Atom C41C           has ADP max/min Ratio .....        3.6 oblate
PLAT213_ALERT_2_C Atom C41B           has ADP max/min Ratio .....        3.6 oblate
PLAT213_ALERT_2_C Atom F3A            has ADP max/min Ratio .....        3.5 prolat
PLAT220_ALERT_2_C Non-Solvent  Resd 2  C   Ueq(max)/Ueq(min) Range       4.2 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference F2B'     --C56B     .       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F6B'     --C57B     .       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C38B     --C39B     .       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F5A      --C57A     .       0.17 Ang.
PLAT244_ALERT_4_C Low    'Solvent' Ueq as Compared to Neighbors of        C3S Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.01369 Ang.
PLAT907_ALERT_2_C Flack x > 0.5, Structure Needs to be Inverted? .       0.66 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).         9 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.597        72 Report
PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage        75 %
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.        0 Info
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite        14 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        21 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large     31.09 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records         9 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records         4 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records         3 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    F1B'     --C56B     .       8.7 s.u.
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of       C56B Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of       C57B Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of       C56A Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of       C57A Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )        13% Note
PLAT432_ALERT_2_G Short Inter X...Y Contact  F2B'     ..C3S            2.93 Ang.
                                                      x,y,z  =      1_555 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  N2S      ..C40B           2.81 Ang.
                                                   x,-1+y,z  =      1_545 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........        30 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1A      (II)      .       2.01 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Cu2A      (II)      .       2.08 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       277 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        44% Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....         1 Note
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 19 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 21 ALERT level G = General information/check it is not something unexpected

  1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
```

```
 18 ALERT type 2 Indicator that the structure model may be wrong or deficient
  9 ALERT type 3 Indicator that the structure quality may be low
 10 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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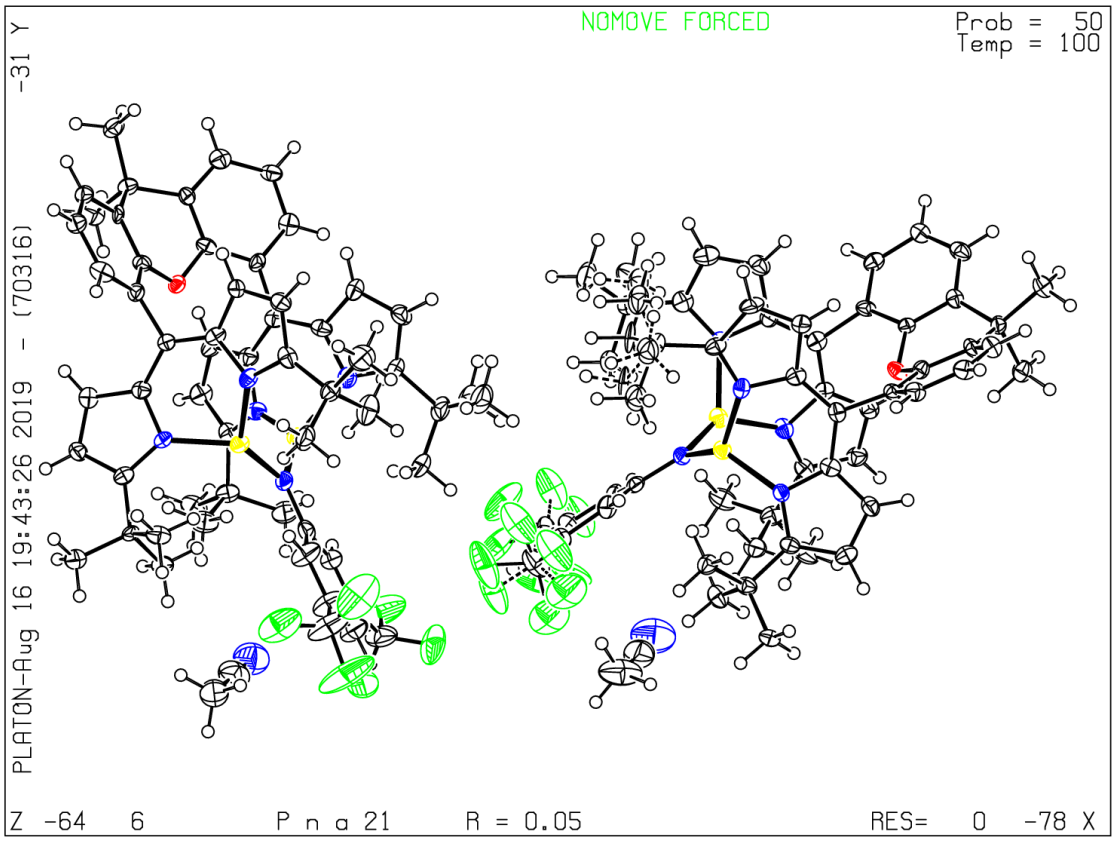
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 6 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 7

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 7

Bond precision: C-C = 0.0050 A Wavelength=1.54184

Cell: a=17.7584(2) b=26.2650(3) c=24.6763(3)
alpha=90 beta=105.2606(12) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	11103.8(2)	11103.8(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C76 H71 Cu2 N5 O2, C18 H36 K N2 O6 [+ solvent]	?
Sum formula	C94 H107 Cu2 K N7 O8 [+ solvent]	C94 H107 Cu2 K N7 O8
Mr	1629.07	1629.04
Dx,g cm-3	0.975	0.974
Z	4	4
Mu (mm-1)	1.171	1.171
F000	3444.0	3444.0
F000’	3438.50	
h,k,lmax	21,31,29	21,31,29
Nref	19610	19446
Tmin,Tmax	0.827,0.871	0.598,0.753
Tmin’	0.672	

Correction method= # Reported T Limits: Tmin=0.598 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.992 Theta(max)= 66.600

R(reflections)= 0.0639(14353) wR2(reflections)= 0.1836(19446)

S = 1.020 Npar= 1024

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT230_ALERT_2_C	Hirshfeld Test Diff for C72 --C73 .	5.3 s.u.
PLAT230_ALERT_2_C	Hirshfeld Test Diff for C73 --C74 .	6.0 s.u.
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.595	165 Report
PLAT978_ALERT_2_C	Number C-C Bonds with Positive Residual Density.	0 Info

---

Alert level G

PLAT072_ALERT_2_G	SHELXL First Parameter in WGHT Unusually Large	0.11 Report
PLAT606_ALERT_4_G	VERY LARGE Solvent Accessible VOID(S) in Structure	! Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (I) .	0.95 Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu2 (I) .	0.95 Info
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	55% Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	4 Note
PLAT992_ALERT_5_G	Repd & Actual _reflns_number_gt Values Differ by	1 Check

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
8 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

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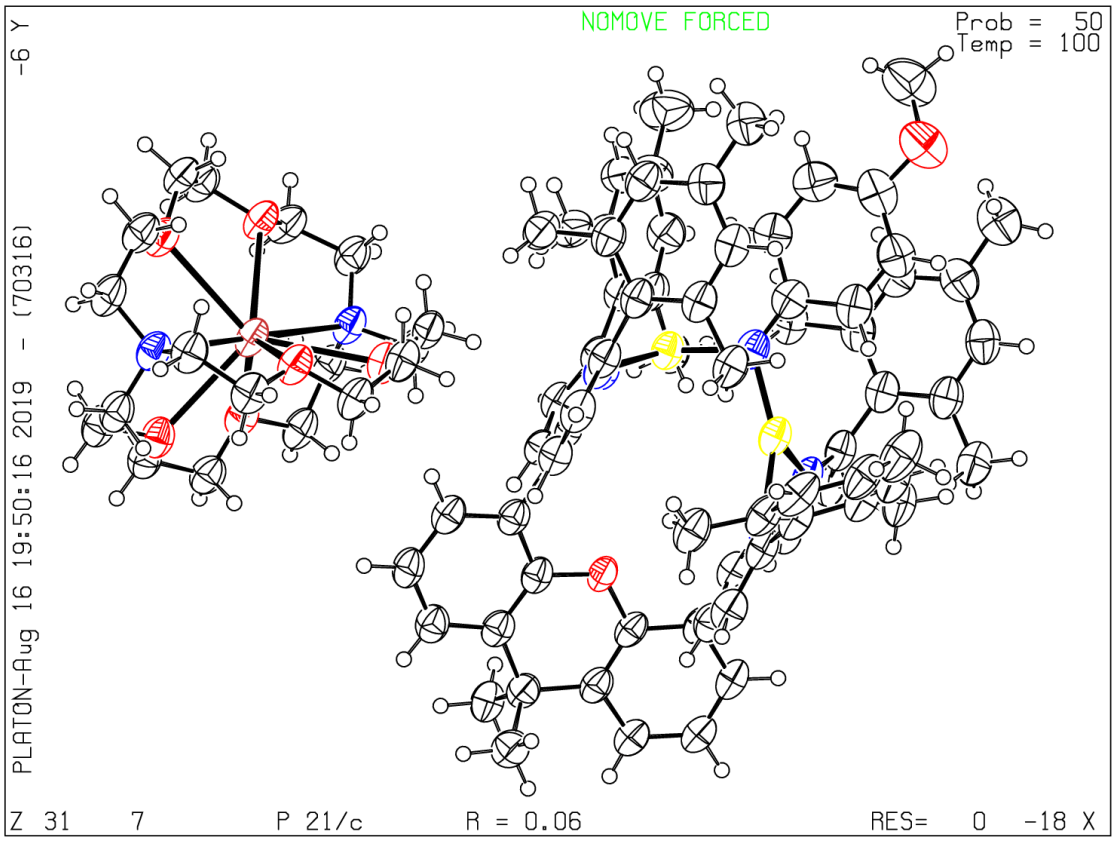
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 7 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 8

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 8

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=17.164(3) b=18.401(3) c=27.309(4)
alpha=90 beta=104.668(4) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	8344(2)	8344(2)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	4(C56 H63 Cu2 N5 O2), 4(C18 H36 K N2 O6), 7(C4 H10 O)	?
Sum formula	C324 H466 Cu8 K4 N28 O39	C81 H116.50 Cu2 K N7 O9.75
Mr	6042.05	1510.48
Dx,g cm-3	1.202	1.202
Z	1	4
Mu (mm-1)	0.617	0.617
F000	3226.0	3226.0
F000'	3230.47	
h,k,lmax	20,21,32	20,21,32
Nref	14787	14724
Tmin,Tmax	0.709,0.807	0.614,0.745
Tmin'	0.534	

Correction method= # Reported T Limits: Tmin=0.614 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.057

R(reflections)= 0.0370(11890) wR2(reflections)= 0.1035(14724)

S = 1.043 Npar= 988

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	O2S	0.101	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	O2T	0.101	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L=	0.596	62	Report
PLAT918_ALERT_3_C	Reflection(s) with I(obs) much Smaller I(calc) .		1	Check

---

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite		29	Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...		5	Report
PLAT045_ALERT_1_G	Calculated and Reported Z Differ by a Factor ...		0.25	Check
PLAT063_ALERT_4_G	Crystal Size Likely too Large for Beam Size		1.00	mm
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large		6.18	Why ?
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records		10	Report
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records		2	Report
PLAT176_ALERT_4_G	The CIF-Embedded .res File Contains SADI Records		4	Report
PLAT187_ALERT_4_G	The CIF-Embedded .res File Contains RIGU Records		1	Report
PLAT230_ALERT_2_G	Hirshfeld Test Diff for C38 --C39 .		12.5	s.u.
PLAT230_ALERT_2_G	Hirshfeld Test Diff for C38 --C40 .		6.0	s.u.
PLAT301_ALERT_3_G	Main Residue Disorder .....(Resd 1)		9%	Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 4)		100%	Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 5)		100%	Note
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 4		5.65	Check
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 5		5.60	Check
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O2T		107.3	Degree
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels		30	Note
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (I) .		0.90	Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints		102	Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .		Please	Do !
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still		63%	Note
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).		1	Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...		7	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.		6	Info

---

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4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
25 **ALERT level G** = General information/check it is not something unexpected

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10 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
10 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

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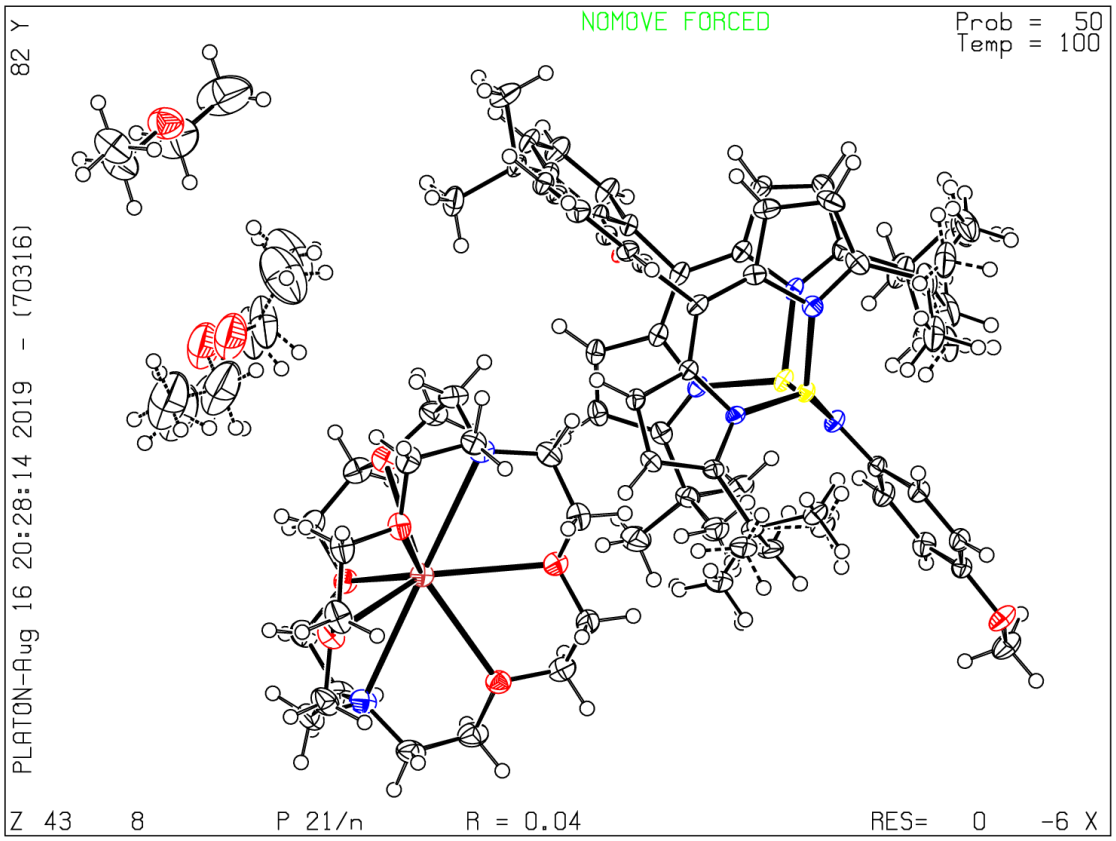
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 8 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 9

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 9

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=13.347(2) b=41.261(6) c=13.763(2)
alpha=90 beta=97.390(3) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	7516.5(19)	7516(2)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C57 H59 Cu2 F6 N5 O, C18 H36 K N2 O6	?
Sum formula	C75 H95 Cu2 F6 K N7 O7	C75 H95 Cu2 F6 K N7 O7
Mr	1486.78	1486.75
Dx,g cm-3	1.314	1.314
Z	4	4
Mu (mm-1)	0.692	0.692
F000	3124.0	3124.0
F000’	3128.70	
h,k,lmax	15,49,16	15,49,16
Nref	13333	13315
Tmin,Tmax	0.723,0.853	0.560,0.745
Tmin’	0.496	

Correction method= # Reported T Limits: Tmin=0.560 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.064

R(reflections)= 0.0402(10685) wR2(reflections)= 0.0932(13315)

S = 1.012 Npar= 920

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	4.5	Ratio
PLAT222_ALERT_3_C	Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range	4.7	Ratio
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	2.111	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.596	18	Report

---

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	14	Note
PLAT063_ALERT_4_G	Crystal Size Likely too Large for Beam Size	1.00	mm
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	10.04	Why ?
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records	6	Report
PLAT176_ALERT_4_G	The CIF-Embedded .res File Contains SADI Records	3	Report
PLAT230_ALERT_2_G	Hirshfeld Test Diff for F6 --C57 .	7.0	s.u.
PLAT230_ALERT_2_G	Hirshfeld Test Diff for F4' --C57 .	20.5	s.u.
PLAT230_ALERT_2_G	Hirshfeld Test Diff for F5' --C57 .	18.0	s.u.
PLAT230_ALERT_2_G	Hirshfeld Test Diff for F6' --C57 .	27.0	s.u.
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C56	Check
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C57	Check
PLAT301_ALERT_3_G	Main Residue Disorder .....(Resd 1)	8%	Note
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	45	Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !	
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	63%	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	6	Info

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0 **ALERT level B** = A potentially serious problem, consider carefully
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16 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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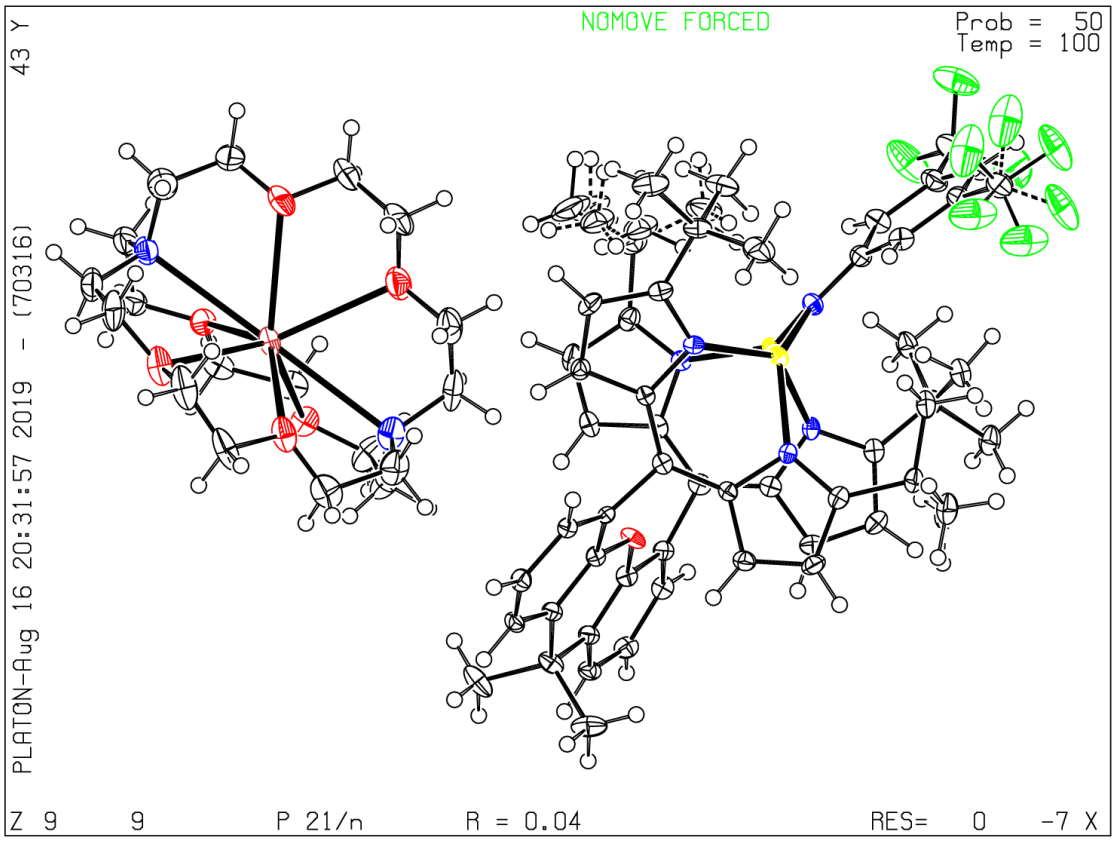
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 9 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 10

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 10

Bond precision: C-C = 0.0077 A Wavelength=0.71073

Cell: a=36.448(4) b=11.0154(11) c=13.4471(12)
alpha=90 beta=105.928(3) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	5191.6(9)	5191.6(9)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	2(C25 H28 Cl2 Cu N3), C2 H3 N	?
Sum formula	C52 H59 Cl4 Cu2 N7	C26 H29.50 Cl2 Cu N3.50
Mr	1050.96	525.47
Dx,g cm-3	1.345	1.345
Z	4	8
Mu (mm-1)	1.067	1.067
F000	2184.0	2184.0
F000’	2189.40	
h,k,lmax	43,13,16	43,13,16
Nref	4616	4558
Tmin,Tmax	0.825,0.870	0.656,0.745
Tmin’	0.758	

Correction method= # Reported T Limits: Tmin=0.656 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.987 Theta(max)= 25.092

R(reflections)= 0.0691(3040) wR2(reflections)= 0.1194(4558)

S = 1.117 Npar= 416

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT213_ALERT_2_C	Atom C21 has ADP max/min Ratio	3.5	prolat
PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	3.6	Ratio
PLAT222_ALERT_3_C	Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range	10.0	Ratio
PLAT245_ALERT_2_C	U(iso) H8 Smaller than U(eq) C8 by	0.011	Ang**2
PLAT245_ALERT_2_C	U(iso) H12A Smaller than U(eq) C12 by	0.013	Ang**2
PLAT245_ALERT_2_C	U(iso) H16A Smaller than U(eq) C16 by	0.019	Ang**2
PLAT341_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00771	Ang.
PLAT391_ALERT_3_C	Deviating Methyl C13 H-C-H Bond Angle	102	Degree
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	7.917	Check
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	2.678	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.597	56	Report
PLAT978_ALERT_2_C	Number C-C Bonds with Positive Residual Density.	0	Info

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Alert level G

PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	3	Report
PLAT045_ALERT_1_G	Calculated and Reported Z Differ by a Factor ...	0.50	Check
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	19.51	Why ?
PLAT128_ALERT_4_G	Alternate Setting for Input Space Group C2/c	I2/a	Note
PLAT164_ALERT_4_G	Nr. of Refined C-H H-Atoms in Heavy-Atom Struct.	27	Note
PLAT187_ALERT_4_G	The CIF-Embedded .res File Contains RIGU Records	1	Report
PLAT300_ALERT_4_G	Atom Site Occupancy of N1S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C1S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C2S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H2SA Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H2SB Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H2SC Constrained at	0.5	Check
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 2)	100%	Note
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	3	Note
PLAT789_ALERT_4_G	Atoms with Negative _atom_site_disorder_group #	6	Check
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (I) .	0.98	Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	9	Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !	
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	41%	Note
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	3	Note

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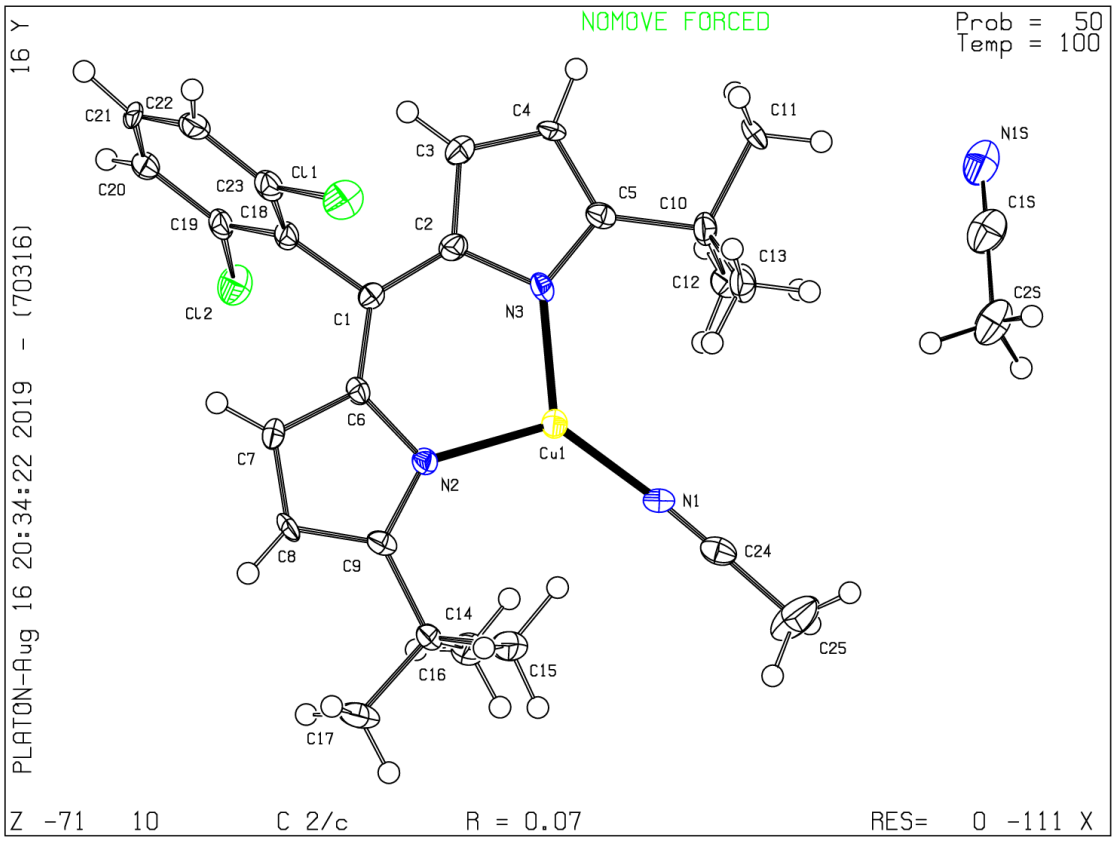
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 10 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 11

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 11

Bond precision: C-C = 0.0063 A Wavelength=0.71073

Cell: a=13.1817(13) b=10.7516(19) c=19.191(3)
alpha=90 beta=95.400(8) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	2707.8(7)	2707.7(7)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C46 H50 Cl6 Cu2 N4, 2(C6 H6)	?
Sum formula	C58 H62 Cl6 Cu2 N4	C29 H31 Cl3 Cu N2
Mr	1154.92	577.45
Dx,g cm-3	1.416	1.417
Z	2	4
Mu (mm-1)	1.124	1.124
F000	1196.0	1196.0
F000’	1199.32	
h,k,lmax	15,12,22	15,12,22
Nref	4809	4789
Tmin,Tmax	0.874,0.914	0.670,0.745
Tmin’	0.874	

Correction method= # Reported T Limits: Tmin=0.670 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.070

R(reflections)= 0.0528(3687) wR2(reflections)= 0.1310(4789)

S = 1.034 Npar= 322

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT341_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00631	Ang.
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	2.948	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.596	16	Report

---

Alert level G

PLAT045_ALERT_1_G	Calculated and Reported Z Differ by a Factor ...	0.50	Check
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	10.02	Why ?
PLAT232_ALERT_2_G	Hirshfeld Test Diff (M-X) Cu1 --Cl1 .	15.3	s.u.
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please	Do !
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	52%	Note
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	4	Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	1	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	5	Info

---

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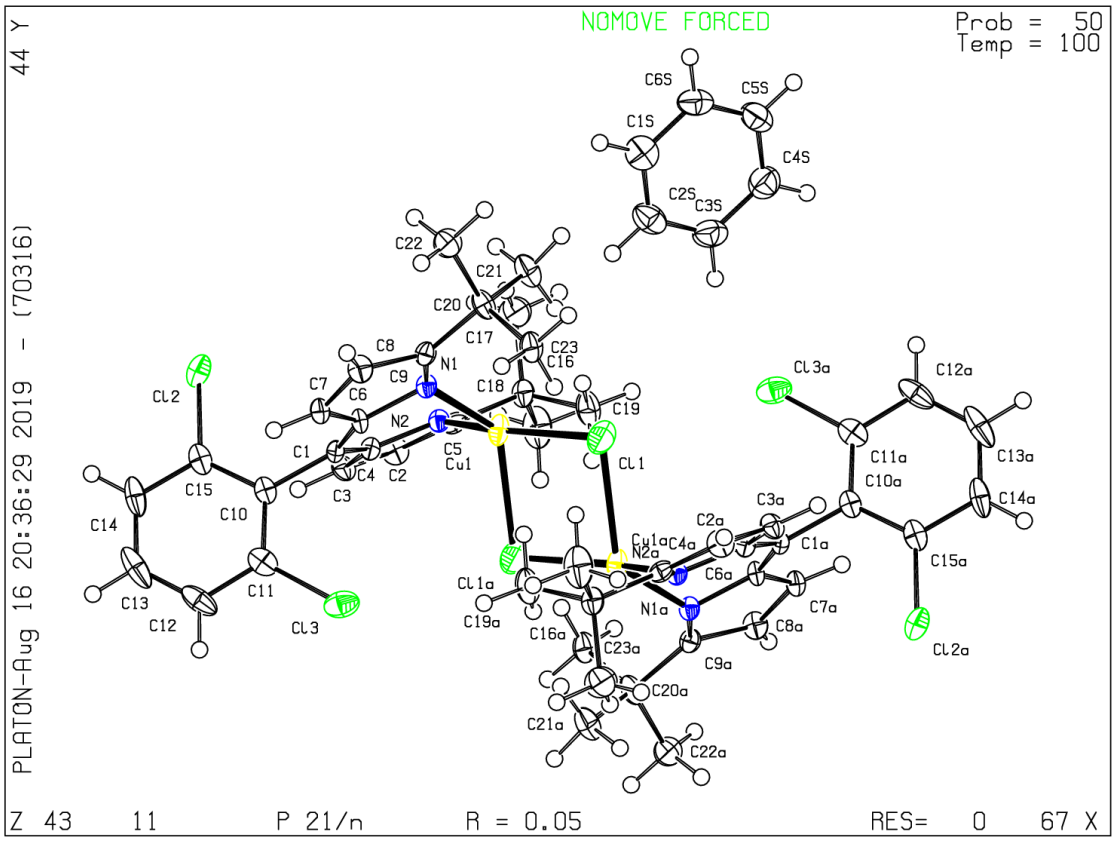
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 11 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 12

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 12

Bond precision: C-C = 0.0055 A Wavelength=0.71073

Cell: a=11.0169(6) b=15.6053(7) c=21.4320(11)
alpha=80.283(4) beta=89.945(4) gamma=74.102(4)
Temperature: 100 K

	Calculated	Reported
Volume	3488.9(3)	3488.9(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C75 H82 Cu2 N4 O P2, C4 H8 O	?
Sum formula	C79 H90 Cu2 N4 O2 P2	C79 H90 Cu2 N4 O2 P2
Mr	1316.60	1316.56
Dx,g cm-3	1.253	1.253
Z	2	2
Mu (mm-1)	0.704	0.704
F000	1392.0	1392.0
F000’	1394.07	
h,k,lmax	13,18,25	13,18,25
Nref	12341	12313
Tmin,Tmax	0.906,0.939	0.701,0.746
Tmin’	0.906	

Correction method= # Reported T Limits: Tmin=0.701 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.026

R(reflections)= 0.0554(7542) wR2(reflections)= 0.1085(12313)

S = 1.007 Npar= 868

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	3.2	Ratio
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	3.545	Check
PLAT910_ALERT_3_C	Missing # of FCF Reflection(s) Below Theta(Min).	6	Note
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.595	22	Report

---

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	10	Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	10	Report
PLAT154_ALERT_1_G	The s.u.'s on the Cell Angles are Equal ..(Note)	0.004	Degree
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records	1	Report
PLAT178_ALERT_4_G	The CIF-Embedded .res File Contains SIMU Records	1	Report
PLAT187_ALERT_4_G	The CIF-Embedded .res File Contains RIGU Records	2	Report
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 2)	100%	Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 3)	100%	Note
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 2	9.41	Check
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 3	3.59	Check
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O1S	108.7	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O1T	108.0	Degree
PLAT411_ALERT_2_G	Short Inter H...H Contact H40 ..H2TB .	2.10	Ang.
	1-x,1-y,2-z =	2_667	Check
PLAT411_ALERT_2_G	Short Inter H...H Contact H41 ..H2TB .	1.81	Ang.
	1-x,1-y,2-z =	2_667	Check
PLAT413_ALERT_2_G	Short Inter XH3 .. XHn H38A ..H2TA .	2.05	Ang.
	-1+x,y,z =	1_455	Check
PLAT413_ALERT_2_G	Short Inter XH3 .. XHn H67A ..H3TA .	1.89	Ang.
	2-x,1-y,2-z =	2_767	Check
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	16	Note
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (I) .	0.93	Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu2 (I) .	0.92	Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	190	Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !	
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	31%	Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	7	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	3	Info

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
24 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
11 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
8 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

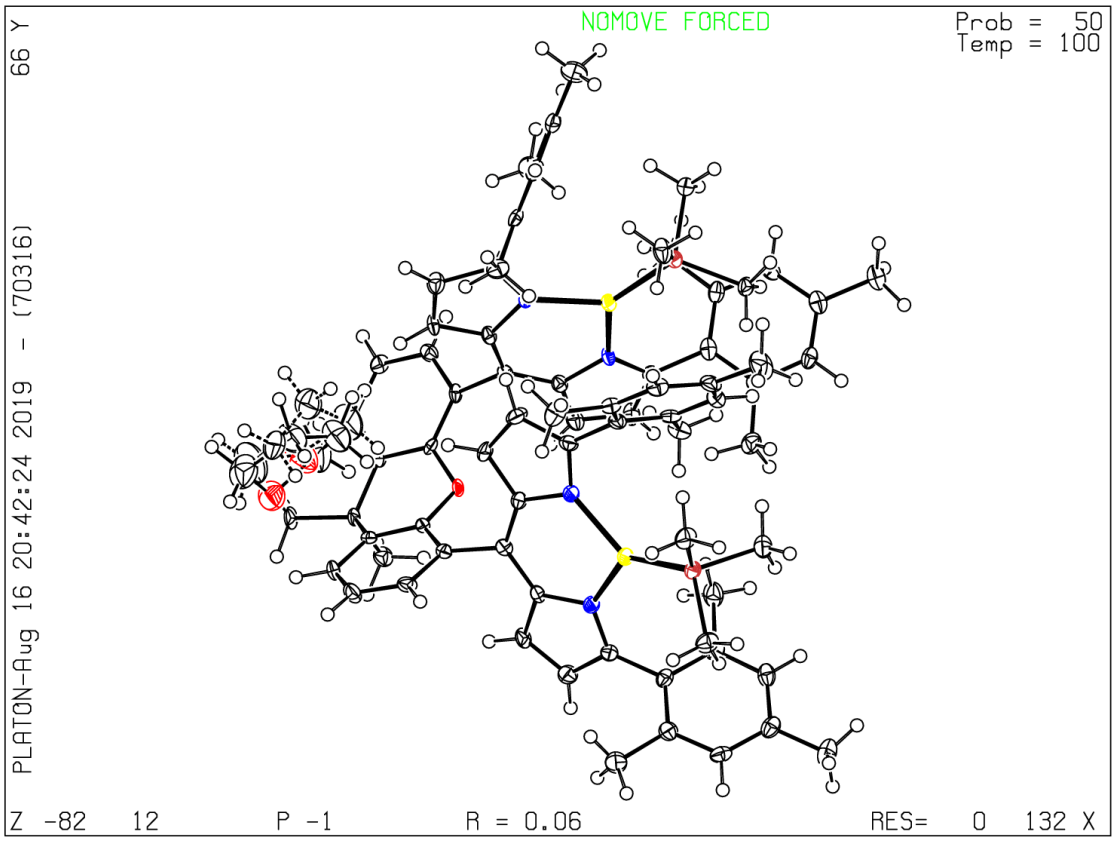
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 12 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 13

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 13

Bond precision: C-C = 0.0085 A Wavelength=0.71073

Cell: a=57.196(11) b=25.306(4) c=26.078(3)
alpha=90 beta=117.092(7) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	33604(9)	33604(10)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	8(C85 H86 Cu2 N4 O P2), 11(C7 H8), 3(C6 H6)	?
Sum formula	C775 H794 Cu16 N32 O8 P16	C96.88 H99.25 Cu2 N4 O P2
Mr	12196.78	1524.57
Dx,g cm-3	1.205	1.205
Z	2	16
Mu (mm-1)	0.594	0.594
F000	12872.0	12872.0
F000’	12889.13	
h,k,lmax	68,30,31	68,30,31
Nref	30364	30048
Tmin,Tmax	0.830,0.922	0.672,0.745
Tmin’	0.798	

Correction method= # Reported T Limits: Tmin=0.672 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.990 Theta(max)= 25.225

R(reflections)= 0.0744(19269) wR2(reflections)= 0.1931(30048)

S = 1.052 Npar= 1990

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta(Min). 22 Note

Author Response: Several reflects are co-incidental with the diffractometer beamstop an

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Alert level C

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.127
PLAT020_ALERT_3_C The Value of Rint is Greater Than 0.12 ..... 0.127 Report
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.25 Report
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 4.2 Ratio
PLAT220_ALERT_2_C Non-Solvent Resd 2 C Ueq(max)/Ueq(min) Range 3.6 Ratio
PLAT222_ALERT_3_C Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range 4.1 Ratio
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C72A Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C6A Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C68A Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C80B Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C83B Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.3 Note
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.3 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including C11S 0.133 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including C21S 0.131 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including C31S 0.108 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including C21T 0.131 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including C31T 0.108 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including C1S 0.102 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including C1T 0.102 Check
PLAT331_ALERT_2_C Small Aver Phenyl C-C Dist C68A -C73A . 1.37 Ang.
PLAT331_ALERT_2_C Small Aver Phenyl C-C Dist C80B -C85B . 1.37 Ang.
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00847 Ang.
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 94 Ang**3
PLAT721_ALERT_1_C Bond Calc 1.41(7), Rep 1.39000 Dev... 0.02 Ang.
C21T -C22T 1.555 1.555 ..... # 503 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 5.704 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 295 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) . 1 Check

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Alert level G

CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: check formula stoichiometry or atom site occupancies.
From the CIF: _cell_formula_units_Z 16
From the CIF: _chemical_formula_sum C96.88 H99.25 Cu2 N4 O P2
TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	1550.08	1550.00	0.08
H	1588.00	1588.00	0.00
Cu	32.00	32.00	0.00
N	64.00	64.00	0.00
O	16.00	16.00	0.00
P	32.00	32.00	0.00

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 39 Note

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PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         27 Report
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       0.13 Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large     266.90 Why ?
PLAT128_ALERT_4_G Alternate Setting for Input Space Group     C2/c       I2/a Note
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records         38 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          7 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records          4 Report
PLAT300_ALERT_4_G Atom Site Occupancy of C11S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C12S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C13S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C14S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C15S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C16S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C17S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H11S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H12S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H13S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15S       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17M       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17N       Constrained at       0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17O       Constrained at       0.75 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )         13% Note
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  2  )          6% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  5  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  6  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  7  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  8  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  9  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  3         11.25 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  5          8.13 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  7          6.87 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  8          6.07 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  9          2.93 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C17S Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C27S Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C37S Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H12A     ..H17A     .        2.09 Ang.
                                                x,y,z  =      1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H40F     ..H16K     .        2.01 Ang.
                                                x,y,z  =      1_555 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H31A     ..H48G     .        2.07 Ang.
                                             x,1-y,1/2+z  =      6_566 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H71A     ..H49I     .        2.11 Ang.
                                             1-x,1-y,1-z  =      5_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H39D     ..H22T     .        2.13 Ang.
                                             x,1-y,1/2+z  =      6_566 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          27 Note
PLAT722_ALERT_1_G Angle   Calc      108.00, Rep      109.50 Dev...        1.50 Degree
            H15A    -C15A    -H15B       1.555  1.555  1.555     #  124 Check
PLAT722_ALERT_1_G Angle   Calc      111.00, Rep      109.50 Dev...        1.50 Degree
            C14A    -C15A    -H15C       1.555  1.555  1.555     #  125 Check
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #          15 Check
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1A      (I)       .        0.95 Info
PLAT802_ALERT_4_G CIF Input Record(s) with more than 80 Characters          1 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        276 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still         36% Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
```

PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 1 Info

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
28 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
60 **ALERT level G** = General information/check it is not something unexpected

7 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
30 ALERT type 2 Indicator that the structure model may be wrong or deficient
13 ALERT type 3 Indicator that the structure quality may be low
38 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

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Publication of your CIF in IUCr journals

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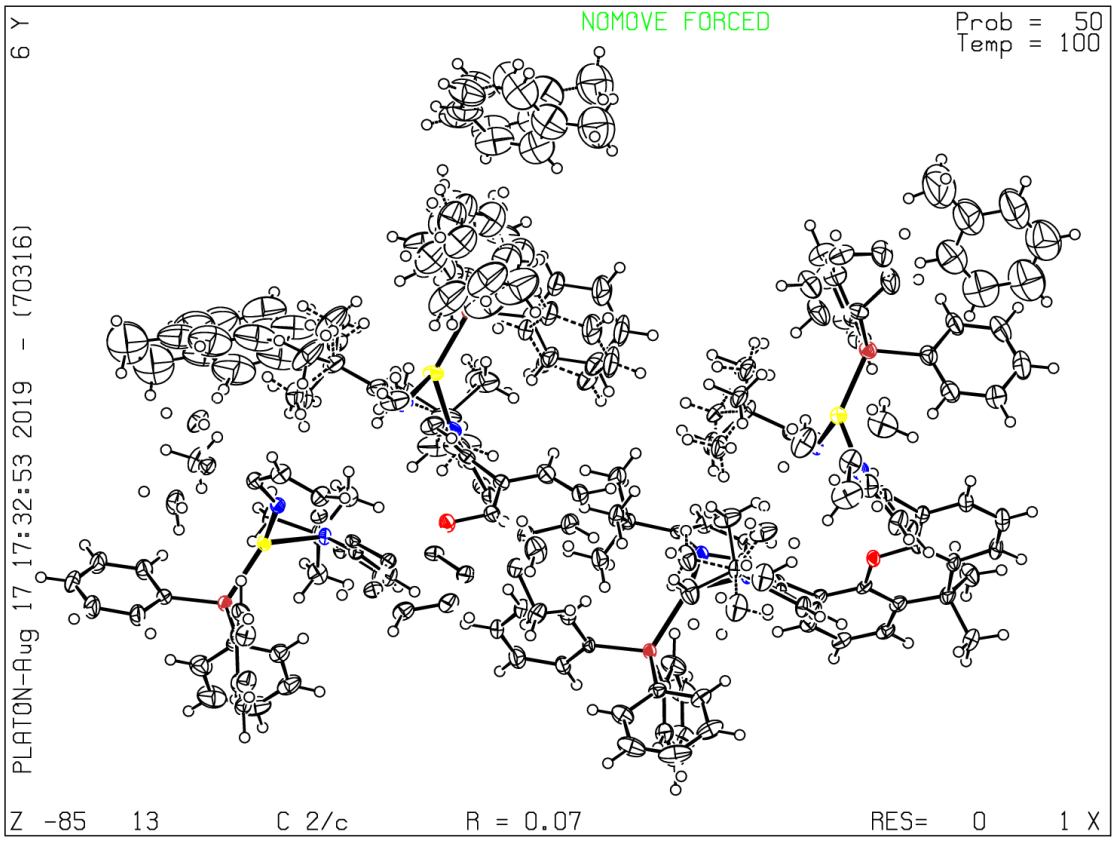
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 13 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 14

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 14

```
Bond precision:  C-C = 0.0064 A          Wavelength=0.71073

Cell:          a=12.031(5)       b=14.049(6)      c=24.368(11)
               alpha=99.925(7)   beta=99.557(8)   gamma=105.278(7)
Temperature:   100 K
```

	Calculated	Reported
Volume	3816(3)	3816(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C79 H82 Cu2 N6 O), 1.5(C4 H10 O), C4 H4 O, 0.5(C4 H8 O)	?
Sum formula	C170 H187 Cu4 N12 O5	C85 H93.50 Cu2 N6 O2.50
Mr	2732.53	1366.23
Dx,g cm-3	1.189	1.189
Z	1	2
Mu (mm-1)	0.608	0.608
F000	1447.0	1447.0
F000’	1448.71	
h,k,lmax	14,16,29	14,16,29
Nref	13862	13626
Tmin,Tmax	0.875,0.934	0.607,0.745
Tmin’	0.777	

```
Correction method= # Reported T Limits: Tmin=0.607 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.983          Theta(max)= 25.277

R(reflections)= 0.0621( 9628)     wR2(reflections)= 0.1921( 13626)

S = 1.021                 Npar= 1022
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT214_ALERT_2_C	Atom C1S (Anion/Solvent) ADP max/min Ratio	4.1 prolat
PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	3.6 Ratio
PLAT234_ALERT_4_C	Large Hirshfeld Difference C76 --C78A .	0.18 Ang.
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	C63 Check
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C76 Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including O2S	0.135 Check
PLAT341_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00638 Ang.
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	2.155 Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	179 Report
PLAT918_ALERT_3_C	Reflection(s) with I(obs) much Smaller I(calc) .	2 Check

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Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	28 Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	27 Report
PLAT045_ALERT_1_G	Calculated and Reported Z Differ by a Factor ...	0.50 Check
PLAT072_ALERT_2_G	SHELXL First Parameter in WGHT Unusually Large	0.11 Report
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	5.28 Why ?
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records	6 Report
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records	4 Report
PLAT176_ALERT_4_G	The CIF-Embedded .res File Contains SADI Records	4 Report
PLAT177_ALERT_4_G	The CIF-Embedded .res File Contains DELU Records	1 Report
PLAT178_ALERT_4_G	The CIF-Embedded .res File Contains SIMU Records	2 Report
PLAT187_ALERT_4_G	The CIF-Embedded .res File Contains RIGU Records	5 Report
PLAT230_ALERT_2_G	Hirshfeld Test Diff for C76 --C77 .	7.2 s.u.
PLAT232_ALERT_2_G	Hirshfeld Test Diff (M-X) Cu2 --C70 .	6.5 s.u.
PLAT300_ALERT_4_G	Atom Site Occupancy of O2S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C5S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C6S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C7S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C8S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H5SA Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H5SB Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H5SC Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H6SA Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H6SB Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H7SA Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H7SB Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H8SA Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H8SB Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H8SC Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of O12S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C15S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C16S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C17S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C18S Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H16D Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H16E Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H17D Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H17E Constrained at	0.5 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of O1S Constrained at	0.25 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C1S Constrained at	0.25 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C2S Constrained at	0.25 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C3S Constrained at	0.25 Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C4S Constrained at	0.25 Check

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PLAT300_ALERT_4_G Atom Site Occupancy of H1SA       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SB       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1SC       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SA       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SB       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SA       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SB       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SA       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SB       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4SC       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O11S       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C11S       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C12S       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C13S       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C14S       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H11A       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H11B       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H12A       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H12B       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H13A       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H13B       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14A       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14B       Constrained at       0.25 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )         7% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  5  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  2          7.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  3          4.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  4          3.75 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  5          3.25 Check
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O12S            97.6 Degree
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H31      ..H42A     .       2.13 Ang.
                                                    x,y,z  =      1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H31      ..H42D     .       2.08 Ang.
                                                    x,y,z  =      1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H40      ..H42B     .       2.09 Ang.
                                                    x,y,z  =      1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H40      ..H42E     .       2.13 Ang.
                                                    x,y,z  =      1_555 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H67A     ..H77C     .       1.82 Ang.
                                                  1+x,y,z  =      1_655 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          21 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #      28 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #       2 Note
              C4 H10 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #       3 Note
              C4 H4 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #       5 Note
              C4 H8 O
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1       (I)       .      0.98 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............     434 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .   Please Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still      48% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).       1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600      57 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...       5 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.       4 Info
```

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0 **ALERT level A** = Most likely a serious problem - resolve or explain

```
 0 ALERT level B = A potentially serious problem, consider carefully
10 ALERT level C = Check. Ensure it is not caused by an omission or oversight
93 ALERT level G = General information/check it is not something unexpected

 2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
19 ALERT type 2 Indicator that the structure model may be wrong or deficient
 8 ALERT type 3 Indicator that the structure quality may be low
73 ALERT type 4 Improvement, methodology, query or suggestion
 1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

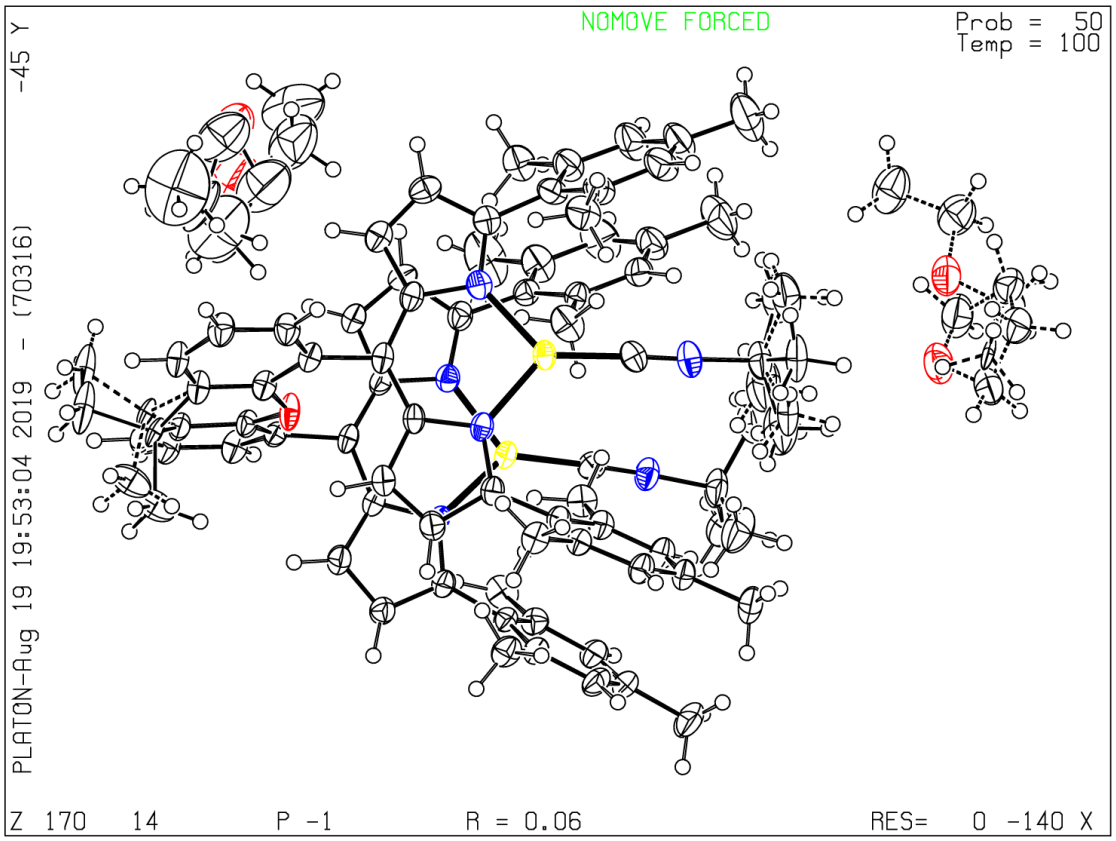
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 14 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 15

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 15

```
Bond precision:  C-C = 0.0032 A          Wavelength=0.71073

Cell:           a=16.3247(7)    b=18.2917(8)        c=20.5023(9)
                alpha=90        beta=106.300(1)     gamma=90
Temperature:    100 K

                Calculated                  Reported
Volume          5876.0(4)                   5876.0(4)
Space group     P 21/n                      P 21/n
Hall group      -P 2yn                      -P 2yn
Moiety formula  C59 H74 Cu2 N6 O, C4 H8 O   ?
Sum formula     C63 H82 Cu2 N6 O2           C63 H82 Cu2 N6 O2
Mr              1082.45                     1082.42
Dx,g cm-3       1.224                       1.224
Z               4                           4
Mu (mm-1)       0.770                       0.770
F000            2304.0                      2304.0
F000'           2307.18
h,k,lmax        19,21,24                    19,21,24
Nref            10431                       10423
Tmin,Tmax       0.871,0.912                 0.688,0.745
Tmin'           0.857

Correction method= # Reported T Limits: Tmin=0.688 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.065

R(reflections)= 0.0342( 7134)     wR2(reflections)= 0.0716( 10423)

S = 0.911                 Npar= 737
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT213_ALERT_2_C	Atom C57 has ADP max/min Ratio	3.1 prolat
PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	5.9 Ratio
PLAT222_ALERT_3_C	Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range	5.8 Ratio
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C56 Check
PLAT905_ALERT_3_C	Negative K value in the Analysis of Variance ...	-0.193 Report
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.596	9 Report

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	19 Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	10 Report
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records	4 Report
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records	2 Report
PLAT176_ALERT_4_G	The CIF-Embedded .res File Contains SADI Records	1 Report
PLAT187_ALERT_4_G	The CIF-Embedded .res File Contains RIGU Records	2 Report
PLAT232_ALERT_2_G	Hirshfeld Test Diff (M-X) Cu1 --C50 .	7.5 s.u.
PLAT232_ALERT_2_G	Hirshfeld Test Diff (M-X) Cu2 --C55 .	5.2 s.u.
PLAT301_ALERT_3_G	Main Residue Disorder .....(Resd 1)	6% Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 2)	100% Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 3)	100% Note
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 2	7.66 Check
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 3	5.34 Check
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O1S	109.2 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O1T	109.5 Degree
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	16 Note
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (I) .	0.94 Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu2 (I) .	0.95 Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	77 Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	45% Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	9 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
22 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
10 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
9 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

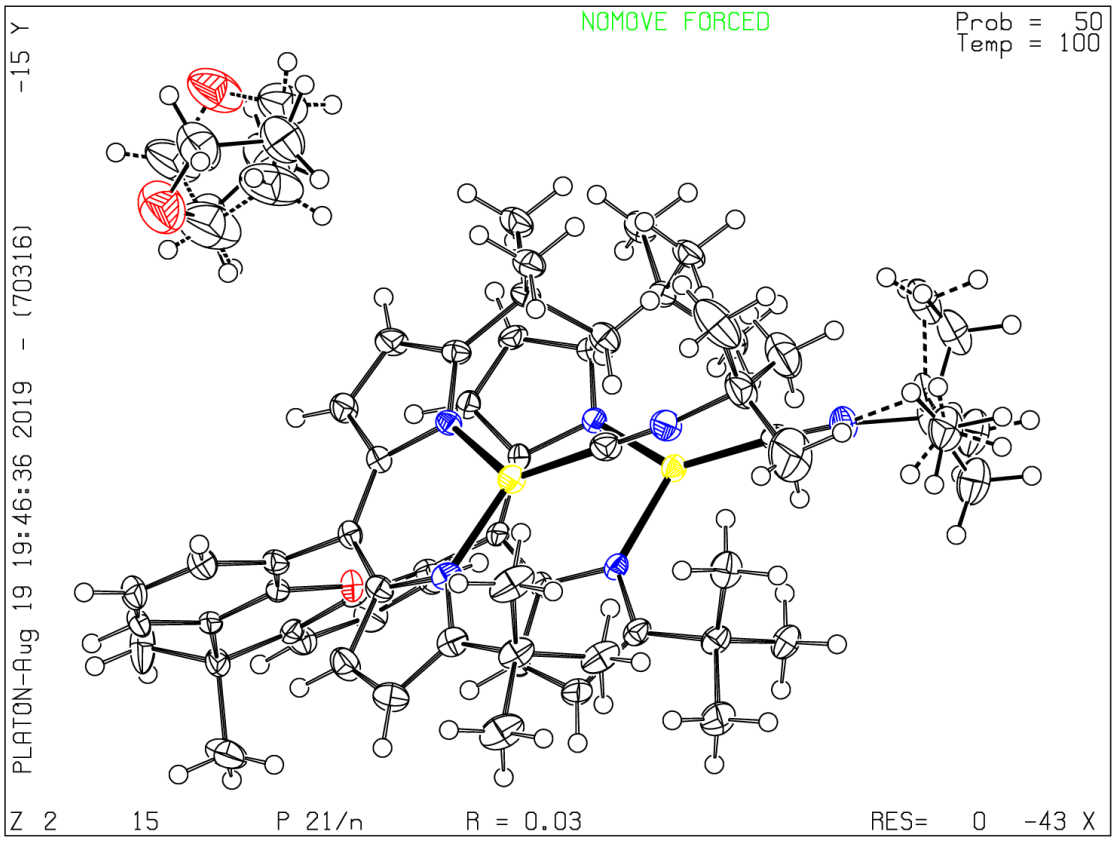
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 15 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 16

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 16

Bond precision: C-C = 0.0081 A Wavelength=0.71073

Cell: a=13.3375(5) b=25.1228(7) c=25.4322(7)
alpha=90 beta=100.624(3) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	8375.6(5)	8375.6(4)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	4(C83 H84 Cu2 N8 O), 5(C4 H10 O), 7(C4 H8 O)	?
Sum formula	C380 H442 Cu8 N32 O16	C95 H110.50 Cu2 N8 O4
Mr	6222.08	1555.49
Dx,g cm-3	1.234	1.234
Z	1	4
Mu (mm-1)	0.564	0.564
F000	3306.0	3306.0
F000’	3309.58	
h,k,lmax	15,29,30	15,29,30
Nref	14858	14837
Tmin,Tmax	0.893,0.893	0.688,0.745
Tmin’	0.893	

Correction method= # Reported T Limits: Tmin=0.688 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.064

R(reflections)= 0.0734(9062) wR2(reflections)= 0.2128(14837)

S = 1.030 Npar= 1153

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT094_ALERT_2_C	Ratio of Maximum / Minimum Residual Density	3.06	Report
PLAT213_ALERT_2_C	Atom C37 has ADP max/min Ratio	3.2	prolat
PLAT213_ALERT_2_C	Atom C37A has ADP max/min Ratio	3.2	prolat
PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	4.0	Ratio
PLAT222_ALERT_3_C	Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range	4.4	Ratio
PLAT230_ALERT_2_C	Hirshfeld Test Diff for N1 --C5 .	5.5	s.u.
PLAT230_ALERT_2_C	Hirshfeld Test Diff for C1 --C2 .	5.8	s.u.
PLAT230_ALERT_2_C	Hirshfeld Test Diff for C8 --C9 .	6.1	s.u.
PLAT234_ALERT_4_C	Large Hirshfeld Difference C7 --C8 .	0.16	Ang.
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including O1S	0.137	Check
PLAT341_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00808	Ang.
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	2.816	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.596	21	Report
PLAT918_ALERT_3_C	Reflection(s) with I(obs) much Smaller I(calc) .	1	Check
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 2.05A From O1S	1.85	eA-3

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	62	Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	25	Report
PLAT045_ALERT_1_G	Calculated and Reported Z Differ by a Factor ...	0.25	Check
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	22.75	Why ?
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records	21	Report
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records	5	Report
PLAT176_ALERT_4_G	The CIF-Embedded .res File Contains SADI Records	4	Report
PLAT178_ALERT_4_G	The CIF-Embedded .res File Contains SIMU Records	1	Report
PLAT187_ALERT_4_G	The CIF-Embedded .res File Contains RIGU Records	5	Report
PLAT300_ALERT_4_G	Atom Site Occupancy of O1S Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C1S Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C2S Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C3S Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C4S Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H1SA Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H1SB Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H1SC Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H2SA Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H2SB Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H3SA Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H3SB Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H4SA Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H4SB Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H4SC Constrained at	0.75	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of O3S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C11S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C12S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C13S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C14S Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H11A Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H11B Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H11C Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H12D Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H12E Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H13D Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H13E Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H14D Constrained at	0.5	Check

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PLAT300_ALERT_4_G Atom Site Occupancy of H14E       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14F       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O4S        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C15S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C16S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C17S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C18S       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H17B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H18A       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H18B       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O2S        Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C5S        Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C6S        Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C7S        Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C8S        Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SA       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H5SB       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SA       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H6SB       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7SA       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7SB       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H8SA       Constrained at       0.25 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H8SB       Constrained at       0.25 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )        17% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  5  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  6  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  7  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  2         11.25 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  3          7.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  4          6.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  5          8.81 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  6          3.25 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  7          4.19 Check
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O4S           110.0 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O5S           107.6 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O5T           107.8 Degree
PLAT411_ALERT_2_G Short Inter H...H Contact  H13E     ..H16      .       2.06 Ang.
                                                    x,y,z  =      1_555 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H21      ..H43D     .       1.98 Ang.
                                    1/2+x,3/2-y,1/2+z  =      4_676 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H34C     ..H48A     .       2.04 Ang.
                                    1/2+x,3/2-y,1/2+z  =      4_676 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H80      ..H42F     .       2.08 Ang.
                                    1/2+x,3/2-y,1/2+z  =      4_676 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          19 Note
PLAT722_ALERT_1_G Angle   Calc      111.00, Rep      109.80 Dev...       1.20 Degree
               C21T    -C22T    -H22D       1.555  1.555  1.555     #  532 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #           4 Note
               C4 H8 O
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1       (I)       .       0.88 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Cu2       (I)       .       0.86 Info
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....           ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        369 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
```

PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	34% Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	2 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	1 Info

---

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 15 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 96 ALERT level G = General information/check it is not something unexpected

  3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 21 ALERT type 2 Indicator that the structure model may be wrong or deficient
  8 ALERT type 3 Indicator that the structure quality may be low
 76 ALERT type 4 Improvement, methodology, query or suggestion
  3 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

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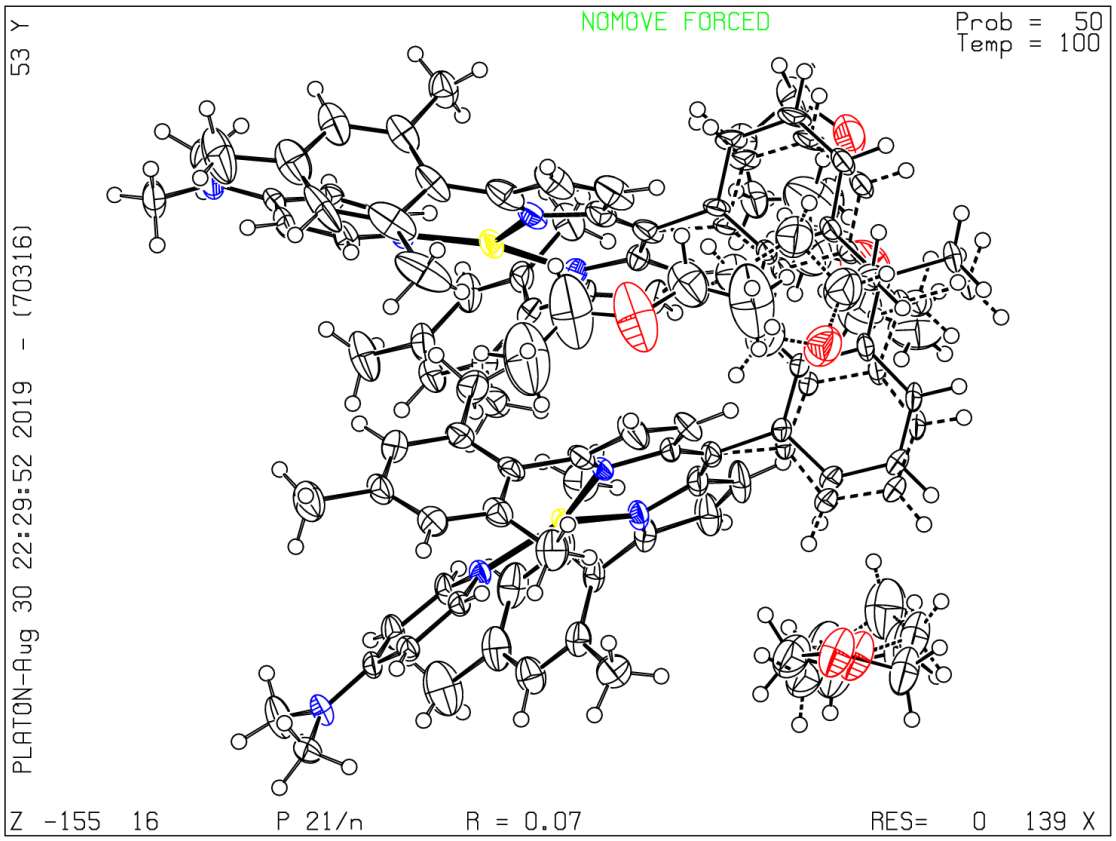
PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock 16 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 18

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 18

```
Bond precision:  C-C = 0.0041 A          Wavelength=0.71073

Cell:            a=11.189(9)     b=17.657(12)      c=22.207(15)
                 alpha=90        beta=95.88(2)     gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	4364(5)	4364(6)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C46 H50 Cl4 Cu2 N4	?
Sum formula	C46 H50 Cl4 Cu2 N4	C46 H50 Cl4 Cu2 N4
Mr	927.80	927.78
Dx,g cm-3	1.412	1.412
Z	4	4
Mu (mm-1)	1.257	1.257
F000	1920.0	1920.0
F000’	1925.34	
h,k,lmax	13,21,26	13,21,26
Nref	7799	7739
Tmin,Tmax	0.578,0.695	0.546,0.745
Tmin’	0.535	

```
Correction method= # Reported T Limits: Tmin=0.546 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.992          Theta(max)= 25.130

R(reflections)= 0.0354( 6072)     wR2(reflections)= 0.0921( 7739)

S = 1.027                 Npar= 517
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT094_ALERT_2_C	Ratio of Maximum / Minimum Residual Density	2.41	Report
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.597	55	Report

Alert level G

PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (I) .	0.79	Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu2 (I) .	0.80	Info
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please	Do !
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	64%	Note
PLAT954_ALERT_1_G	Reported (CIF) and Actual (FCF) Kmax Differ by .	1	Units
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	6	Info

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Datablock 18 - ellipsoid plot