Electronic Supplementary Information (ESI)

Using Internal Electrostatic Fields to Manipulate the Valence Manifolds of Copper Complexes

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General considerations

All experiments were carried out under an atmosphere of purified nitrogen using standard Schlenk line techniques or in a dry, oxygen-free glovebox. All glassware, molecular sieves, stir bars, cannulas, and Celite were dried in a 150 °C oven for at least 12 h prior to use. Solvents (tetrahydrofuran, acetonitrile, isobutyronitrile, *n*-pentane, o-difluorobenzene, diethyl ether) were dried by passage through a column of activated alumina and stored over 4 Å molecular sieves under an inert atmosphere, while dibutyl ether was dried with sodium/benzophenone and distilled under an inert atmosphere of dinitrogen. Deuterated solvents were purchased from Cambridge Isotope Laboratory, dried over Na^0/benzophenone (C_6D_6) or CaH_2 (CD_3CN), isolated via vacuum transfer or distillation, and stored under an inert atmosphere over 3 Å molecular sieves. Trimethylphosphine and tris(azido)tren were prepared according to modified literature procedures (see below), and $CuBArF_4$•4MeCN was prepared according to a literature procedure.[1] All other reagents were obtained from commercial sources and used without further purification. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker UNI 400 spectrometer. All chemical shifts (δ) are reported in units of ppm and referenced to the residual proteo-solvent resonance for ^1H and $^{13}C\{^1H\}$ chemical shifts. External H_3PO_4 was used for referencing ^{31}P chemical shifts. Elemental analyses were performed by Midwest Microlab, LLC or on a Costech ECS 4010 analyzer at the University of Pennsylvania.

Synthetic Procedures

Synthesis of trimethylphosphine (PMe_3)

Trimethylphosphine was prepared in bulk according to the following procedure, which is a modification of that reported in the literature:[2] Magnesium turnings (101 g, 4.15 mol) were rigorously flame-dried in a 3 L, 2-necked Schlenk flask, followed by the addition of 1.5 L dry and degassed dibutyl ether (Bu_2O) and a large magnetic stir bar. Several crystals of iodine (I_2) was added to activate the magnesium surface, and the mixture was stirred until the solution became colorless. The flask containing the reaction suspension was cooled in ice bath (0 °C), and methyl iodide (240 mL, 3.85 mol) was added dropwise over the course of 2 h. The reaction was warmed to room temperature and stirred under N_2 overnight to ensure the full formation of the Grignard. The flask containing the Grignard was cooled in a -10 °C salt/ice bath, and a Bu_2O solution (300 mL) of triphenyl phosphite (300 mL, 1.14 mol) was added dropwise via cannula over the course of 2.5 h. Upon completion of the addition of triphenyl phosphite, the reaction was warmed to room temperature, and the flask was fitted with a distillation apparatus connected by a 15-inch Vigreux column with a 250 mL Schlenk flask containing a stir bar as the receiving vessel. The reaction mixture was distilled, and fractions were collected until the thermometer read 110 °C. The donor pot was quenched via addition of excess (> 85 g, 1.14 mol) sodium hypochlorite (left to stir overnight to ensure full quenching prior to disposal). The collected fractions were again distilled, this time with use of a 6-inch Vigreux column. The product was collected at 38 °C in a 100 mL Schlenk bomb (73.8 g, 85% yield). The identity of the pure phosphine was confirmed via NMR spectroscopy, and the material was used without further purification. **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 0.90 (d, 9H, J_{PH} = 4 Hz) ppm. **$^{31}P\{^1H\}$ NMR:** (162 MHz, C_6D_6, 300 K): δ = -62.60 (s) ppm.

Synthesis of 2-azido-N,N-bis(2-azidoethyl)ethaneamine (*tris*(azido)tren)

WARNING: extreme caution should be used when using organic azides, especially with such high percent-nitrogen content. We have not experienced any safety issues with this particular molecule under the conditions described below; however, the use of proper personal protective equipment and blast shields is recommended to ensure safe handling. We also recommend keeping the molecule in solution at all times to lower the chance of runaway (explosive) thermal decomposition.

Tris(azido)tren was prepared according to the following procedure, which is a modification of that reported in the literature:[3] 2-chloro-*N*,*N*-*bis*(2-chloroethyl)ethanammonium chloride (1.6 g, 6.64 mmol) was combined with sodium azide (2.4 g, 36.92 mmol) in DMSO (50 mL) while open to the air. The resulting reaction mixture was heated to 92 °C for 8 h. Upon cooling to room temperature, cold deionized water (300 mL) was added, and the resulting aqueous mixture was basified with sodium

carbonate (3.2 g, 30.2 mmol). The aqueous mixture was extracted with diethyl ether (3 x 200 mL), and the combined organic layers were washed with deionized water (3 x 100 mL), and brine (100 mL). The diethyl ether solution was dried with sodium sulfate, then transferred to a Schlenk bomb where oxygen was removed via 3 freeze-pump-thaw cycles. Extreme caution was exercised to keep the product in solution at all times to lower the possibility of detonation. The diethyl ether mixture was dried rigorously over CaH_2 for 2-4 d, after which time the heterogeneous mixture was filtered through a plug of Celite. The product was used without further purification while assuming quantitative yields.

Synthesis of $^{Me3}P_3$tren

A Schlenk tube containing a diethyl ether solution (~50 mL) of *tris*(azido)tren (6.64 mmol) was cooled to 0 °C. Trimethylphosphine (2.03 mL, 19.92 mmol) was added quickly via an air-tight syringe, and the solution was stirred at 0 °C for 5 min before warming to room temperature. The resulting reaction mixture was stirred at room temperature for 6 h while open to a mineral oil bubbler to prevent a buildup of pressure from N_2 evolution. Volatile materials were then removed *in vacuo*, and the resulting white solid was washed with *n*-pentane. The phases were separated via cannula filtration, and the resulting white solid was dried under vacuum for 30 min (1.5 – 1.8 g, 62-74% yield). **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 3.60 (dt, 6H, J_{HH} = 8 Hz, J_{PH} = 24 Hz), δ = 3.16 (t, 6H, J_{HH} = 8 Hz), δ = 0.93 (d, 27H, J_{PH} = 12 Hz) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6 300 K): δ = 63.49 (d, J_{PC} = 17 Hz), δ = 45.60 (d, J_{PC} = 7 Hz), δ = 16.63 (d, J_{PC} = 65 Hz) ppm. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6, 300 K): δ = 3.40 (s) ppm.

Synthesis of $^{Me2Ph}P_3$tren

A Schlenk flask containing a diethyl ether solution (~50 mL) of *tris*(azido)tren (6.64 mmol) was cooled to 0 °C. Dimethylphenylphosphine (2.83 mL, 19.92 mmol) was added quickly via an air-tight syringe. The resulting solution was warmed to room temperature and stirred for 6 h while open to a mineral oil bubbler to prevent a buildup of pressure from N_2 evolution. Volatile materials were removed *in vacuo* to generate a clear, viscous oil. The product was crystallized from a 1:1 mixture of diethyl ether and *n*-hexane at -78 °C, and the phases were separated via cannula filtration. Upon warming to room temperature, the material lost crystallinity and formed a liquid, which was washed extensively with *n*-hexane to remove residual phosphine. The product was further dried under vacuum for a minimum of 30 min. The resulting liquid was washed with cold diethyl ether, and upon removal of all volatile materials, the product was isolated as a free-flowing solid (2.28 g, 62%). **^{1}H NMR** (400 MHz, C_6D_6, 300K): δ = 7.62 (m, 6H), δ = 7.12 (m, 9H), δ = 3.65 (dt, 6H, J_{HH} = 8 Hz, J_{PH} = 20 Hz), δ = 3.25 (t, 6H, J_{HH} = 8 Hz), δ = 1.23 (d, 18H, J_{PH} = 12 Hz) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 300K): δ = 137.12 (d, J_{PC} = 86 Hz), δ = 130.72 (d, J_{PC} = 8 Hz), δ = 130.40 (d, J_{PC} = 2 Hz), δ = 128.46 (d, J_{PC} = 10 Hz), δ = 63.20 (d, J_{PC} = 18 Hz), δ = 45.42 (d, J_{PC} = 6 Hz), δ = 16.12 (d, J_{PC} = 68 Hz) ppm. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6, 300K): δ = 2.60 (s) ppm.

Synthesis of $^{MePh2}P_3$tren

A Schlenk tube containing a diethyl ether (~50 mL) solution of *tris*(azido)tren (6.64 mmol) was cooled to 0 °C. Methyldiphenylphosphine (3.71 mL, 19.92 mmol) was added in one portion via an air-tight syringe. The resulting solution was warmed to room temperature and stirred for 6 h while open to a mineral oil bubbler to prevent a buildup of pressure from N_2 evolution. All volatile materials were then removed *in vacuo*, and the resulting pale oil was washed with *n*-hexane. The phases were separated via cannula filtration, and the resulting oil was dried under vacuum for 30 minutes. The resulting solid was washed with cold diethyl ether, and upon removal of all volatile materials *in vacuo*, the product was isolated as a white free-flowing powder (3.09 g 63%). **^{1}H NMR** (400 MHz, C_6D_6, 300K): δ = 7.67 (m, 12H), δ = 7.05 (m, 18H), δ = 3.68 (m, 6H), δ = 3.28 (t, 6H, J_{HH} = 8 Hz), δ = 1.55 (d, 9H, J_{PH} = 20 Hz) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 300K): δ = 135.80 (d, J_{PC} = 93 Hz), δ = 131.62 (d, J_{PC} = 9 Hz), δ = 130.49 (d, J_{PC} = 3 Hz), δ = 128.39 (d, J_{PC} = 10 Hz), δ = 62.90 (d, J_{PC} = 19 Hz), δ = 45.22 (d, J_{PC} = 6 Hz), δ = 14.98 (d, J_{PC} = 67 Hz) ppm. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6, 300K): δ = 1.81 (s) ppm.

Synthesis of $^{Ph3}P_3$tren

A Schlenk tube containing a diethyl ether solution (~50 mL) of *tris*(azido)tren (6.64 mmol) was cooled to 0 °C. A THF solution (5 mL) of triphenylphosphine (5.22, 19.92 mmol) was added to the reaction mixture via cannula transfer. The resulting solution was warmed to room temperature and stirred for 6 h while open to a mineral oil bubbler to prevent a buildup of pressure from N_2 evolution. All volatile materials were then removed *in vacuo*, and the resulting white solid was washed with *n*-hexane. The phases were separated via cannula filtration, and the product was extracted into diethyl ether (10 mL), which was filtered through a plug of Celite. The resulting solution was allowed to sit at -20 °C overnight to crystallize unreacted triphenylphosphine. The mother liquor was separated by filtration and all volatile materials of the filtrate were removed *in vacuo*. The resulting white solid was dried under vacuum for a minimum of 30 min (3.39 g, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K): δ = 7.57 (m, 18H), δ = 7.42 (m, 9H), δ = 7.33 (m, 18H), δ = 3.11 (m, 6H), δ = 2.65 (t, 6H, J_{HH} = 8 Hz) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 300K): δ = 133.62 (d, J_{PC} = 19 Hz), δ = 132.67 (d, J_{PC} = 9 Hz), δ = 131.11 (d, J_{PC} = 3 Hz), δ = 128.39 (d, J_{PC} = 11 Hz), δ = 61.21 (d, J_{PC} = 18 Hz), δ = 44.44 (d, J_{PC} = 6 Hz) ppm. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 300K): δ = 11.52 (s) ppm.

Synthesis of $^{Me2(NEt2)}P_3$tren

A Schlenk tube containing a diethyl ether solution (~50 mL) of *tris*(azido)tren (1.33 mmol) was cooled to 0 °C. A diethyl ether solution (100 mL) of $PMe_2(NEt_2)$ (500 mg, 3.75 mmol) was added to the reaction mixture via cannula transfer. The resulting solution was warmed to room temperature and stirred for 6 h while open to a mineral oil bubbler to prevent a buildup of pressure from N_2 evolution. All volatile materials were then removed *in vacuo*, and the resulting white solid was washed with *n*-hexane. The phases were separated via cannula filtration, and the resulting white solid was dried under vacuum for a minimum of 30 min (431 mg, 60%). **^{1}H NMR** (400 MHz, C_6D_6, 300K): δ = 3.60 (dt, 6H, J_{HH} = 8 Hz, J_{PH} = 20 Hz), δ = 3.25 (t, 6H, J_{HH} = 8 Hz), δ = 2.73 (m, 12H), δ = 1.07 (d, 18H, J_{PH} = 12 Hz), δ = 0.84 (d, 18H, J_{HH} = 6 Hz) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 300K): δ = 62.77 (d, J_{PC} = 21 Hz), δ = 44.76 (d, J_{PC} = 7 Hz), δ = 38.30 (d, J_{PC} = 2 Hz), δ = 14.48 (d, J_{PC} = 19 Hz), δ = 13.72 (s) ppm. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6, 300K): δ = 20.79 (s) ppm.

Synthesis of [$^{Me3}P_3$tren-Cu^{I}]BAr$^{F}_4$ (1^{PMe3})

[*Tetrakis*(acetonitrile)copper(I)][*tetrakis*(pentafluorophenyl)borate] ($CuBAr^{F}_4$•4MeCN) (400 mg, 0.44 mmol) was dissolved in THF (30 mL), and the Schlenk flask containing the solution was cooled to -78 °C. One equivalent of $^{Me3}P_3$tren (162 mg, 0.44 mmol) dissolved in THF (10 mL) was transferred to the flask via cannula, resulting in the formation of a colorless solution. The reaction mixture was warmed to room temperature and stirred for an additional 20 min. Volatile materials were then removed *in vacuo*, resulting in the formation of a white solid. The product was extracted with diethyl ether (30 mL) and filtered through a plug of Celite. Volatile materials were again removed *in vacuo*, and the resulting white solid was washed with *n*-pentane. The phases were separated via cannula filtration, and the product was dried under vacuum for 30 min (350 mg, 72%). Single crystals suitable for crystallographic analysis were obtained by storing a saturated diethyl ether solution at -78 °C for two days. **^{1}H NMR** (400 MHz, CD_3CN, 300 K): δ = 2.99 (dt, 6H, J_{HH} = 6 Hz, J_{PH} = 16 Hz), δ = 2.51 (t, 6H, J_{HH} = 4 Hz), δ = 1.49 (d, 27H, J_{PH} = 16 Hz) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN, 300 K) δ = 58.49 (d, J_{PC} = 10 Hz), δ = 45.27 (d, J_{PC} = 2 Hz), δ = 15.81 (d, J_{PC} = 68 Hz) ppm. **^{31}P{^{1}H} NMR** (162 MHz, CD_3CN, 300 K): δ = 24.39 (s) ppm. **Anal. Calcd.** For $C_{39}H_{39}BCuF_{20}N_4P_3$: C, 42.16; H, 3.54; N, 5.04. **Found**: C, 42.52; H, 3.56; N, 5.00.

Synthesis of [$^{Me2Ph}P_3$tren-Cu^{I}]BAr$^{F}_4$ (1^{PMe2Ph})

$CuBAr^{F}_4$•4MeCN (400 mg, 0.44 mmol) was dissolved in THF (30 mL), and the Schlenk flask containing the solution was cooled to -78 °C. One equivalent of $^{Me2Ph}P_3$tren (244 mg, 0.44 mmol) dissolved in THF (10 mL) was transferred to the flask via cannula, resulting in the formation of a yellow solution. The reaction mixture was warmed to room temperature and stirred for an additional 20 min. Volatile materials were removed *in vacuo*, resulting in the formation of a yellow solid. The product was washed with diethyl ether (3 x 30 mL), the phases were separated via cannula filtration, and the resulting yellow solid was dried under vacuum for 30 min (420 mg, 74%). Single crystals suitable crystallographic analysis were obtained following diffusion of *n*-pentane into a THF solution of **1^{PMe2Ph}** at room temperature. **^{1}H NMR**

(400 MHz, CD_3CN, 300K): δ = 7.81 (m, 9H), δ = 7.55 (m, 3H), δ = 7.49 (m, 9H), δ = 3.00 (dt, 6H, J_{HH} = 6 Hz, J_{PH} = 18 Hz), δ = 2.52 (t, 6H, J_{HH} = 6 Hz), δ = 1.72 (d, 18H, J_{PH} = 12 Hz) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, CD_3CN, 300K): δ = 134.07 (d, J_{PC} = 85 Hz), δ = 132.63 (d, J_{PC} = 3 Hz), δ = 131.47 (d, J_{PC} = 9 Hz), δ = 129.73 (d, J_{PC} = 11 Hz), δ = 57.82 (d, J_{PC} = 14 Hz), δ = 45.43 (d, J_{PC} = 2 Hz), δ = 15.70 (d, J_{PC} = 73 Hz) ppm. **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_3CN, 300K): δ = 22.23 (s) ppm. **Anal. Calcd.** for $C_{54}H_{45}BCuF_{20}N_4P_3$: C, 50.00; H, 3.50; N, 4.32. **Found**: C, 49.96; H, 3.38; N, 4.57.

Synthesis of [^{MePh2}P$_3$tren-Cu^I]BAr$^F_4$ (1^{PMePh2})

$CuBAr^F_4$•4MeCN (400 mg, 0.44 mmol) was dissolved in THF (30 mL) and charged to a Schlenk flask that was cooled to -78 °C. One equivalent of $^{MePh2}P_3$tren (326 mg, 0.44 mmol) dissolved in THF (10 mL) was transferred to the flask via cannula, resulting in the formation of a yellow solution. The reaction mixture was warmed to room temperature and stirred for an additional 20 min. Volatile materials were then removed *in vacuo*, resulting in the formation of a yellow foam. The product was extracted with diethyl ether (30 mL) and filtered through a plug of Celite. Volatile materials were again removed *in vacuo*, and the resulting yellow solid was washed with *n*-pentane. The phases were separated via cannula filtration, and the product was dried under vacuum for 30 min (450 mg, 69%). **^{1}H NMR** (400 MHz, CD_3CN, 300K): δ = 7.65 (m, 12H), δ = 7.54 (m, 6H), δ = 7.41 (m, 12H), δ = 3.05 (dt, 6H, J_{HH} = 6 Hz, J_{PH} = 20 Hz), δ = 2.52 (t, 6H, J_{HH} = 6 Hz), δ = 1.84 (d, 9H, J_{PH} = 12 Hz) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, CD_3CN, 300K): δ = 132.92 (d, J_{PC} = 2 Hz), δ = 132.41 (d, J_{PC} = 9 Hz), δ = 132.40 (d, J_{PC} = 92 Hz), δ = 129.73 (d, J_{PC} = 12 Hz), δ = 58.05, δ = 45.90, δ = 15.29 (d, J_{PC} = 78 Hz) ppm. **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_3CN, 300K): δ = 21.83 (s) ppm. **Anal. Calcd.** for $C_{69}H_{57}BCuF_{20}N_4P_3$: C, 55.87; H, 3.47; N, 3.78. **Found**: C, 55.82; H, 3.52; N, 3.83.

Synthesis of [^{Ph3}P$_3$tren-Cu^I]OTf (1^{PPh3})

$^{Ph3}P_3$tren (408 mg, 0.44 mmol) was dissolved in THF (30 mL) and transferred to a Schlenk tube containing $[CuOTf]_2$•C_6H_6 (110 mg, 0.22 mmol) via cannula, resulting in the formation of a yellow solution. The reaction mixture was stirred for 30 min. Volatile materials were then removed *in vacuo*, resulting in the formation of a yellow solid. The product was washed with toluene (30 mL), followed by *n*-pentane (3 x 10 mL). The product was then dried under vacuum for 30 min, resulting in a yellow solid (450 mg, 69%). Single crystals suitable for crystallographic analysis were obtained by diffusion of *n*-pentane into a THF solution of **1^{PPh3}** at room temperature. **^{1}H NMR** (400 MHz, CD_3CN, 300K): δ = 7.64 (m, 18H), δ = 7.47 (m, 9H), δ = 7.25 (m, 18H), 3.08 (dt, 6H, J_{HH} = 4 Hz, J_{PH} = 16 Hz), δ = 2.47 (t, 6H, J_{HH} = 6 Hz) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, CD_3CN, 300K): δ = 133.64 (d, J_{PC} = 21 Hz), δ = 133.01 (d, J_{PC} = 3 Hz), δ = 130.57 (d, J_{PC} = 97 Hz), δ = 129.66 (d, J_{PC} = 12 Hz), δ = 58.61 (d, J_{PC} = 14 Hz), δ = 46.22 ppm. **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_3CN, 300K): δ = 22.29 (s) ppm. **Anal. Calcd.** for $C_{61}H_{57}CuF_3N_4O_3P_3S$: C, 64.29; H, 5.04; N, 4.92. **Found**: C, 64.21; H, 5.42; N, 4.86.

Synthesis of [$^{Me2(NEt2)}$P$_3$tren-Cu^I]BAr$^F_4$ (1$^{PMe2(NEt2)}$)

$CuBAr^F_4$•4MeCN (80 mg, 0.088 mmol) was dissolved in THF (5 mL), and one equivalent of $^{Me2(NEt2)}P_3$tren (47.6 mg, 0.088 mmol) dissolved in THF (2 mL) was transferred to the vial via pipet, resulting in the formation of a pale yellow solution. The reaction mixture was stirred for an additional 20 min. Volatile materials were removed *in vacuo*, resulting in the formation of a tan solid. The product was extracted with diethyl ether (10 mL) and filtered through a plug of Celite. Volatile materials were again removed *in vacuo*, and the resulting tan solid was washed with *n*-pentane. The phases were separated via cannula filtration, and the product was dried under vacuum for 30 min (86 mg, 79%). **^{1}H NMR** (400 MHz, CD_3CN, 300 K): δ = 3.01 (m, 18H), δ = 2.55 (t, 6H, J_{HH} = 6 Hz), δ = 1.49 (d, 18H, J_{PH} = 16 Hz), δ = 1.06 (t, 18H, J_{HH} = 8 Hz) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, CD_3CN, 300K): δ = 59.74 (s), δ = 45.25 (s), δ = 39.66 (d, J_{PC} = 3 Hz), δ = 15.09 (d, J_{PC} = 88 Hz), δ = 14.91 (d, J_{PC} = 2 Hz) ppm. **Anal. Calcd.** for $C_{48}H_{60}BCuF_{20}N_7P_3$: C, 44.96; H, 4.72; N, 7.65. **Found**: C, 44.60; H, 4.92; N, 8.67.

Synthesis of [^{Me3}P$_3$tren-Cu^{II}][OTf]$_2$ (2^{PMe3})

$^{Me3}P_3$tren (101 mg, 0.274 mmol) was dissolved in MeCN (5 mL), and the resulting solution was transferred via cannula into a solution of $Cu(OTf)_2$ (90 mg, 0.249 mmol) in MeCN (10 mL). The solution quickly turned to a dark red color and was allowed to stir for 5 min, after which time all volatile materials were removed *in vacuo*. The resulting dark oil was washed with THF (3 x 30 mL), followed by trituration with *n*-pentane. The resulting crimson solid was dried under vacuum for 30 min and was used without further purification. Single crystals suitable for crystallographic analysis were obtained by diffusion of *n*-pentane into an *o*-difluorobenzene solution of the product. **Anal. Calcd.** for $C_{17}H_{39}CuF_6N_4O_6P_3S_2$: C, 27.97; H, 5.38; N, 7.67. **Found**: C, 27.64; H, 5.48; N, 7.89.

Syntheses of [$^{Me3}P_3$tren-Cu^{II}-Cl]BAr^F_4 (3^{PMe3})

Synthesis of 3^{PMe3}, method A:

Triphenylmethyl chloride (14 mg, 0.0504 mmol) was dissolved in THF (3 mL), forming a colorless solution that was transferred via cannula into a THF solution (5 mL) of $\mathbf{1^{PMe3}}$ (56 mg, 0.0504 mmol). The resulting mixture immediately turned to a vibrant green color. The solution was allowed to stir for 5 min, at which point all volatile materials were removed *in vacuo*. The resulting green, oily solid was washed extensively with *n*-hexane, followed by extraction into diethyl ether. Single crystals suitable for crystallographic analysis were obtained by storing a saturated diethyl ether solution of the material at -78 °C; however, the resulting material did not provide suitable microanalytical data. One reason may be the incomplete removal of Gomberg's dimer, which has a similar solubility profile to that of $\mathbf{3^{PMe3}}$.

Synthesis of 3^{PMe3}, method B:

Step 1: Formation of [$^{Me3}P_3$tren-Cu^{II}-Cl]Cl

$^{Me3}P_3$tren (200 mg, 0.54 mmol) was dissolved in MeCN (10 mL), and the resulting solution was cannula transferred into a MeCN slurry (5 mL) of $CuCl_2$ (66 mg, 0.49 mmol). The reaction mixture was stirred for 30 min at room temperature, at which point a green solution had formed. The reaction was filtered through Celite, to give a clear, green filtrate. Following concentration under vacuum, the product was precipitated via addition of diethyl ether. The resulting yellow solid was washed extensively with pentane and was used without further purification. Single crystals suitable for crystallographic analysis were obtained by diffusion of diethyl ether into a concentrated MeCN solution of the complex (see supplementary information) (176 mg, 71% yield). **Anal. Calcd.** For $C_{15}H_{39}Cl_2CuN_4P_3$: C, 35.83; H, 7.82; N, 11.14. **Found**: C, 36.21; H, 7.84; N, 10.90.

Step 2: Formation of $\mathbf{3^{PMe3}}$

To a MeCN solution (10 mL) of [$^{Me3}P_3$trenCuCl]Cl (150 mg, 0.30 mmol) was added a solution of $AgBAr^F_4$•4MeCN (259 mg, 0.27 mmol) in MeCN (5 mL). A white solid (AgCl) was observed to precipitate immediately after addition. The reaction was stirred in the dark for an additional 10 min, at which point the reaction mixture was filtered through Celite. Volatile materials were removed *in vacuo* to yield a green, *pseudo*-solid. The product was extracted into diethyl ether, forming a green solution that was filtered through Celite to remove insoluble materials. The filtrate was concentrated under vacuum, then precipitated by addition of *n*-pentane to produce a pale green solid. The phases were separated via filtration, and the resulting green solid was dried under vacuum for 30 min to afford $\mathbf{3^{PMe3}}$, which was used without further purification (164 mg, 53 % yield). **Anal. Calcd.** For $C_{39}H_{39}BClCuF_{20}N_4P_3$: C, 40.86; H, 3.43; N, 4.89. **Found**: C, 40.69; H, 3.31; N, 4.93.

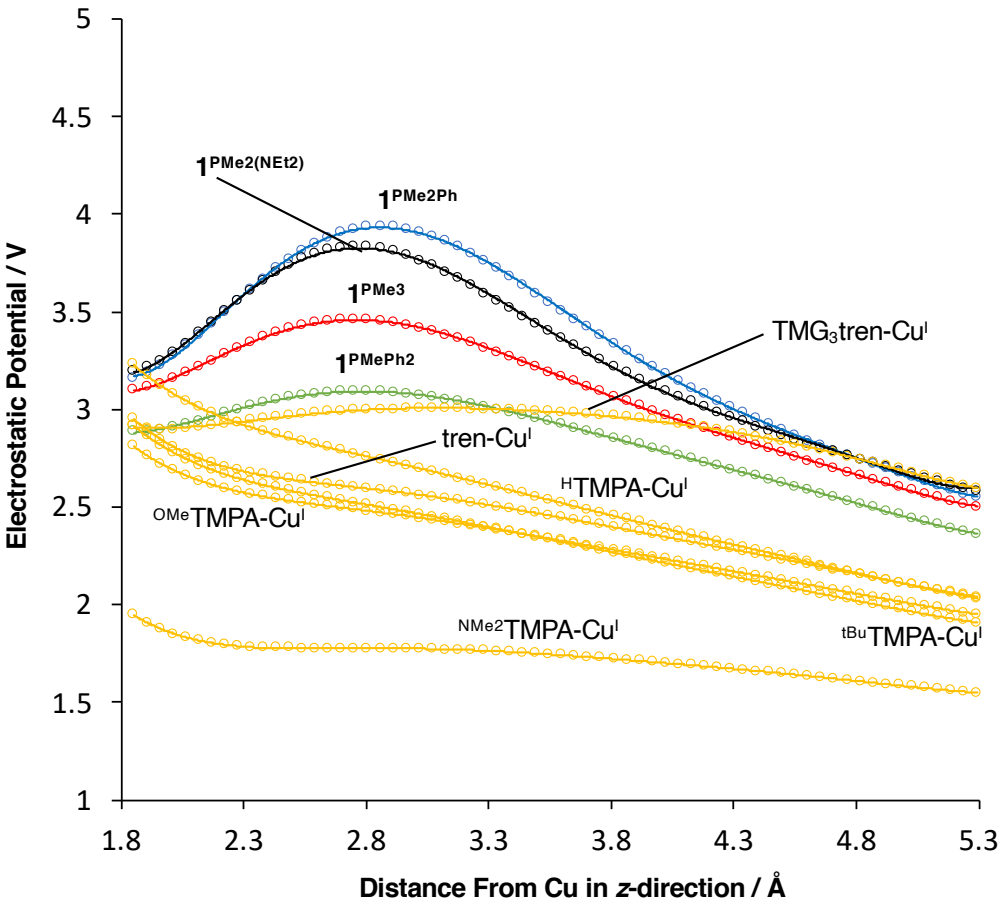


Fig S1. Electrostatic potential as a function of distance from copper in the canonical *z*-direction. Solid lines represent 6th order polynomial fits to the calculated data. The functions that fit the data for each complex are shown below. These functions are necessary for calculating electrostatic fields along the canonical z-axes of the complexes, which is represented by the gradient in electrostatic potential with respect to distance.

$\mathbf{1}^{PMe3}$

$y = 0.02323x^6 - 0.52311x^5 + 4.78372x^4 - 22.58878x^3 + 57.54229x^2 - 74.26552x + 40.94026$

$R^2 = 0.99986$

$\mathbf{1}^{PMe2Ph}$

$y = 0.04038x^6 - 0.93125x^5 + 8.72286x^4 - 42.20006x^3 + 110.21054x^2 - 145.94353x + 79.55198$

$R^2 = 0.99990$

$\mathbf{1}^{PMePh2}$

$y = 0.01308x^6 - 0.29478x^5 + 2.70363x^4 - 12.84060x^3 + 32.97521x^2 - 42.97510x + 25.02208$

$R^2 = 0.99983$

$\mathbf{1}^{PMe2(NEt2)}$

$y = 0.04712x^6 - 1.05818x^5 + 9.64554x^4 - 45.40547x^3 + 115.48734x^2 - 149.25834x + 79.61112$

$R^2 = 0.99970$

TMG_3tren-Cu^I

$y = 0.00763x^6 - 0.16669x^5 + 1.49140x^4 - 6.99171x^3 + 18.00632x^2 - 23.93301x + 15.66221$

$R^2 = 0.99916$

^{H}TMPA-Cu^I

$y = 0.00695x^6 - 0.16225x^5 + 1.55793x^4 - 7.86623x^3 + 21.99933x^2 - 32.57947x + 23.00252$

$R^2 = 0.99997$

^{tBu}TMPA-Cu^I

$y = 0.00697x^6 - 0.16279x^5 + 1.56415x^4 - 7.90484x^3 + 22.12619x^2 - 32.71709x + 22.69368$

$R^2 = 0.99996$

^{OMe}TMPA-Cu^I

$y = 0.00702x^6 - 0.16391x^5 + 1.57486x^4 - 7.95579x^3 + 22.23588x^2 - 32.71777x + 22.43461$

$R^2 = 0.99995$

^{NMe2}TMPA-Cu^I

$y = 0.00711x^6 - 0.16624x^5 + 1.59880x^4 - 8.08678x^3 + 22.62029x^2 - 33.11195x + 21.57856$

$R^2 = 0.99965$

tren-Cu^I

$y = 0.00863x^6 - 0.20144x^5 + 1.93574x^4 - 9.78233x^3 + 27.35089x^2 - 40.20054x + 26.99751$

$R^2 = 0.99992$

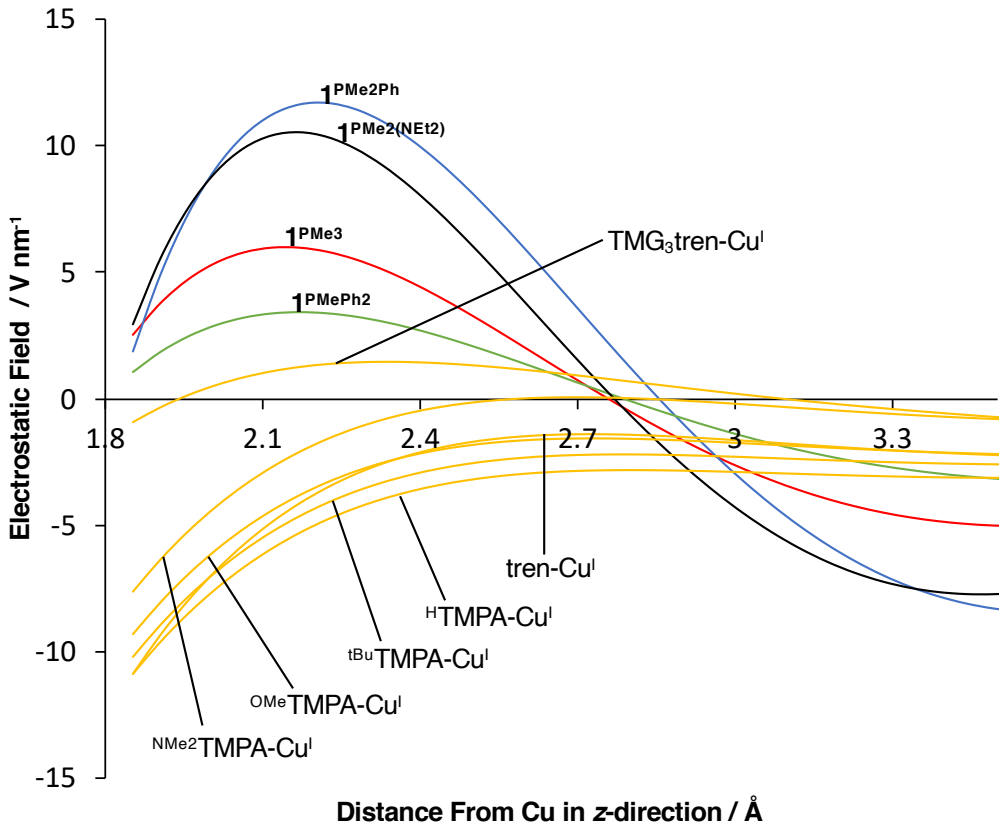
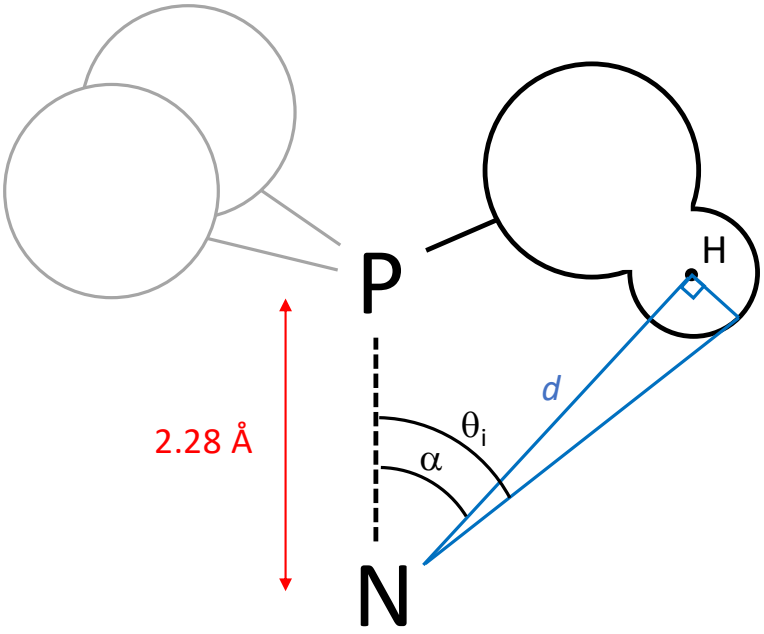


Fig S2. Electrostatic field strength along the canonical *z*-axes of various C_3-symmetric trigonal-pyramidal copper complexes. The metal is placed at the origin in these calculations. Negative ESF values correspond to a force that would move a positive charge away from the metal center at that position along the *z*-axis.

Complex	Max. ESF (V nm^{-1})	Dist. from Cu (Å)
1^{PMe3}	5.99	2.12
1^{PMe2Ph}	11.72	2.22
1^{PMePh2}	3.43	2.17
$1^{PMe2(NEt2)}$	10.56	2.17
$TMG_3tren\text{-}Cu^{I}$	1.47	2.33

Fig S3. Tabulated maxima in electrostatic field strength along the *z*-axes for $\mathbf{1}^{PR3}$ and TMG_3tren.



$$\theta_i = \alpha + 180/\pi \times \tan^{-1}(r_H/d)$$

$$\theta^* = 2/3 \sum_{i=1}^{3} \theta_i$$

Fig S4. Illustration of the method used to determine the cone angles (θ*). The q* values were determined by analyzing the phosphonium components in the optimized structures of the $\mathbf{1}^{PR3}$. The P-N bond lengths were first increased to 2.28 Å, such that a more direct comparison could be made to Tolman cone angles.[4] Doubling the average of the three q_i angles gave the cone angle for a phosphinimine, and the final value for q* was determined by averaging this value across the three phosphinimines in each metal complex. A van der Waals radius of 1.2 Å was used for hydrogen.

Electrochemistry of Cu^{I} complexes (1^{PR3})

Cyclic voltammetry and square-wave measurements were carried out using a BASi Epsilon Eclipse electrochemistry analyzer. All electrochemical measurements were performed under an N_2 atmosphere inside of a glovebox. A platinum disk was used as the working electrode, and platinum wire was used as the counter electrode. An isobutyronitrile (IBN) solution of $Ag/AgNO_3$ contained within a solution cell was used as the reference electrode. The measurements were performed at room temperature in IBN containing 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. A concentration of 1 mM was used for the analyte in all electrochemical experiments presented here.

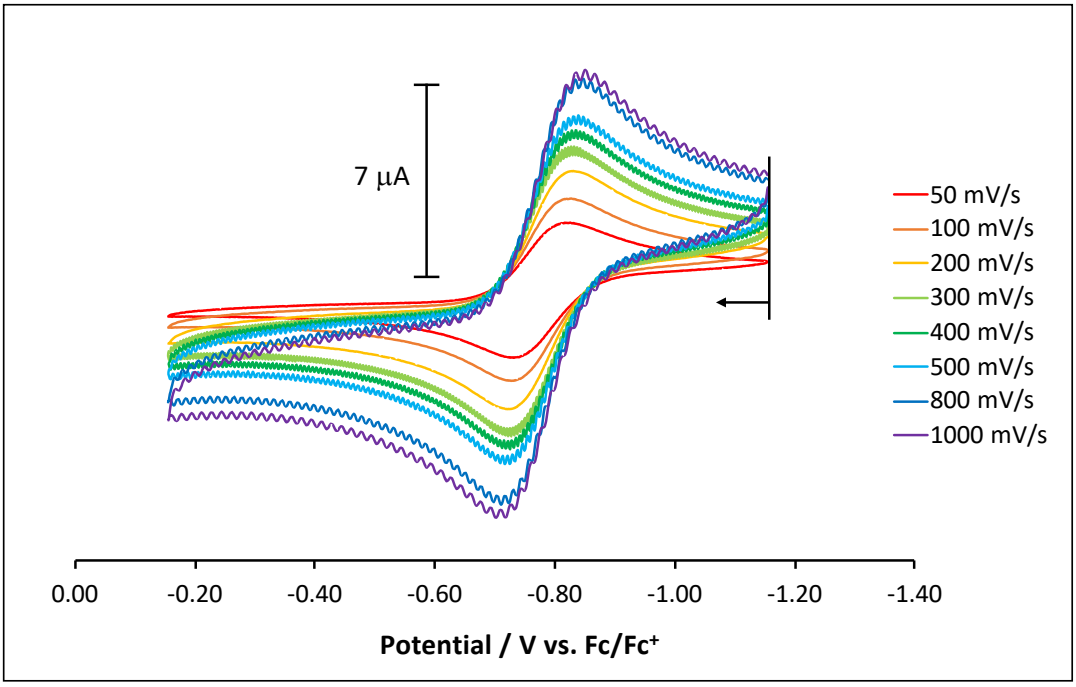


Fig S5. Cyclic voltammograms of $\mathbf{1}^{PMe3}$.

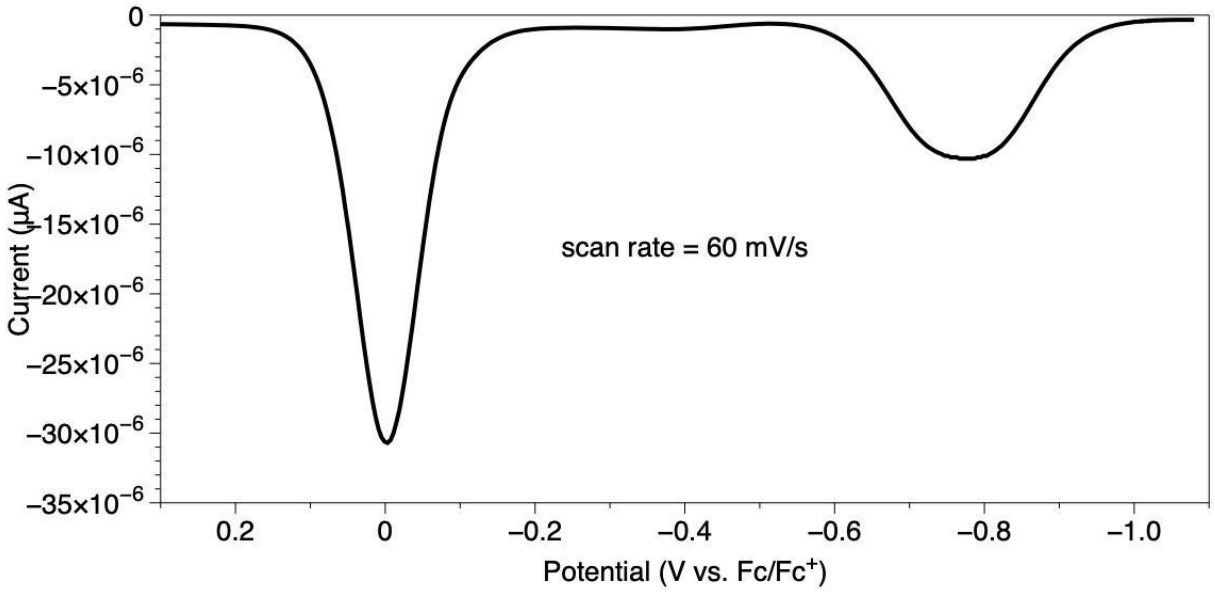


Fig S6. Square wave measurements of **1**^{PMe3} with an internal Fc reference.

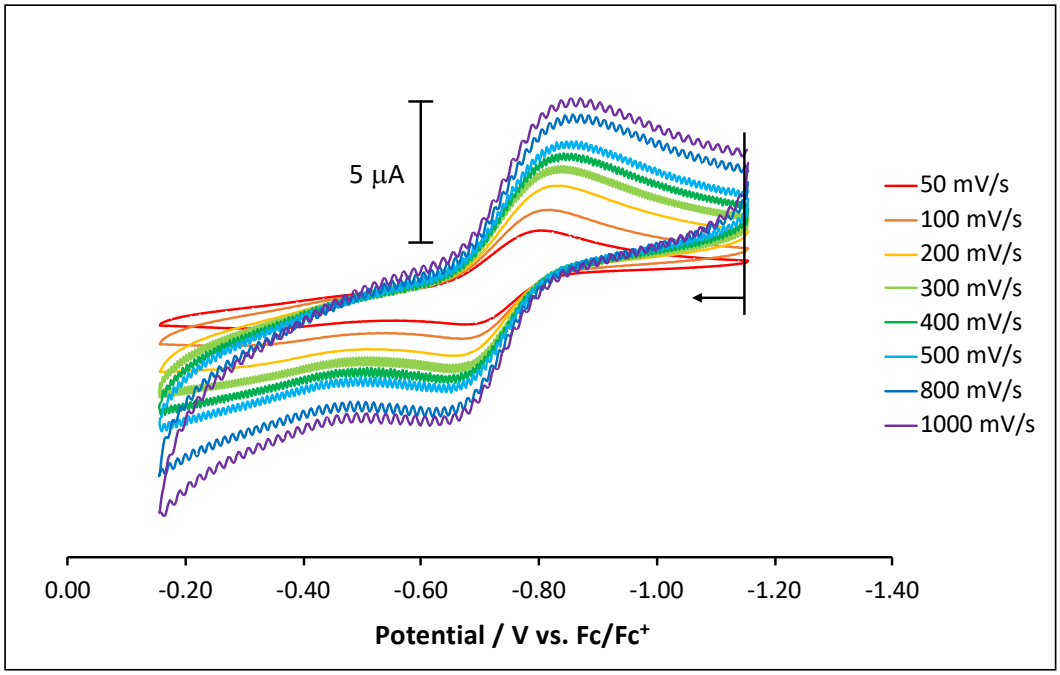


Fig S7. Cyclic voltammograms of **1**^{PMe2Ph}.

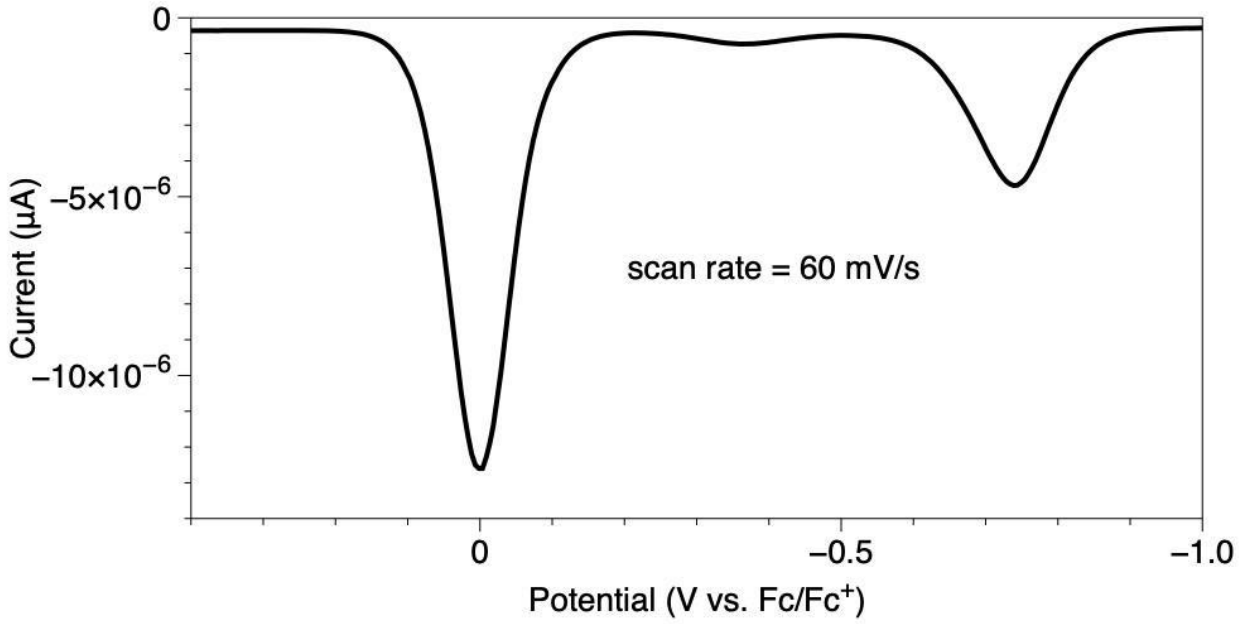


Fig S8. Square wave measurement of $\mathbf{1}^{\mathbf{PMe2Ph}}$ with an internal Fc reference.

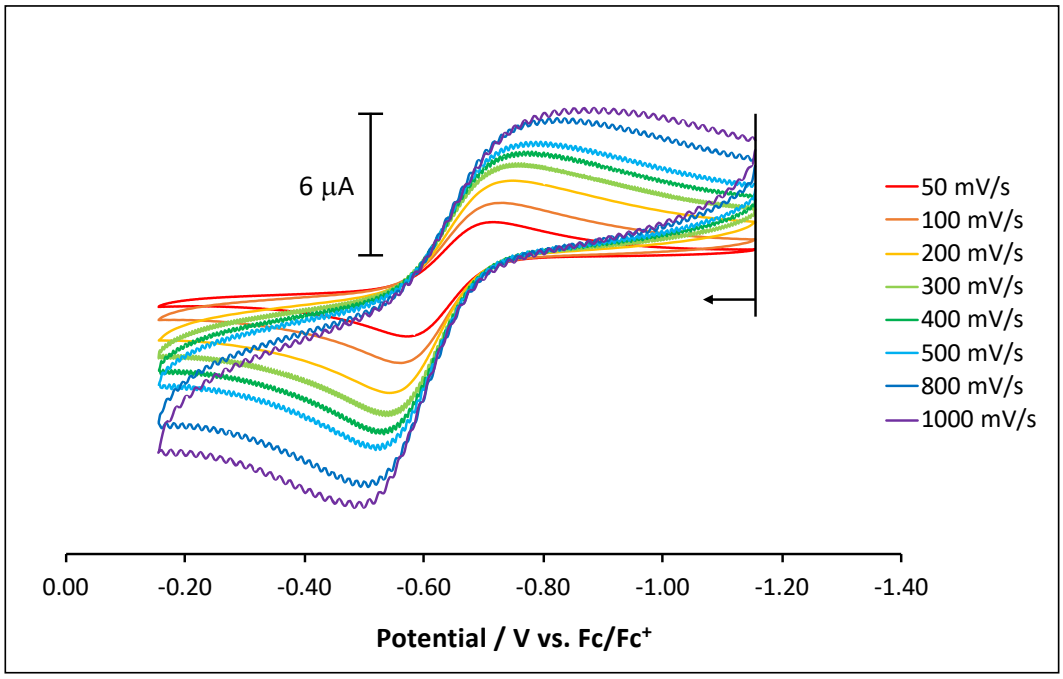


Fig S9. Cyclic voltammograms of $\mathbf{1}^{\mathbf{PMePh2}}$.

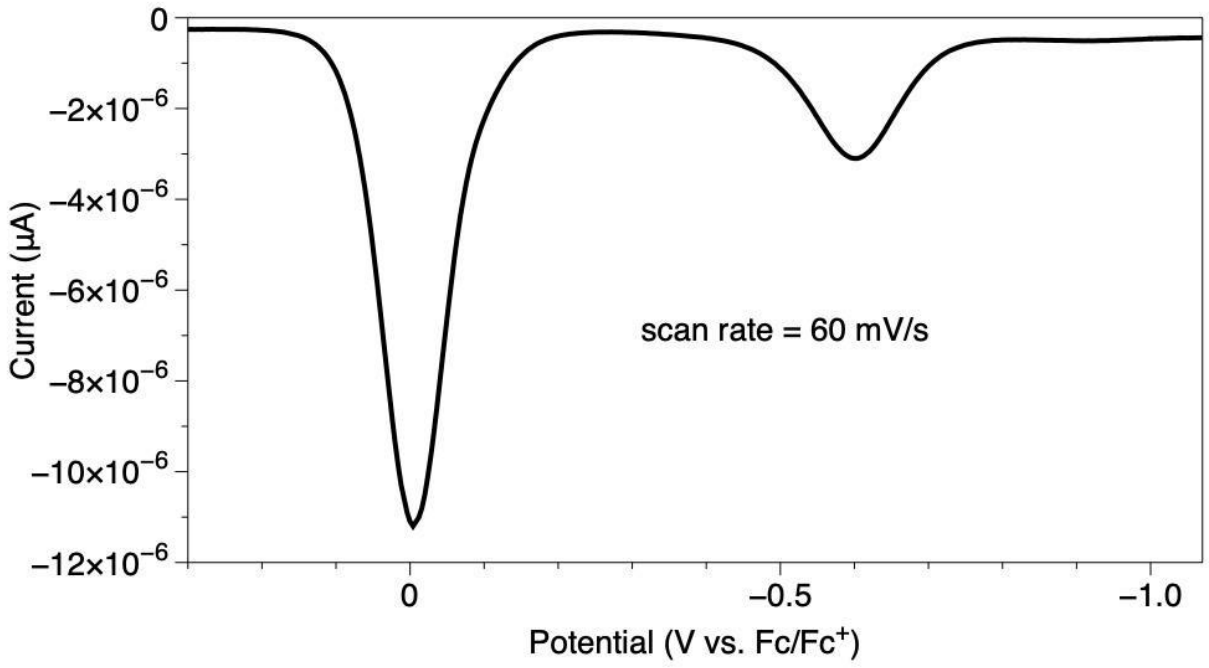


Fig S10. Square wave measurements of $\mathbf{1}^{\mathbf{PMePh2}}$ with an internal Fc reference.

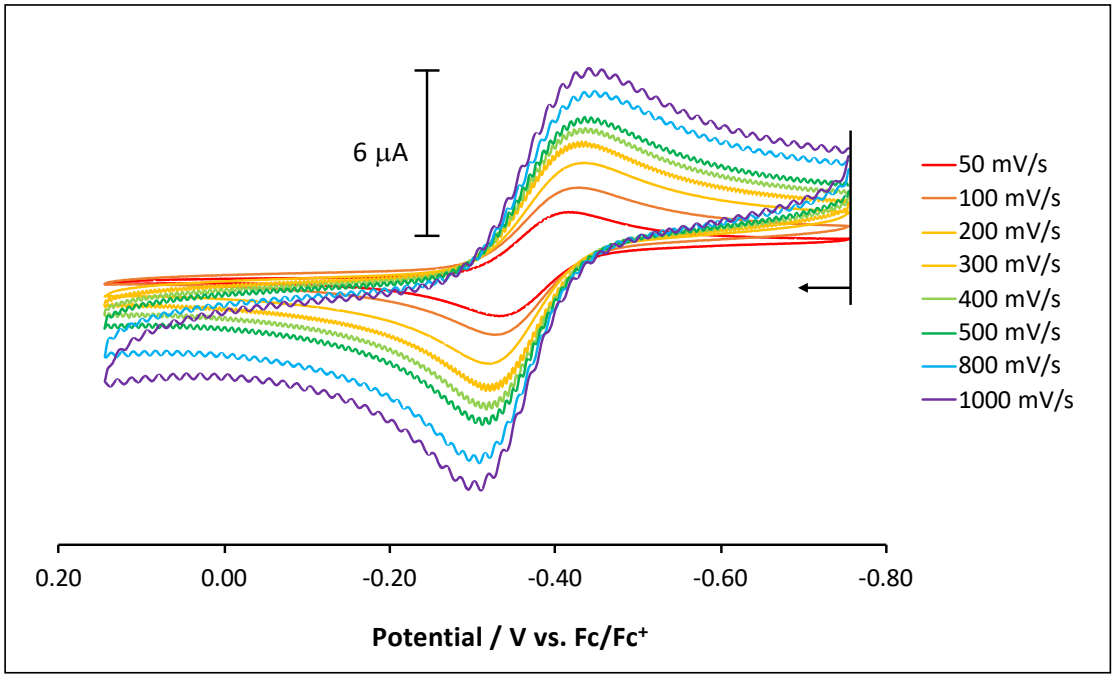


Fig S11. Cyclic voltammograms of $\mathbf{1}^{\mathbf{PPh3}}$.

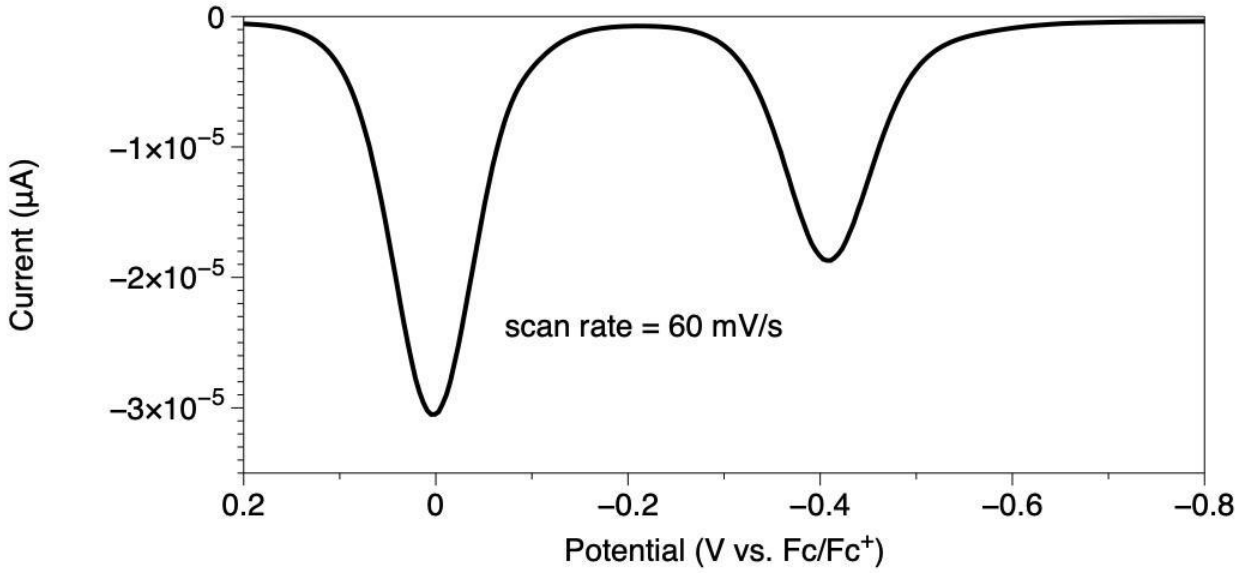


Fig S12. Square wave measurements of $\mathbf{1}^{\mathbf{PPh3}}$ with an internal Fc reference.

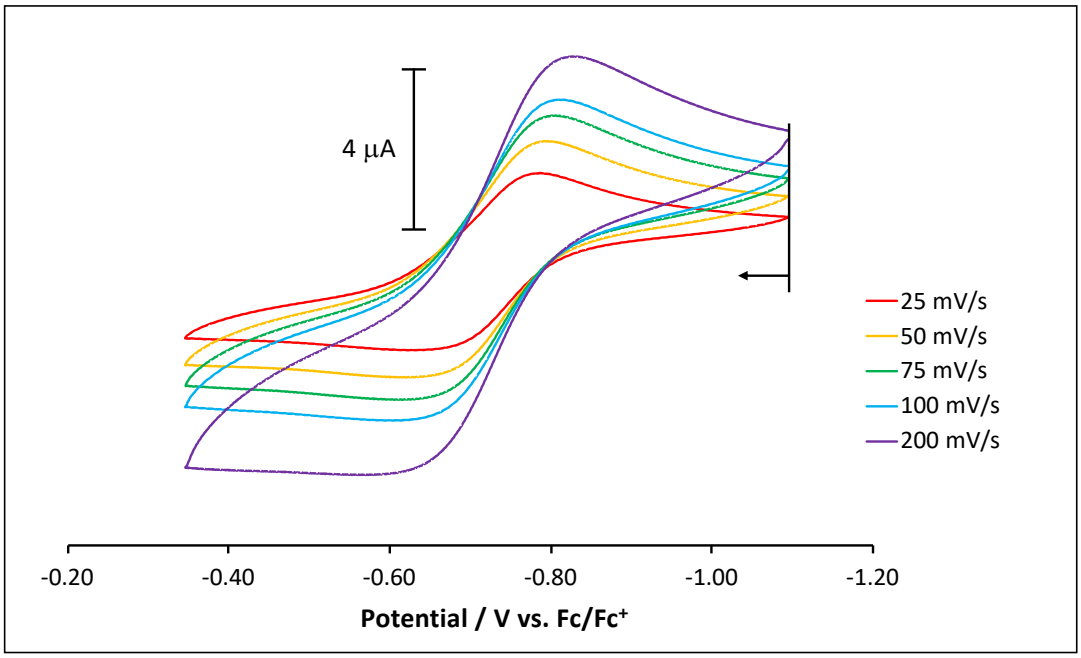


Fig S13. Cyclic voltammograms of $\mathbf{1}^{\mathbf{PMe2(NEt2)}}$.

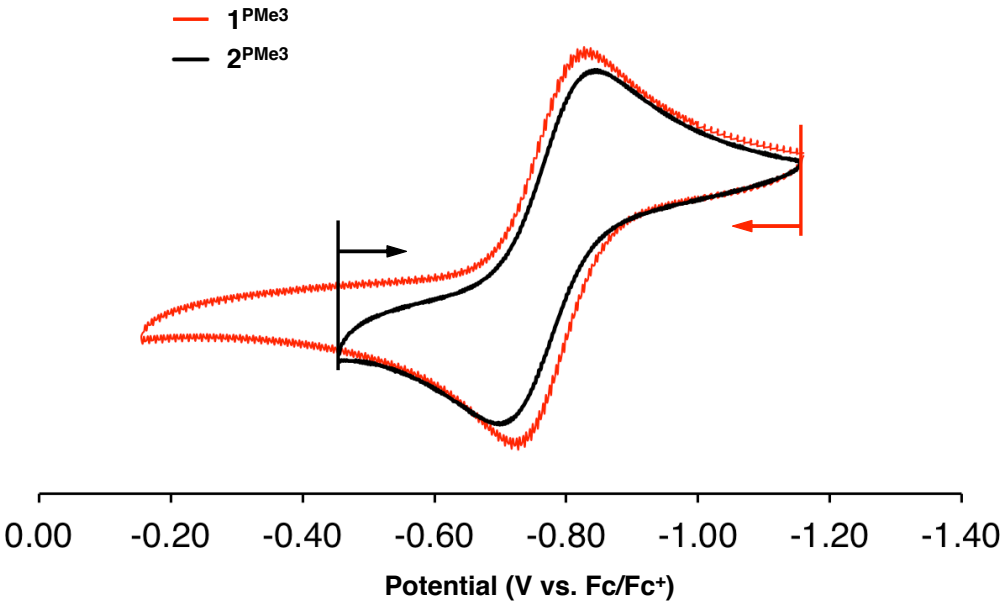


Fig S14. Overlaid cyclic voltammograms of $\mathbf{1}^{PMe3}$ and $\mathbf{2}^{PMe3}$.

NMR Spectra of Ligands and Cu^{I} Complexes (1^{PR3})

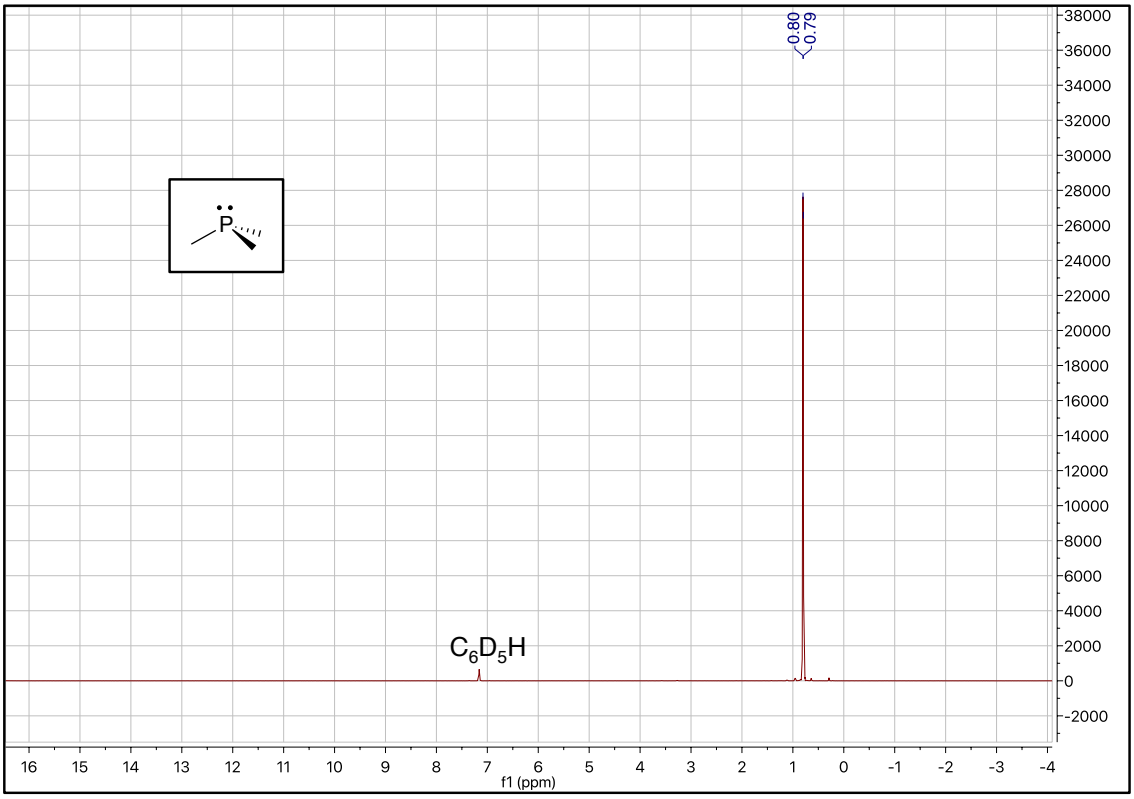


Fig S15. ^{1}H NMR (400 MHz) spectrum of PMe_3 in C_6D_6 (T = 298 K).

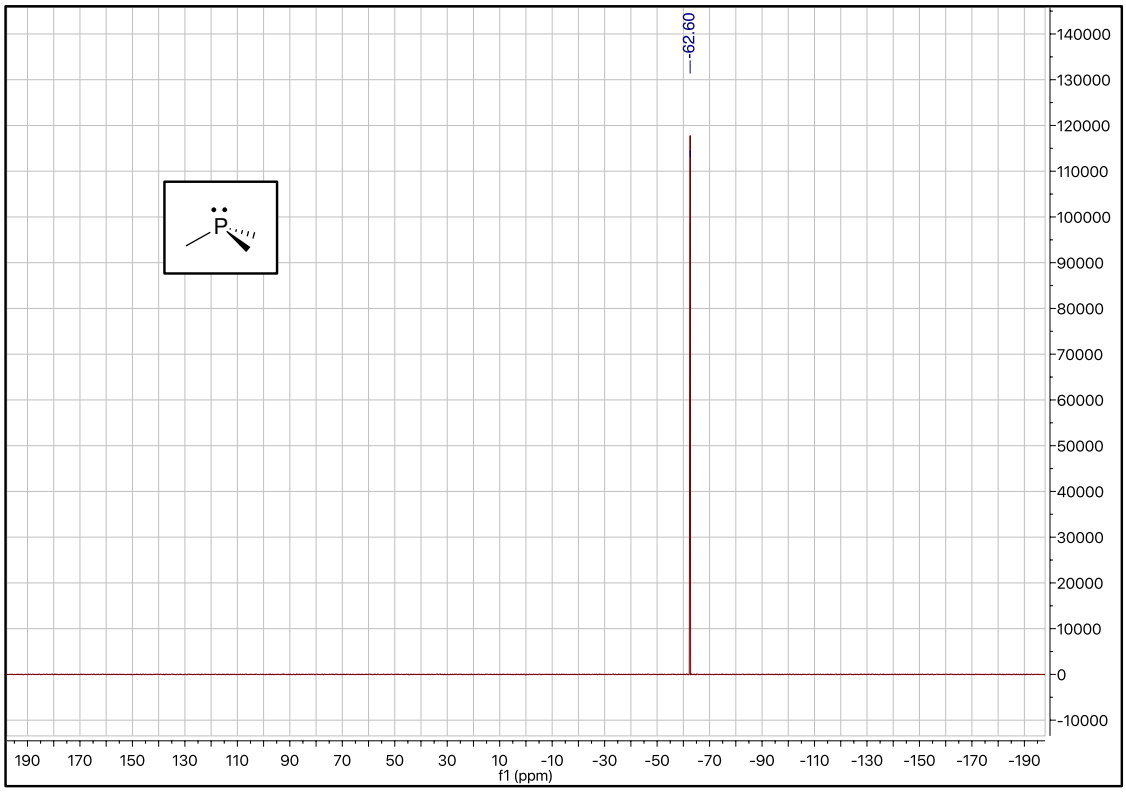


Fig S16. $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of PMe_3 in C_6D_6 (T = 298 K).

Fig S17. ^{1}H NMR (400 MHz) spectrum of $^{Me3}P_3$tren in C_6D_6 (T = 298 K).

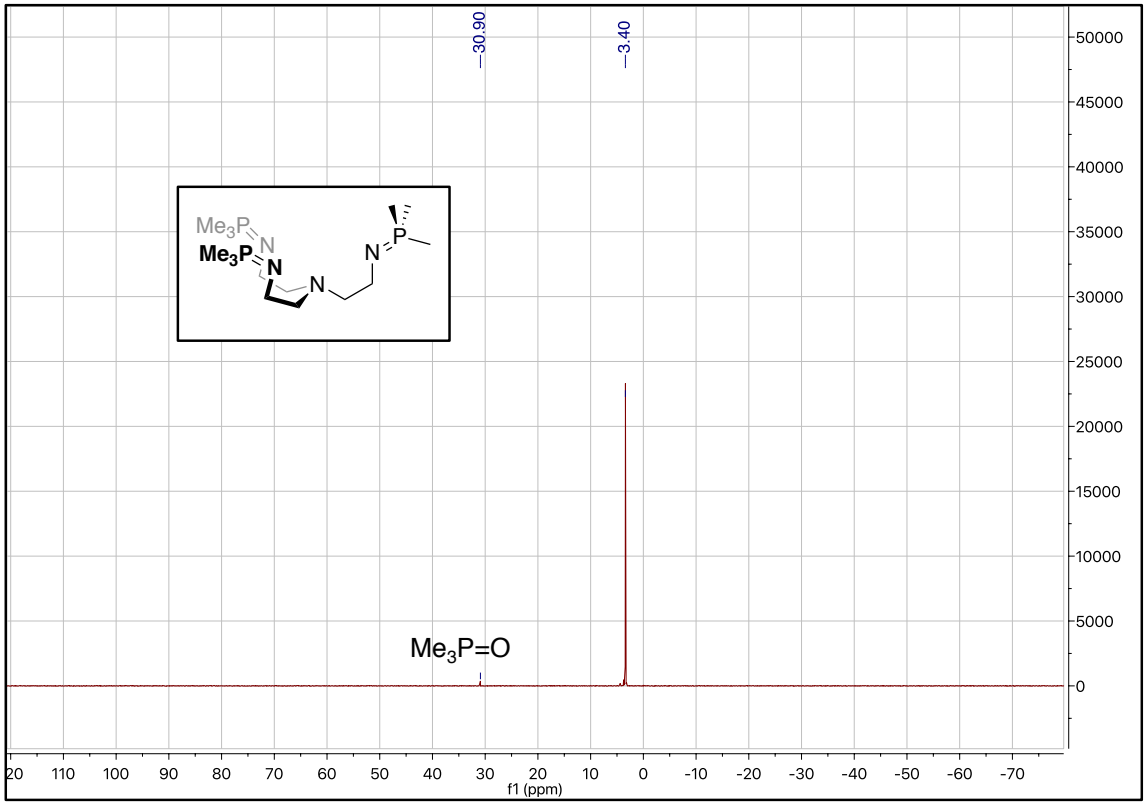


Fig S18. ^{31}P{^{1}H} NMR (162 MHz) spectrum of $^{Me3}P_3$tren in C_6D_6 (T = 298 K).

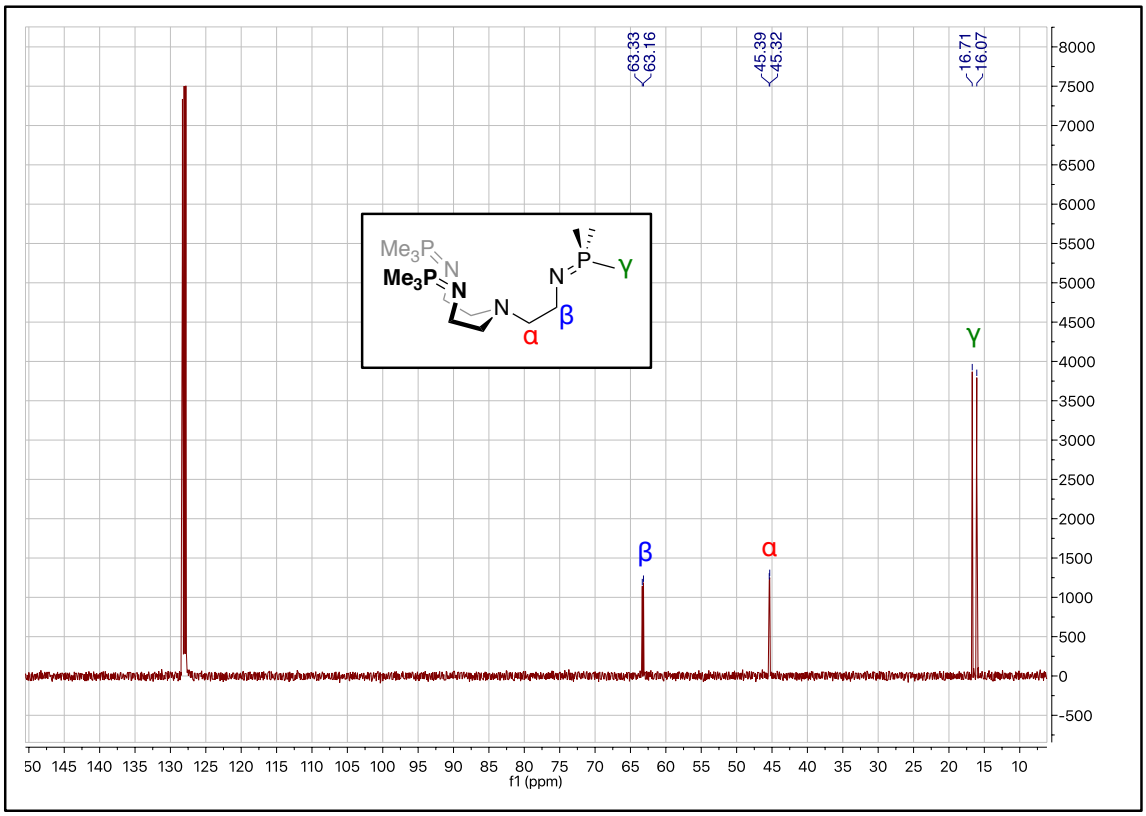


Fig S19. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of $^{Me3}P_3$tren in C_6D_6 (T = 298 K).

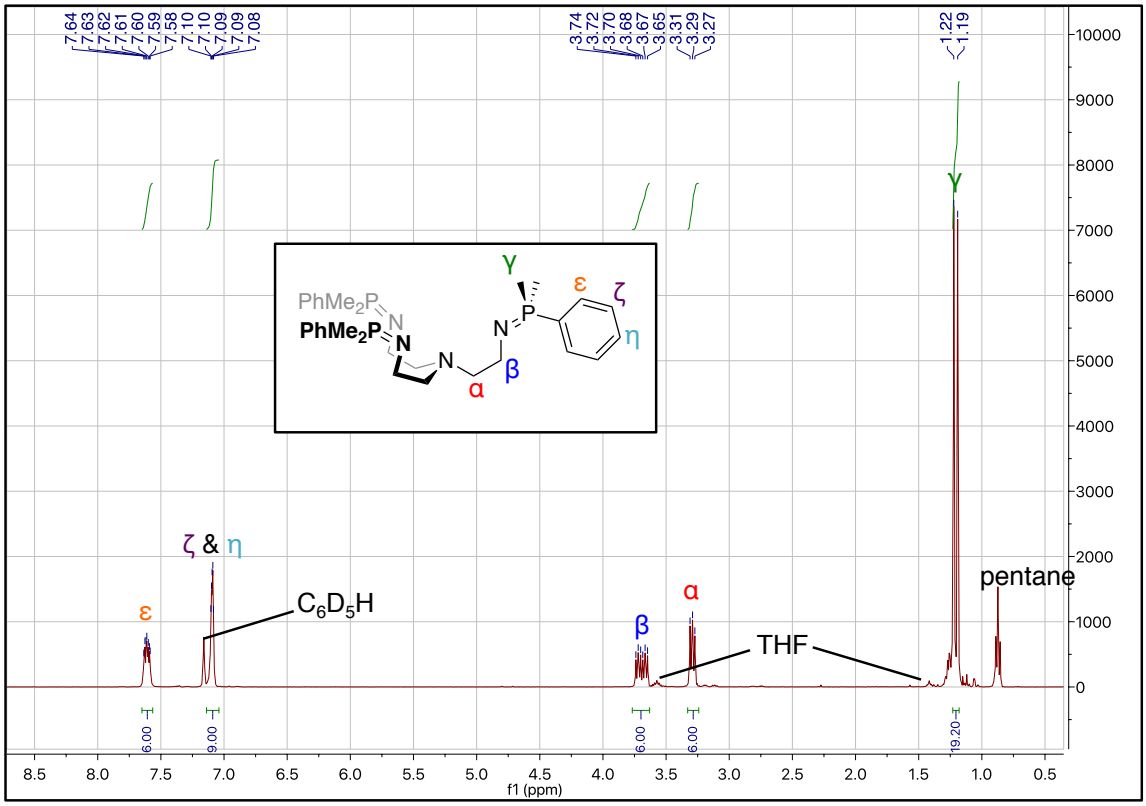


Fig S20. ^{1}H NMR (400 MHz) spectrum of $^{Me2Ph}P_3$tren in C_6D_6 (T = 298 K).

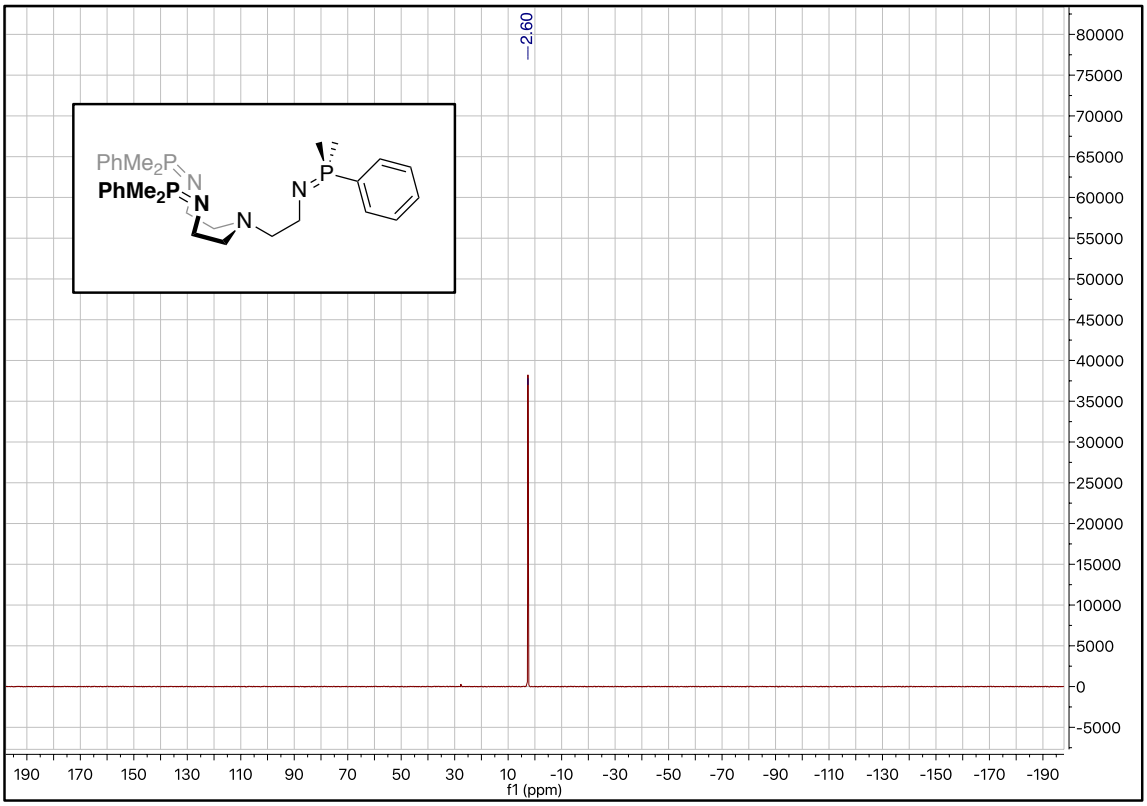


Fig S21. $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of $^{Me2Ph}P_3$tren in C_6D_6 (T = 298 K).

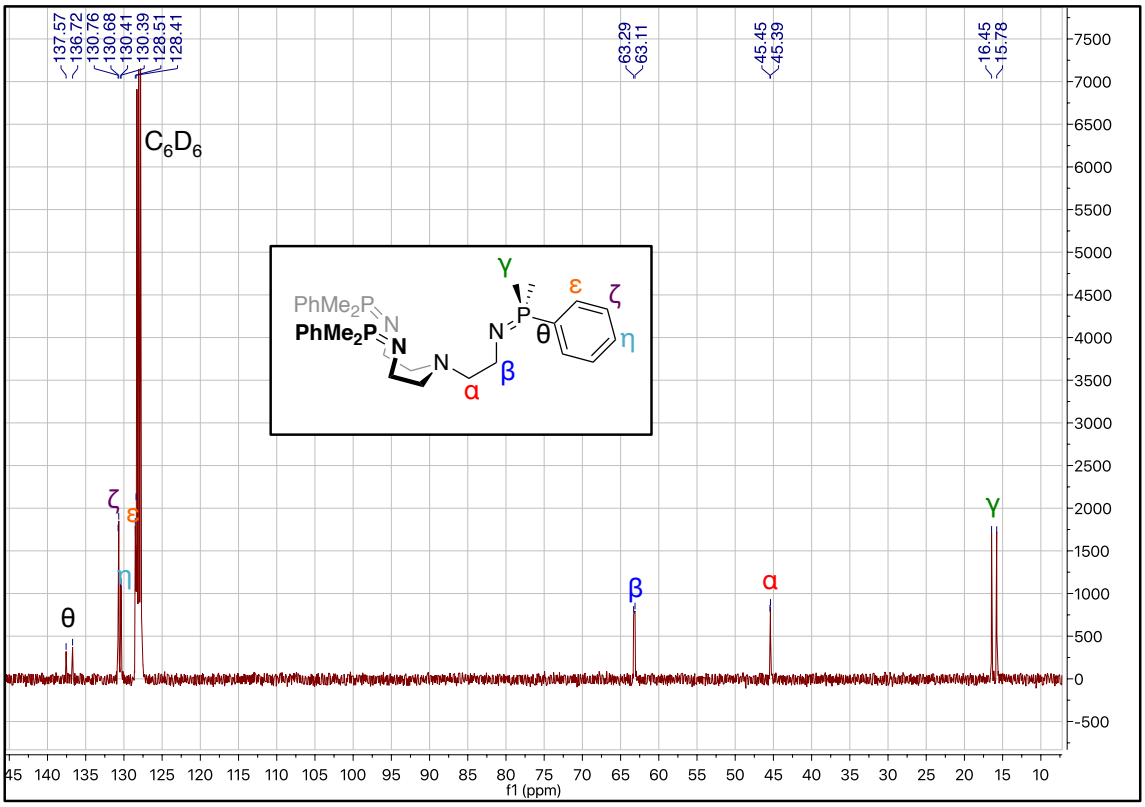


Fig S22. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of $^{Me2Ph}P_3$tren in C_6D_6 (T = 298 K).

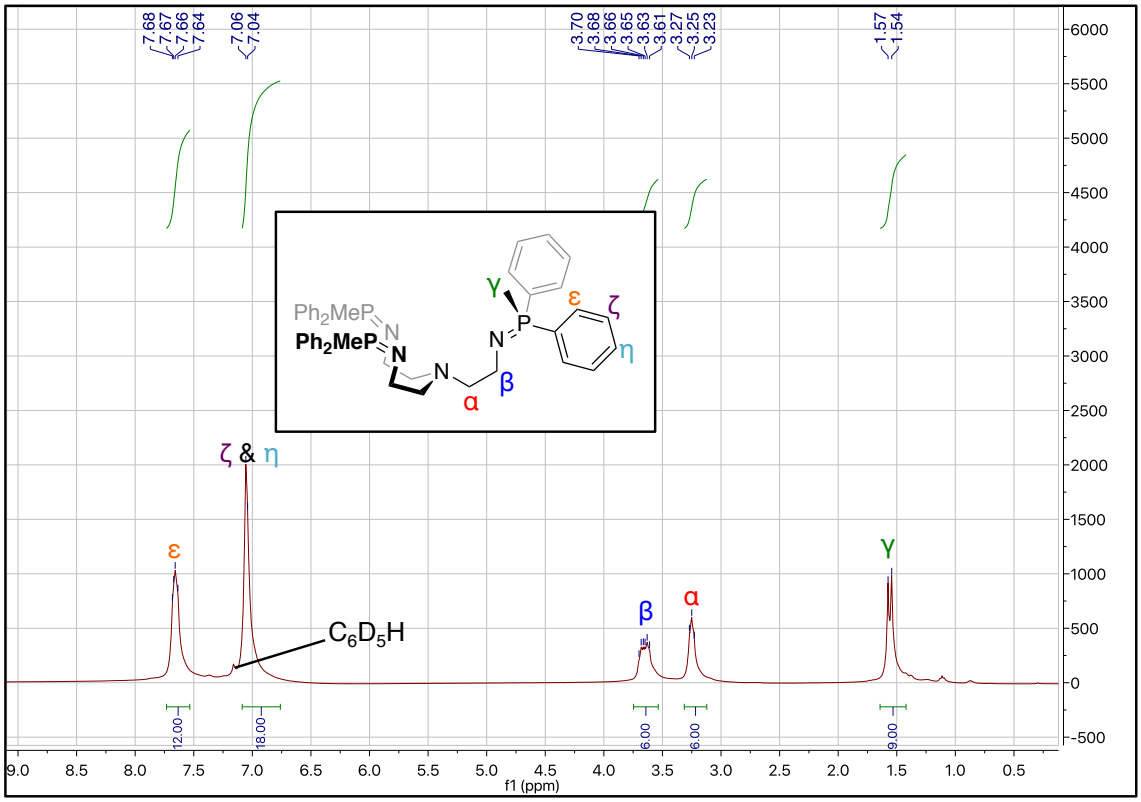


Fig S23. ^{1}H NMR (400 MHz) spectrum of $^{MePh2}P_3$tren in C_6D_6 (T = 298 K).

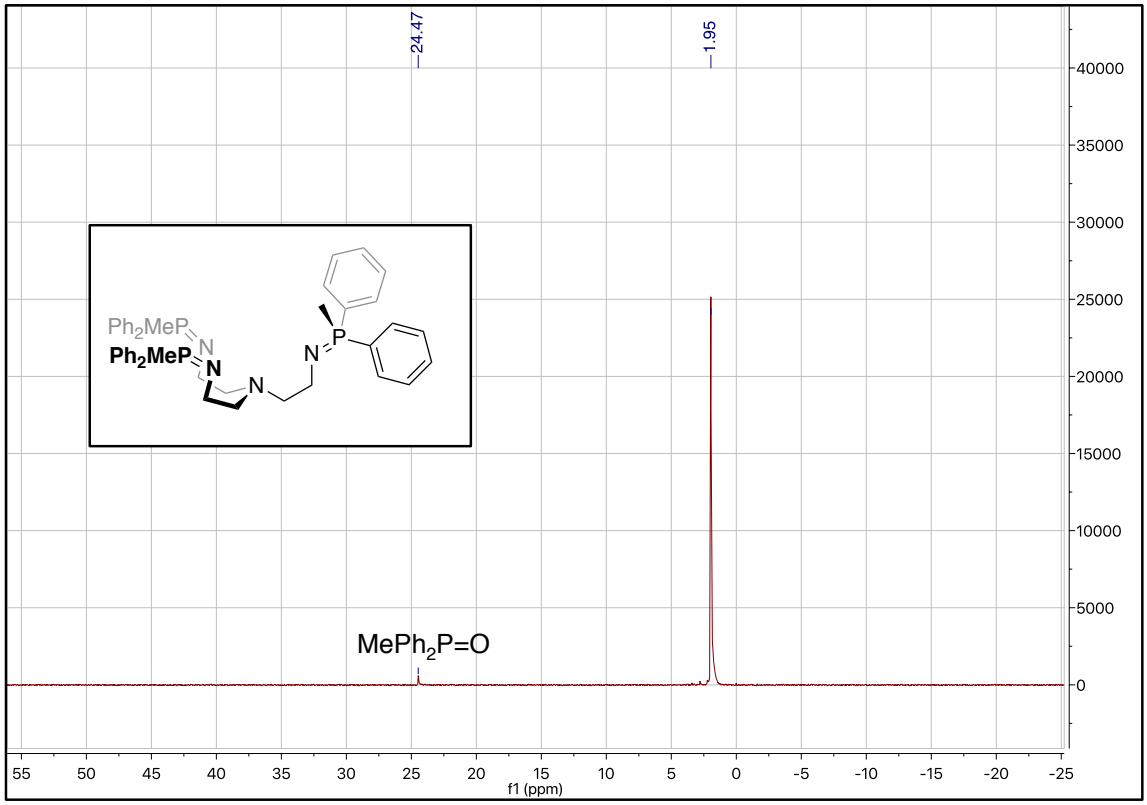


Fig S24. ^{31}P{^{1}H} NMR (162 MHz) spectrum of $^{MePh2}P_3$tren in C_6D_6 (T = 298 K).

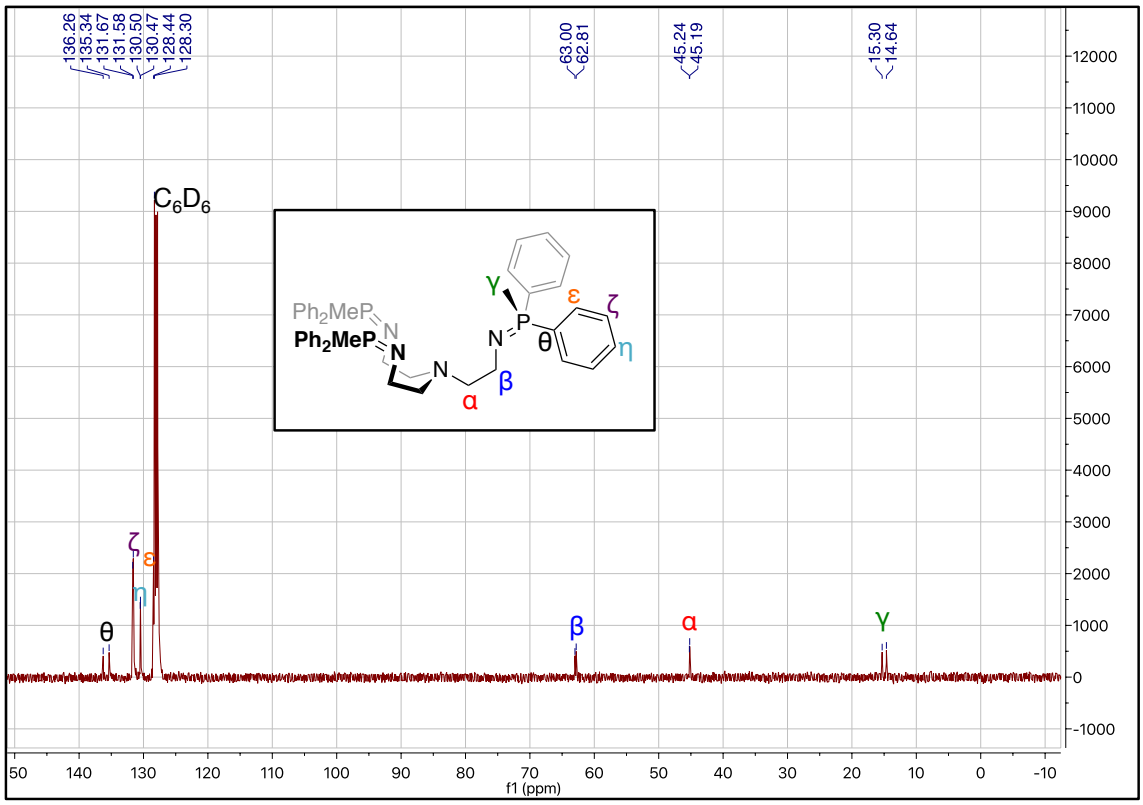


Fig S25. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of $^{MePh2}P_3$tren in C_6D_6 (T = 298 K).

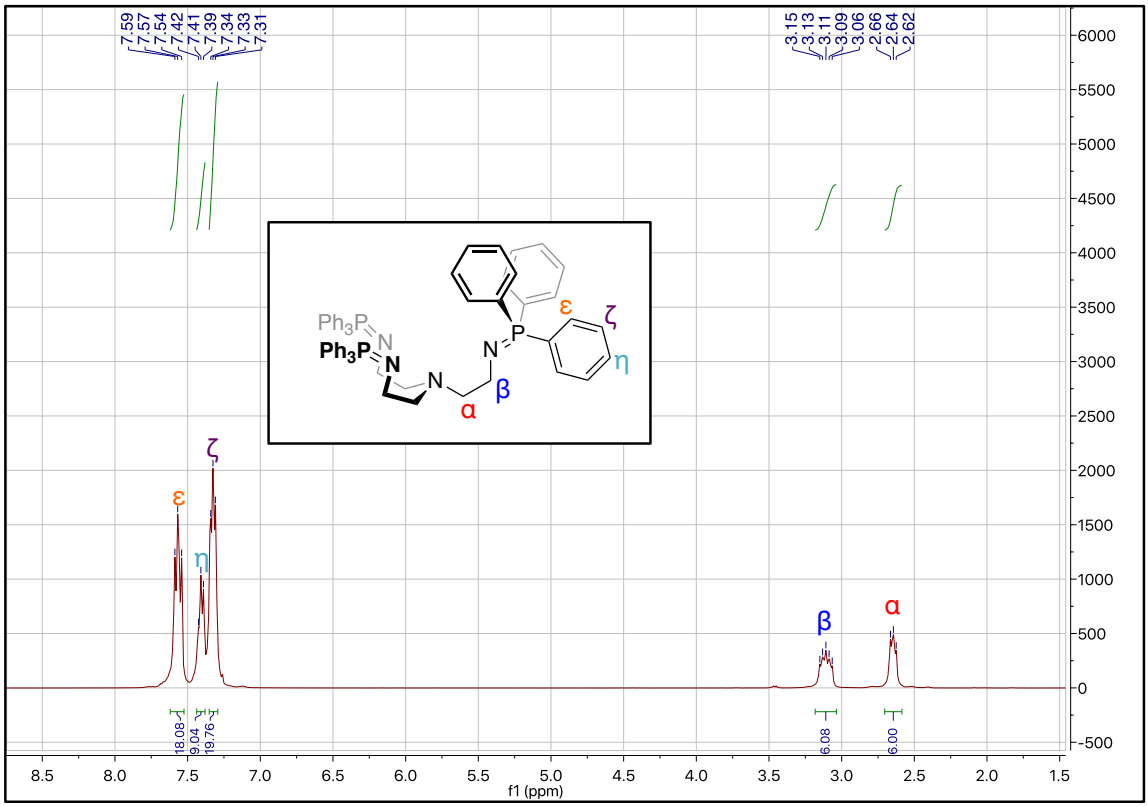


Fig S26. ^{1}H NMR (400 MHz) spectrum of $^{Ph3}P_3$tren in CD_3Cl (T = 298 K).

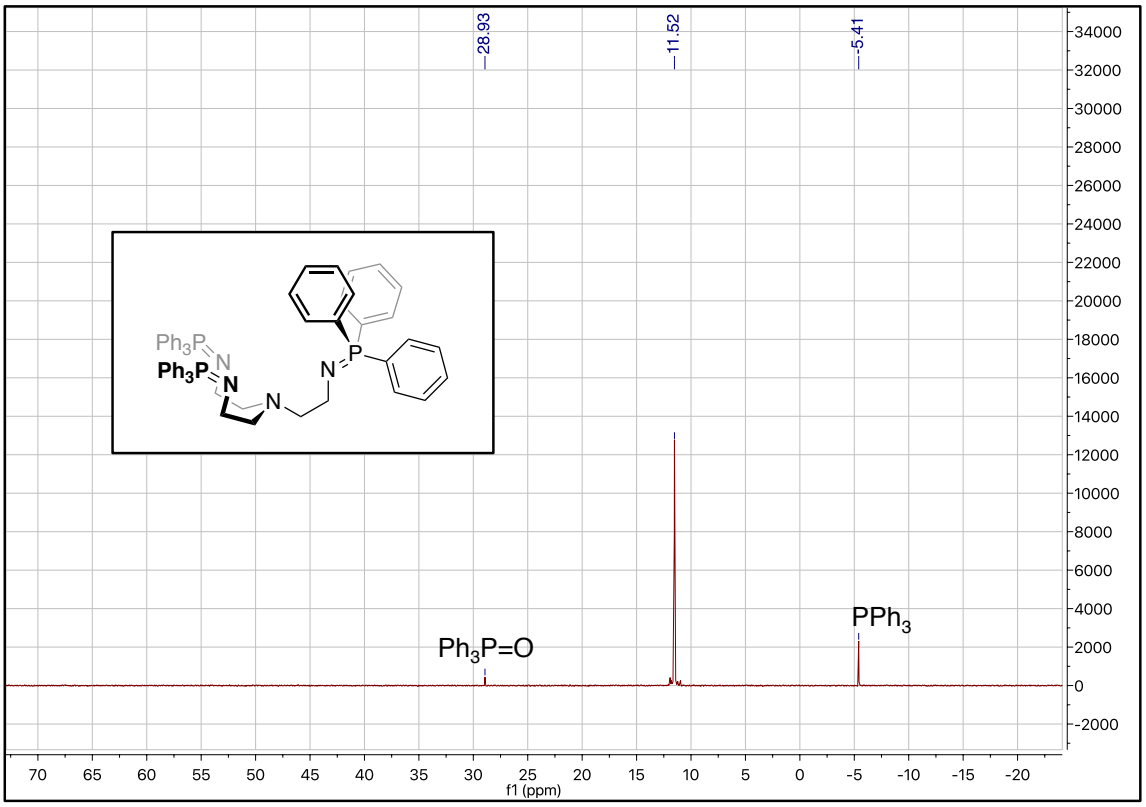


Fig S27. $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of $^{Ph3}P_3$tren in CD_3Cl (T = 298 K).

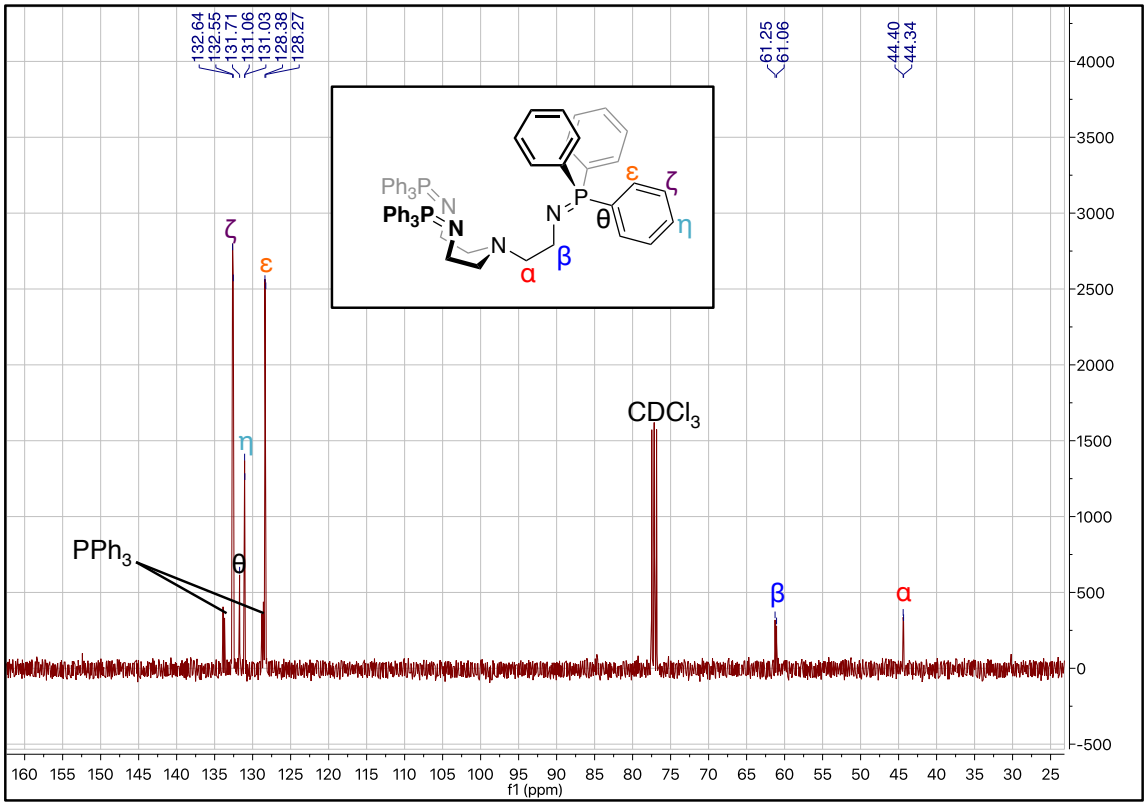


Fig S28. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of $^{Ph3}P_3$tren in CD_3Cl (T = 298 K).

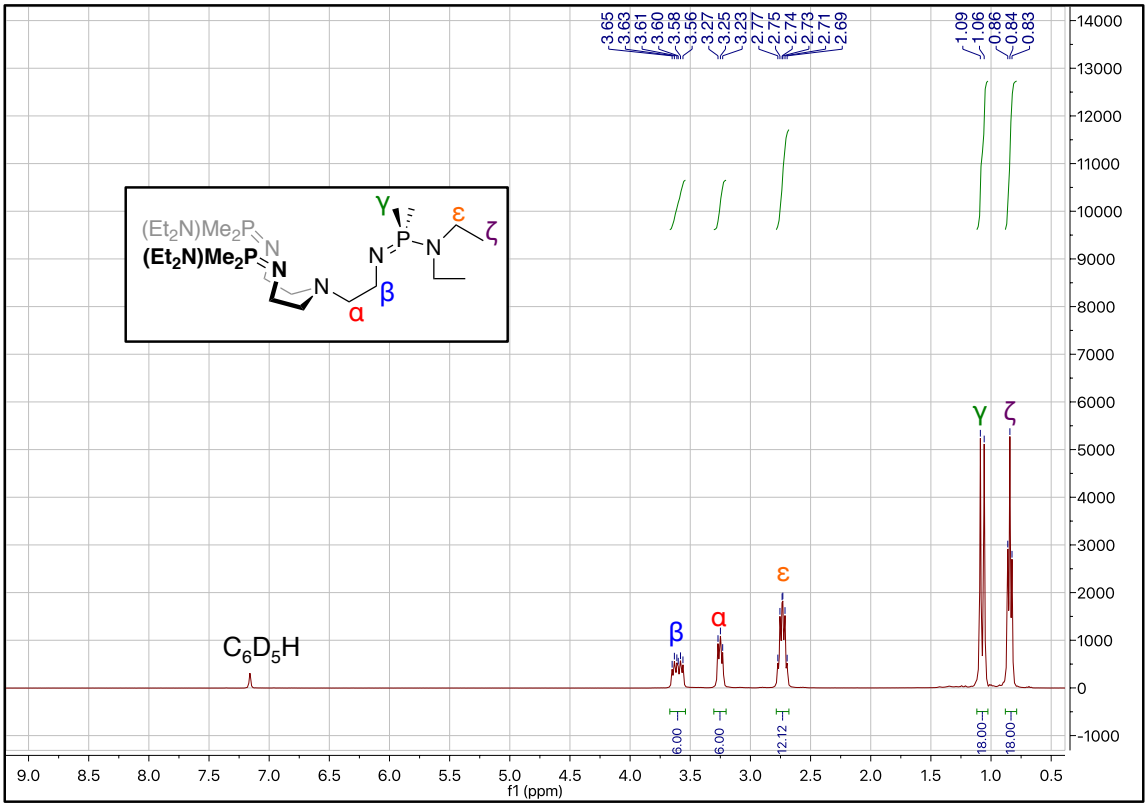


Fig S29. ^{1}H NMR (400 MHz) spectrum of $^{Me2(NEt2)}P_3$tren in C_6D_6 (T = 298 K).

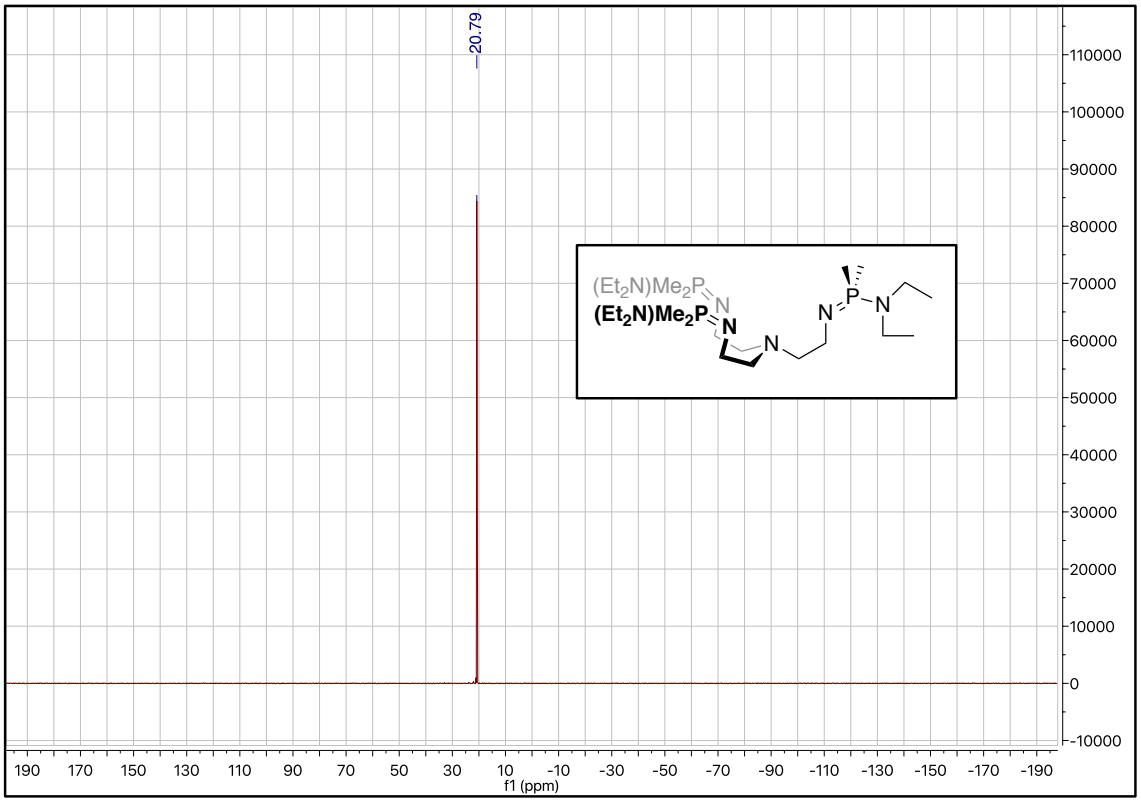


Fig S30. ^{31}P{^{1}H} NMR (162 MHz) spectrum of $^{Me2(NEt2)}P_3$tren in C_6D_6 (T = 298 K).

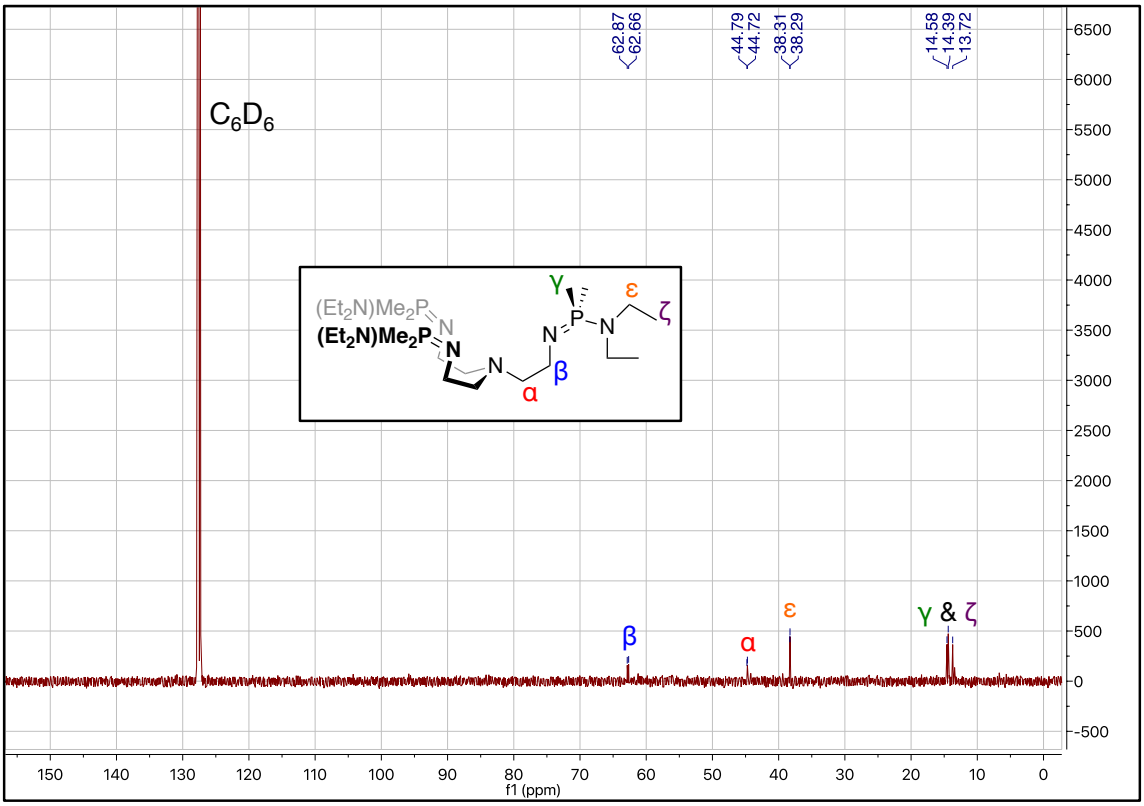


Fig S31. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of $^{Me2(NEt2)}P_3$tren in C_6D_6 (T = 298 K).

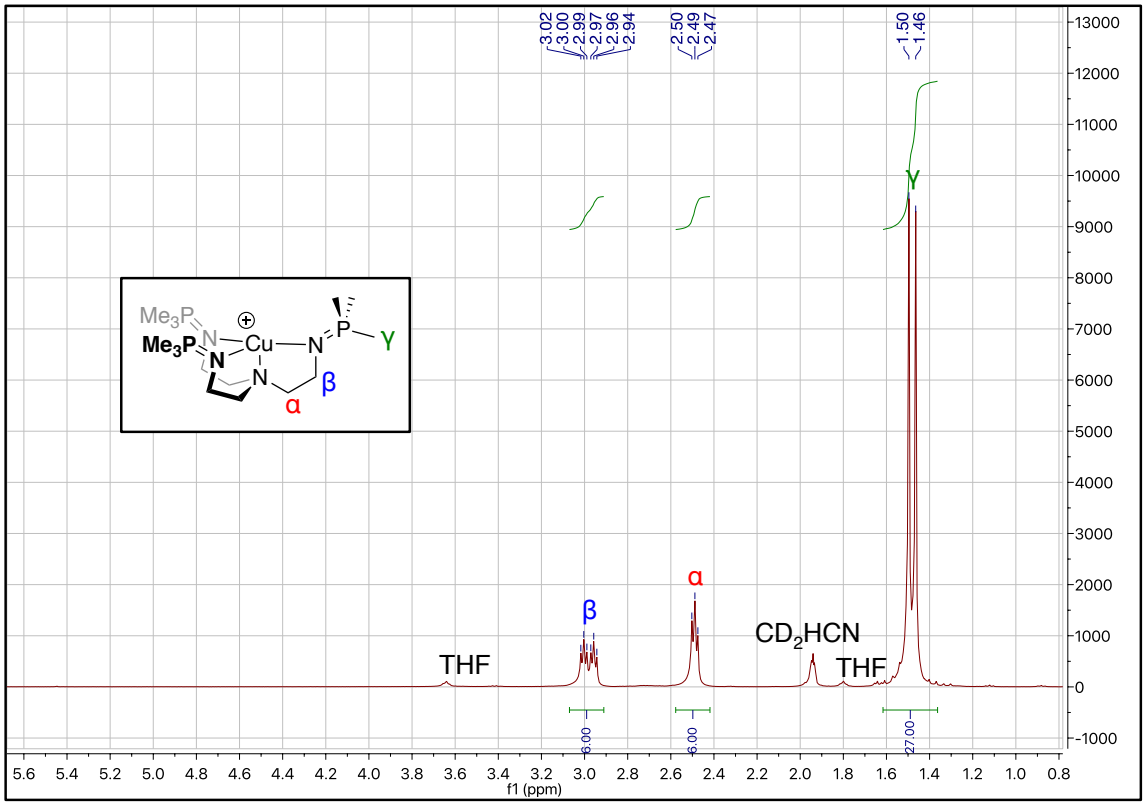


Fig S32. ^{1}H NMR (400 MHz) spectrum of $\mathbf{1}^{\mathbf{PMe3}}$ in CD_3CN (T = 298 K).

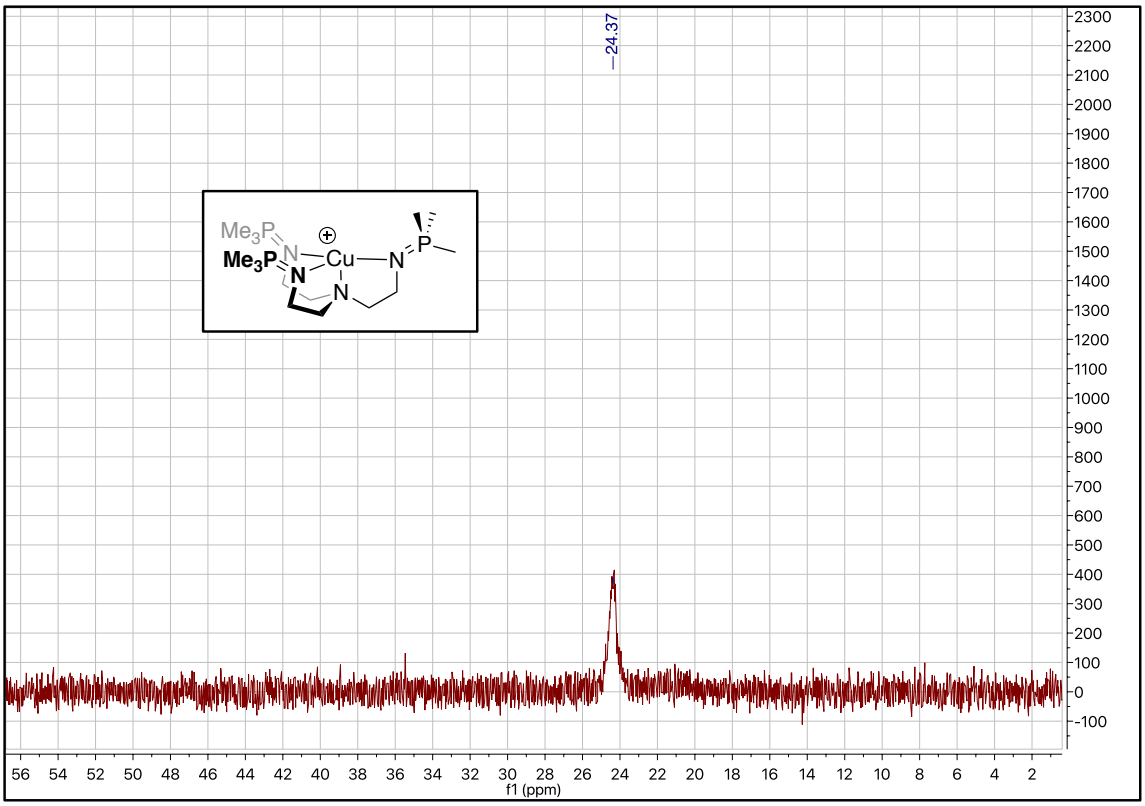


Fig S33. $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of $\mathbf{1}^{\mathbf{PMe3}}$ in CD_3CN (T = 298 K).

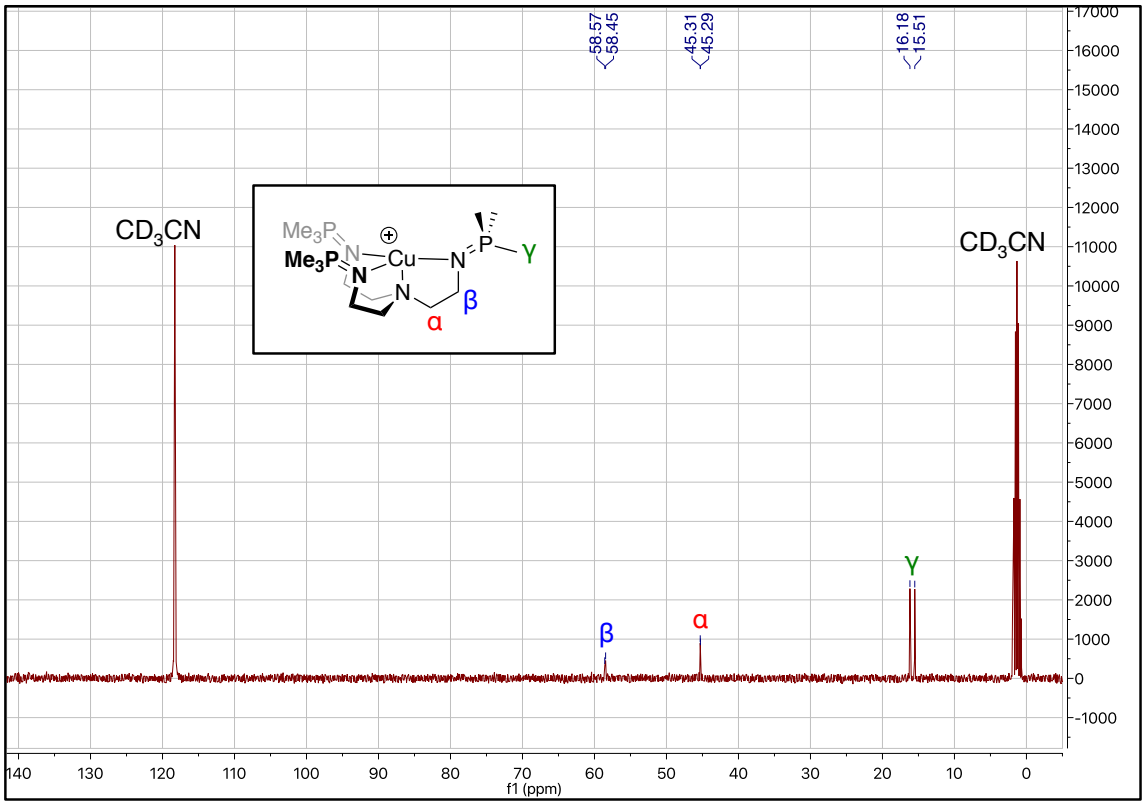


Fig S34. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of $\mathbf{1}^{\mathbf{PMe3}}$ in CD_3CN (T = 298 K).

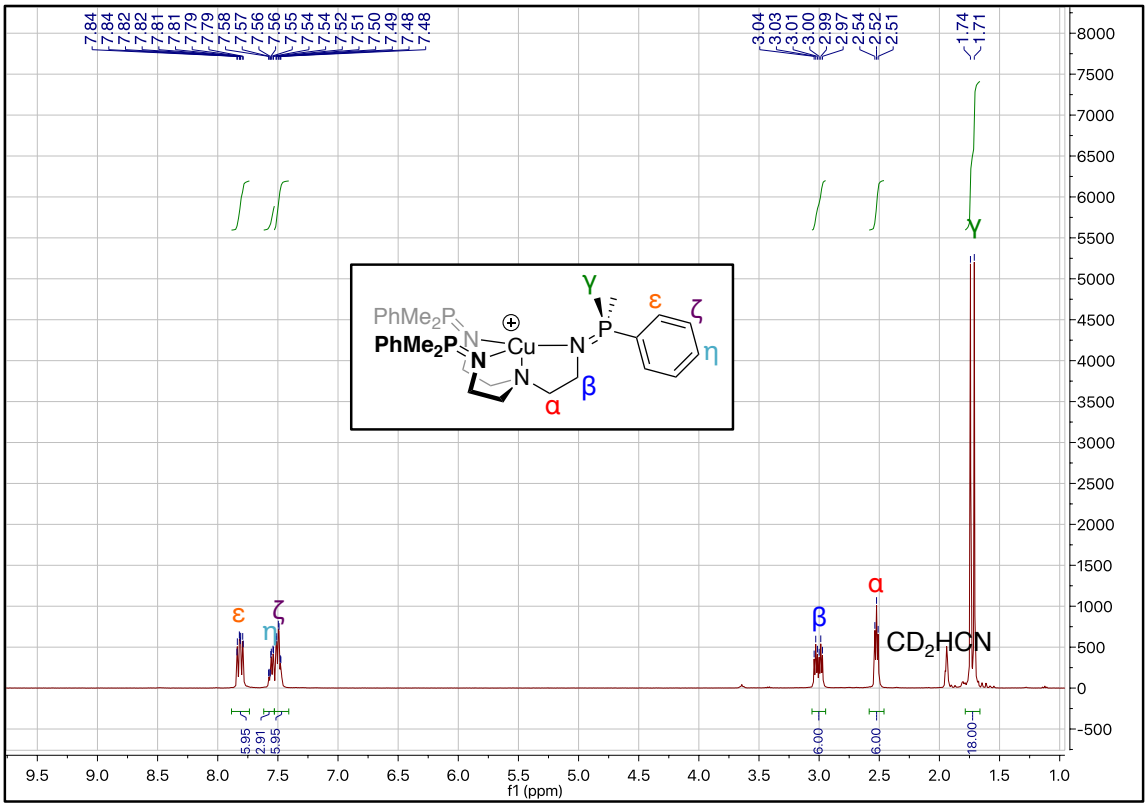


Fig S35. ^{1}H NMR (400 MHz) spectrum of **1**$^{\mathbf{PMe2Ph}}$ in CD_3CN (T = 298 K).

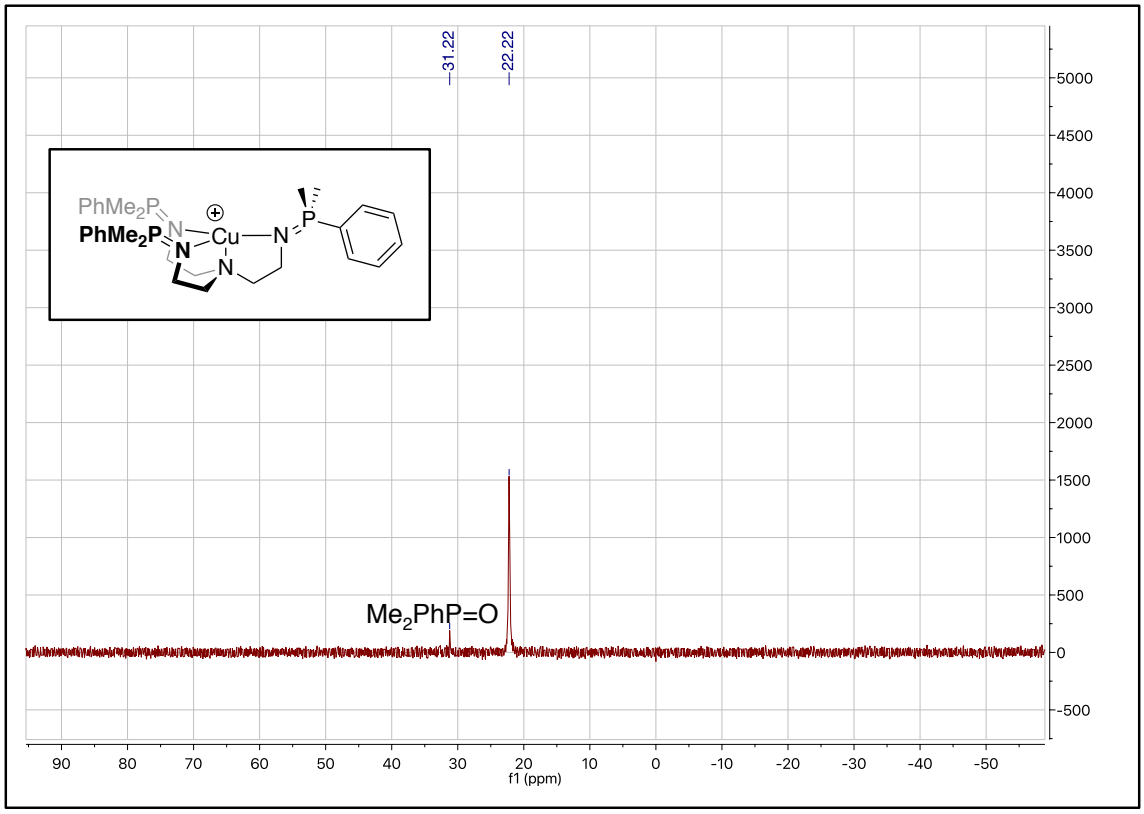


Fig S36. ^{31}P{^{1}H} NMR (162 MHz) spectrum of **1**$^{\mathbf{PMe2Ph}}$ in CD_3CN (T = 298 K).

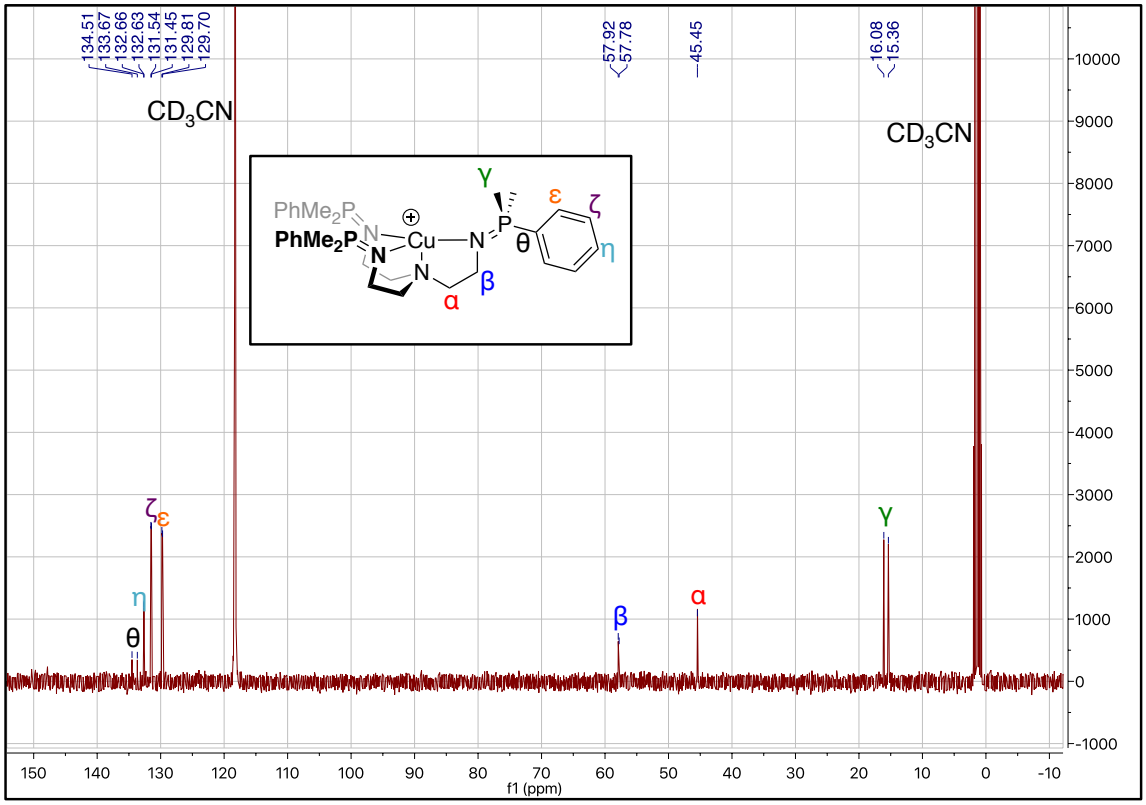


Fig S37. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **1**^{PMe2Ph} in CD_3CN (T = 298 K).

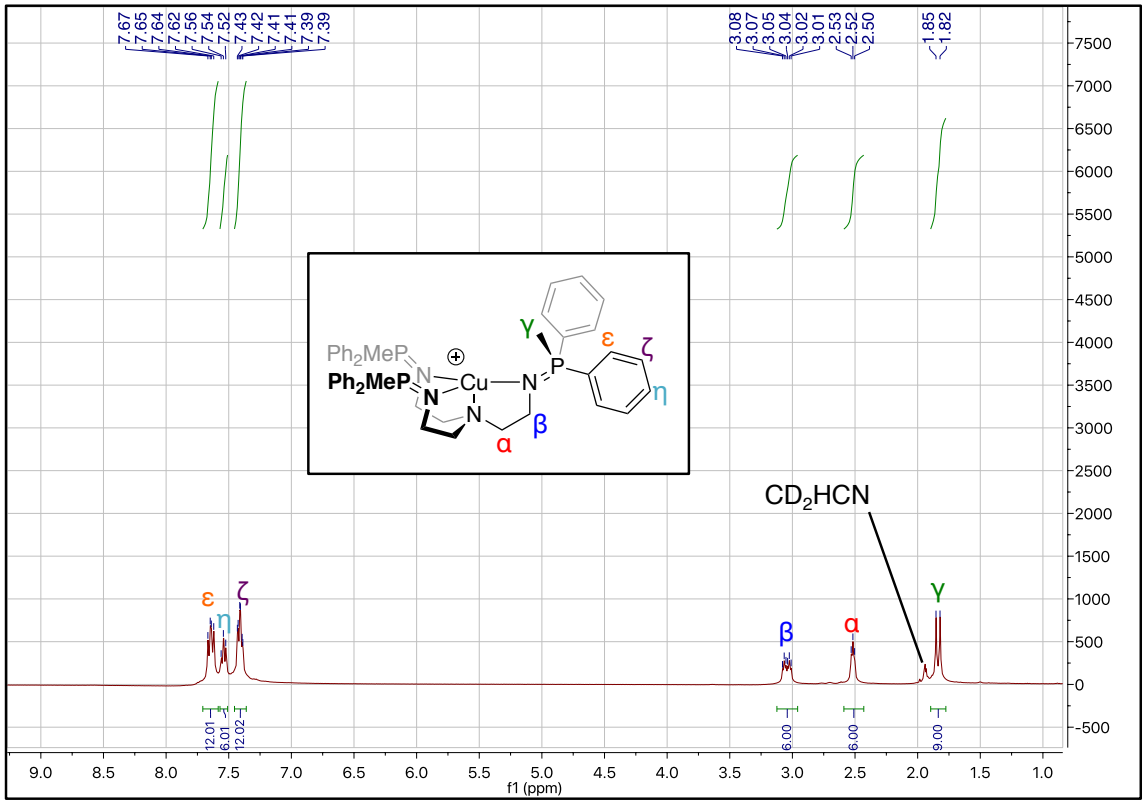


Fig S38. ^{1}H NMR (400 MHz) spectrum of **1**^{PMePh2} in CD_3CN (T = 298 K).

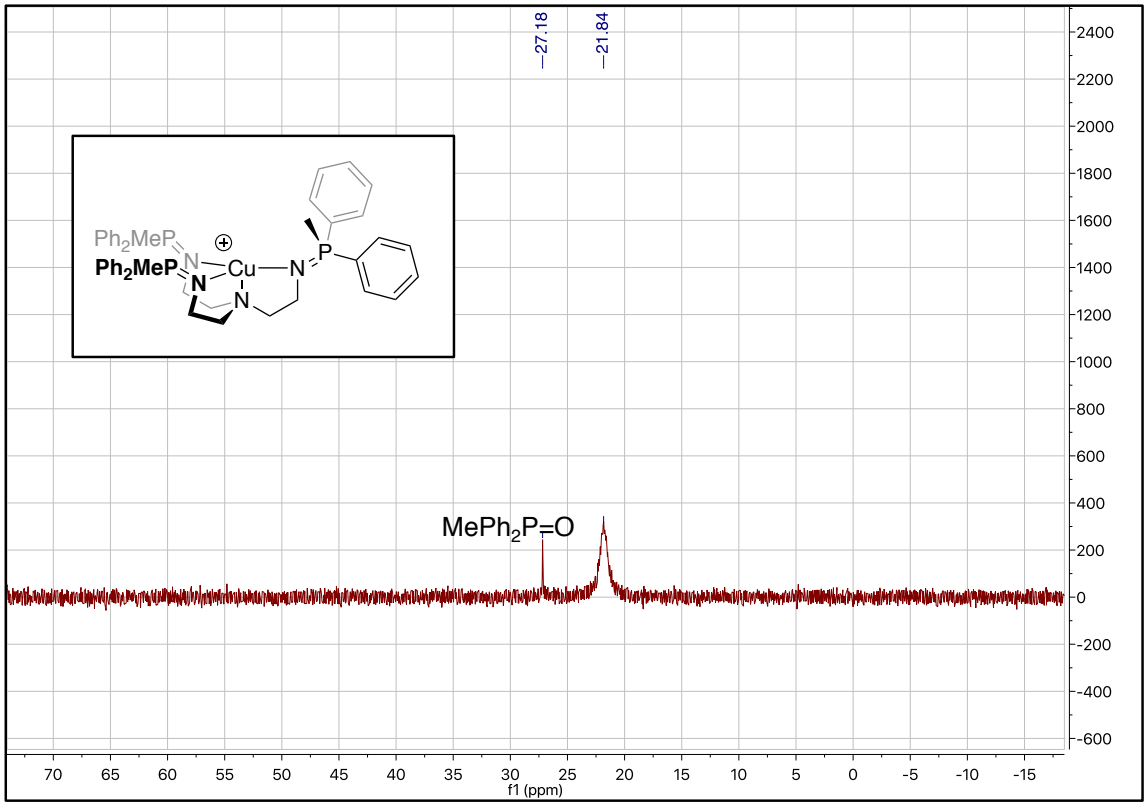


Fig S39. $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of $\mathbf{1}^{\mathbf{PMePh2}}$ in CD_3CN (T = 298 K).

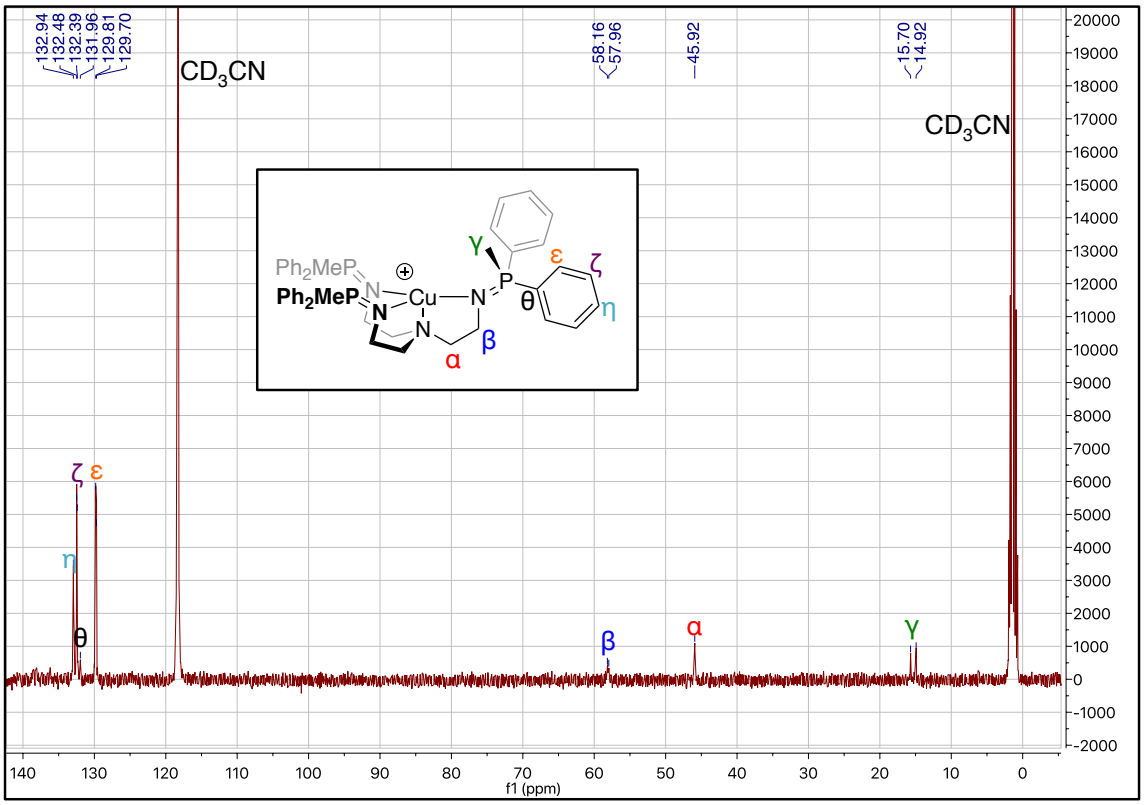


Fig S40. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of $\mathbf{1}^{\mathbf{PMePh2}}$ in CD_3CN (T = 298 K).

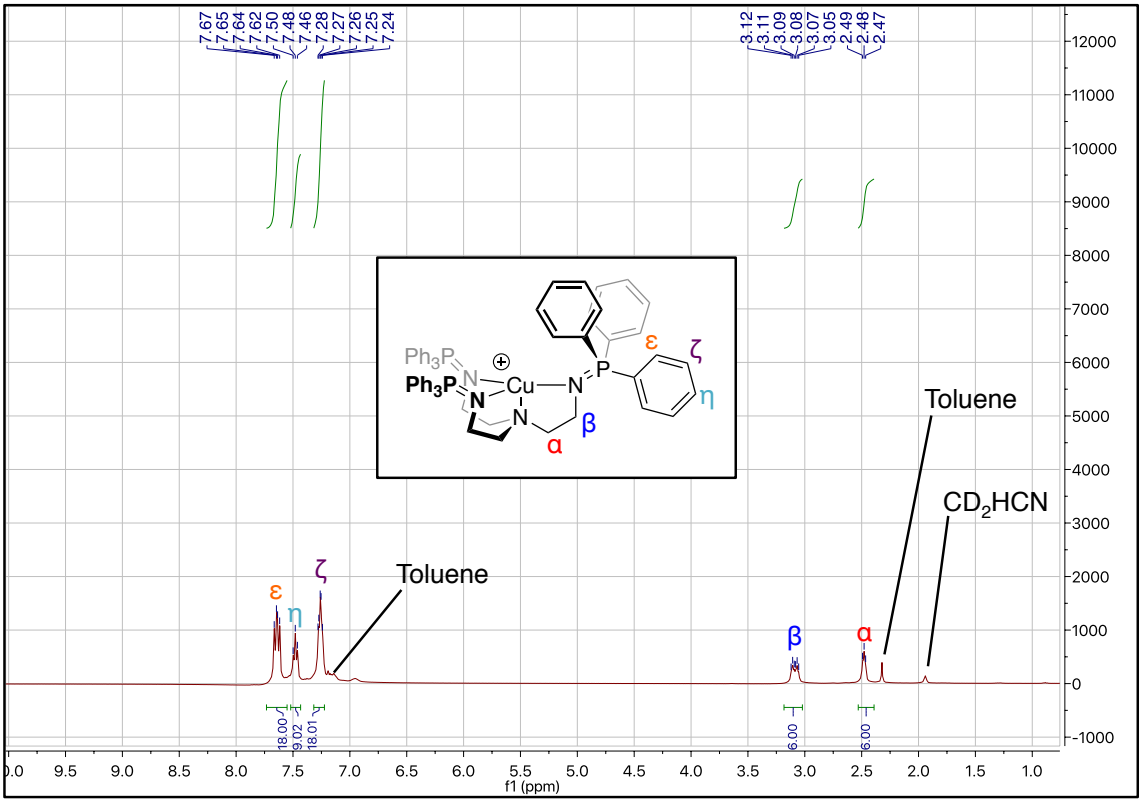


Fig S41. ^{1}H NMR (400 MHz) spectrum of **1**^{PPh3} in CD_3CN (T = 298 K).

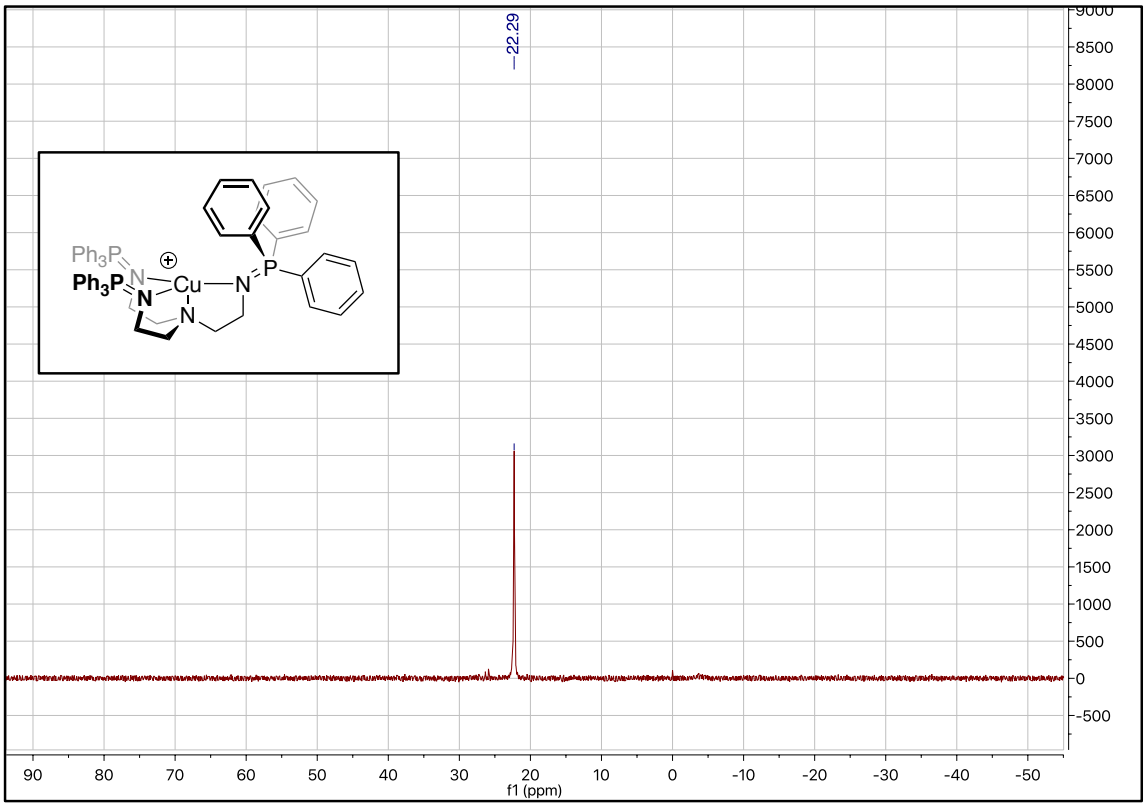


Fig S42. $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of **1**^{PPh3} in CD_3CN (T = 298 K).

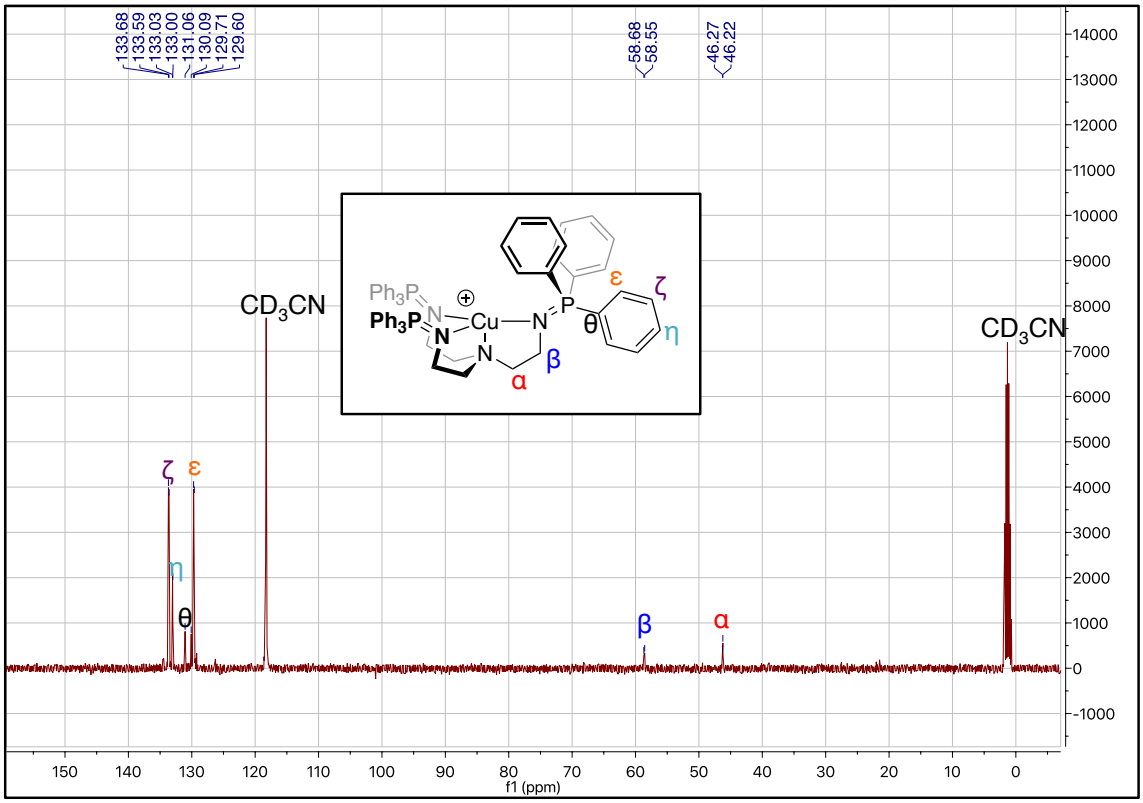


Fig S43. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of $\mathbf{1}^{\mathbf{PPh3}}$ in CD_3CN (T = 298 K).

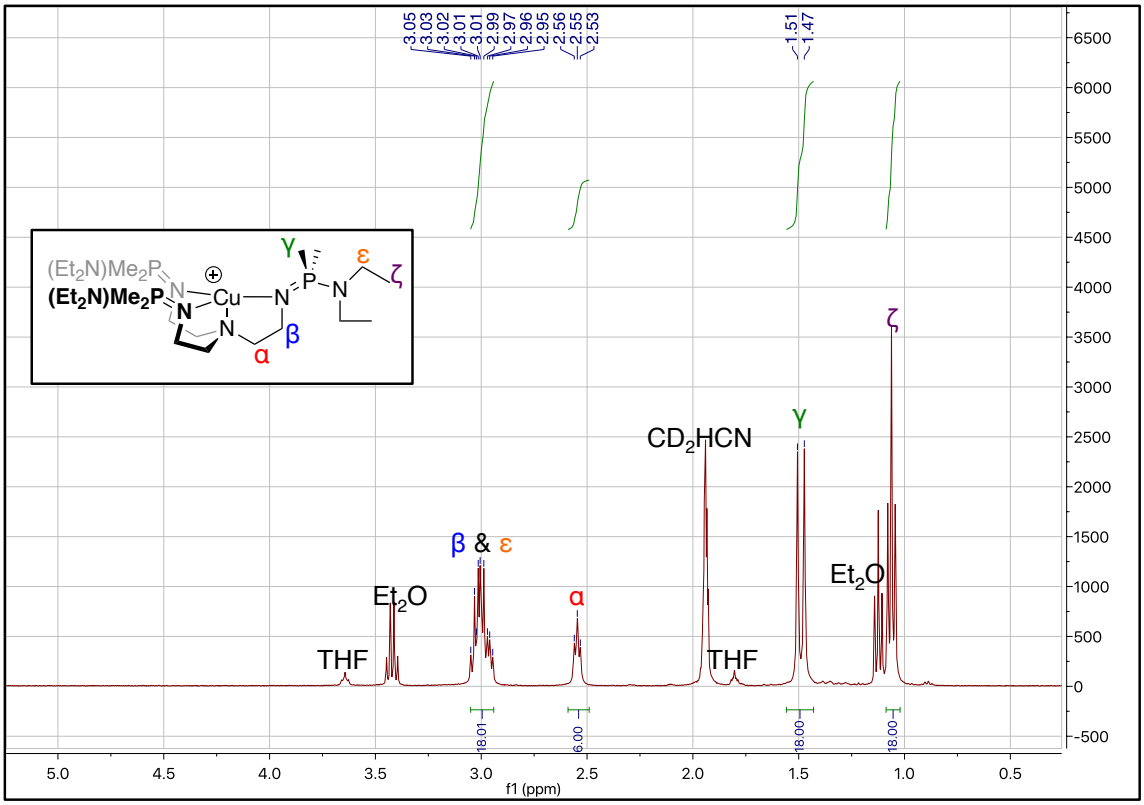


Fig S44. ^{1}H NMR (400 MHz) spectrum of $\mathbf{1}^{\mathbf{PMe2(NEt2)}}$ in CD_3CN (T = 298 K).

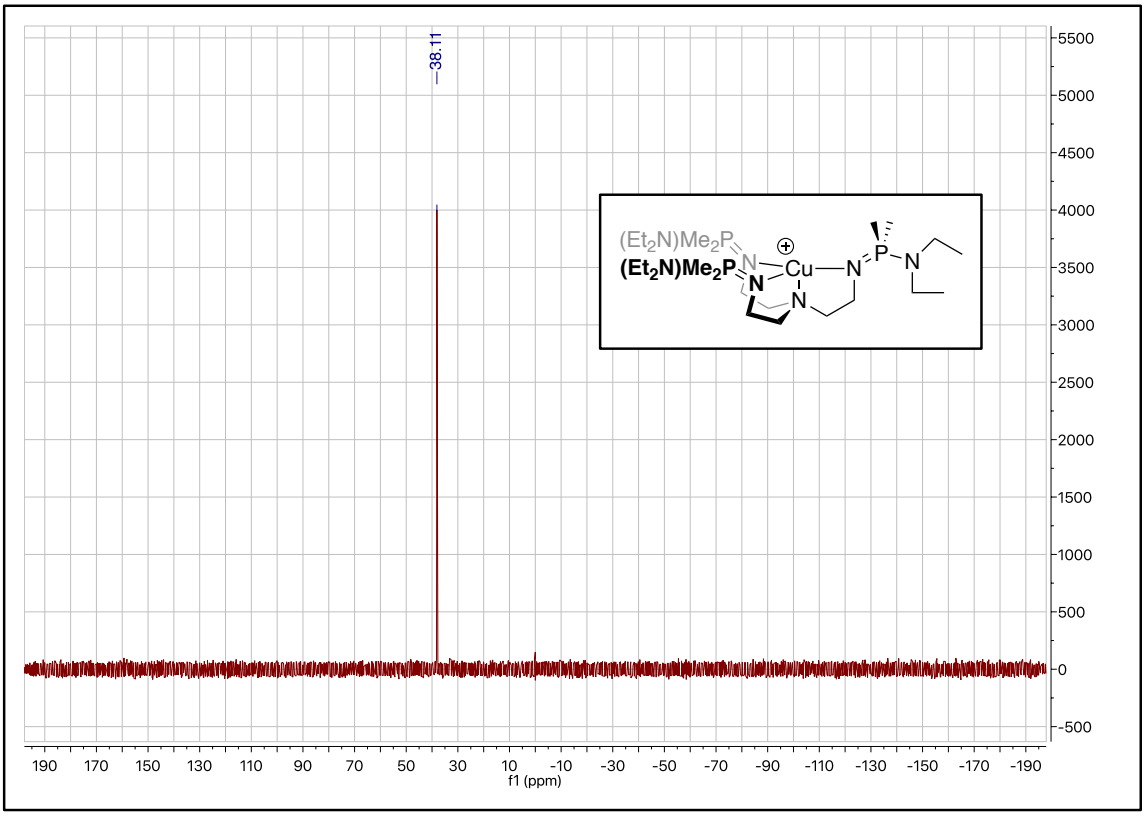


Fig S45. $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of **1**$^{\mathbf{PMe2(NEt2)}}$ in CD_3CN (T = 298 K).

X-ray Crystallographic Details

X-ray intensity data were collected on a Bruker D8QUEST CMOS area detector or on a Bruker APEXII CCD area detector, employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 100 K. Rotation frames were integrated using SAINT, producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[5] The structure was solved by direct methods – ShelXT.[6] Refinement was done by full-matrix least squares based on F^2 using SHELXL-2017[6] or SHELXL-2018.[7] All reflections were used during refinement. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 9.9284P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Crystals of $\mathbf{2}^{\mathbf{PMe3}}$ were weakly diffracting and required use of a Cu-Kα radiation source (λ = 1.5406 Å) at a temperature of 100 K. Long X-ray exposure times during the data collection led to consistent radiation decay of the sample, resulting in incomplete data sets (60 – 70%) for the sample. Bond lengths and angles in the solid-state structure of $\mathbf{2}^{\mathbf{PMe3}}$ are therefore less reliable than other structures reported herein, however the resolution was sufficient to determine the presence of a Jahn-Teller distortion in $\mathbf{2}^{\mathbf{PMe3}}$.

Summary of Structure Determination of **1**^{PMe3}

Empirical formula	$C_{39}H_{39}BCuF_{20}N_4P_3$
Formula weight	1111.00
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	13.4430(19)Å
b	14.253(2)Å
c	14.599(2)Å
α	93.503(7)°
β	105.397(6)°
γ	107.916(6)°
Volume	2534.8(6)Å^3
Z	2
d_{calc}	1.456 g/cm^3
μ	0.631 mm^{-1}
F(000)	1120.0
Crystal size, mm	0.17 × 0.14 × 0.08
2θ range for data collection	2.93 - 55.068°
Index ranges	-15 ≤ h ≤ 17, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	43606
Independent reflections	11597[R(int) = 0.0372]
Data/restraints/parameters	11597/0/622
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0873
Final R indexes [all data]	R_1 = 0.0558, wR_2 = 0.0964
Largest diff. peak/hole	0.55/-0.57 eÅ^{-3}

Summary of Structure Determination of **1**^{PMe2Ph}

Empirical formula	$C_{54}H_{45}BCuF_{20}N_4P_3$
Formula weight	1297.20
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a	12.8794(5)Å
b	28.2479(10)Å
c	15.6613(6)Å
β	110.7600(10)°
Volume	5327.9(3)Å^3
Z	4
d_{calc}	1.617 g/cm^3
μ	0.614 mm^{-1}
F(000)	2624.0
Crystal size, mm	0.33 × 0.29 × 0.12
2θ range for data collection	5.144 - 55.124°
Index ranges	-16 ≤ h ≤ 16, -36 ≤ k ≤ 36, -20 ≤ l ≤ 20
Reflections collected	130044
Independent reflections	12282[R(int) = 0.0756]
Data/restraints/parameters	12282/0/754
Goodness-of-fit on F^2	1.104
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.0835
Final R indexes [all data]	R_1 = 0.0657, wR_2 = 0.0897
Largest diff. peak/hole	0.42/-0.42 eÅ^{-3}

Summary of Structure Determination of **1**^{PPh3}

Empirical formula	$C_{66}H_{67}CoF_6N_4O_7P_3S_2$
Formula weight	1358.19
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a	16.9769(4)Å
b	15.0310(3)Å
c	24.8133(5)Å
β	94.0320(10)°
Volume	6316.2(2)Å^3
Z	4
d_{calc}	1.428 g/cm^3
μ	0.489 mm^{-1}
F(000)	2820.0
Crystal size, mm	0.25 × 0.12 × 0.1
2θ range for data collection	3.17 - 55.1°
Index ranges	-22 ≤ h ≤ 22, -18 ≤ k ≤ 19, -32 ≤ l ≤ 32
Reflections collected	85004
Independent reflections	14579[R(int) = 0.0421]
Data/restraints/parameters	14579/0/802
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0846
Final R indexes [all data]	R_1 = 0.0451, wR_2 = 0.0908
Largest diff. peak/hole	0.72/-0.48 eÅ^{-3}

Summary of Structure Determination of **3**^{PMe3}

Empirical formula	$C_{43}H_{49}N_4OBF_{20}ClP_3Cu$
Formula weight	1220.57
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a	16.4423(16)Å
b	20.7390(19)Å
c	15.7833(15)Å
β	104.388(5)°
Volume	5213.2(9)Å^3
Z	4
d_{calc}	1.555 g/cm^3
μ	0.672 mm^{-1}
F(000)	2476.0
Crystal size, mm	0.35 × 0.18 × 0.08
2θ range for data collection	2.558 - 55.028°
Index ranges	-21 ≤ h ≤ 21, -26 ≤ k ≤ 26, -20 ≤ l ≤ 20
Reflections collected	133454
Independent reflections	11993[R(int) = 0.0330]
Data/restraints/parameters	11993/0/678
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.1009
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.1059
Largest diff. peak/hole	1.60/-0.88 eÅ^{-3}

Summary of Structure Determination of [$^{Me3}P_3$tren-Cu^{II}-Cl]Cl

Empirical formula	$C_{15}H_{39}Cl_2CuN_4P_3$
Formula weight	502.85
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbca
a	16.2129(7)Å
b	16.8046(7)Å
c	17.8201(8)Å
Volume	4855.1(4)$Å^3$
Z	8
d_{calc}	1.376 g/cm^3
μ	1.325 mm^{-1}
F(000)	2120.0
Crystal size, mm	0.33 × 0.14 × 0.13
2θ range for data collection	4.172 - 55.042°
Index ranges	$-21 \le h \le 20$, $-21 \le k \le 21$, $-23 \le l \le 22$
Reflections collected	118076
Independent reflections	5586[R(int) = 0.0321]
Data/restraints/parameters	5586/0/235
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0197, wR_2 = 0.0516
Final R indexes [all data]	R_1 = 0.0222, wR_2 = 0.0531
Largest diff. peak/hole	0.47/-0.53 $eÅ^{-3}$

Computational Details for Copper Complexes

All density functional theory (DFT) calculations were performed with the ORCA program package, v3.0.3.[6] Geometry optimizations were carried out at the restricted (Cu^{I} complexes) or unrestricted (Cu^{II} complexes) B97-D3 level of DFT. The def2-TZVP basis sets and the def2-TZVP/J auxiliary basis sets (used to expand the electron density in the resolution-of-identity (RI) approach) were used for all atoms except carbon and hydrogen, which were described using the def2-SVP basis sets and def2-SV/J auxiliary basis sets.[8–12] These functional/basis set combinations were chosen for their convenient balance of accuracy and computational cost and for their ability to capture non-covalent interactions and dispersion forces. The conductor-like screening model (COSMO; dipole moment corresponding to acetonitrile) was implemented for all calculations. Time-dependent density functional theory (TDDFT) calculations were carried out using the same methodology described above. The 20 lowest-energy excited states were calculated for each complex. Transition assignments were based on the majority/plurality orbital contributions to a given state; however, some transitions result from a non-negligible mixture of either donor or acceptor orbitals (or both), thereby leading to higher-than-expected transition probabilities for some "d-to-d" excitations.

The SCF calculations were tightly converged ($1x10^{-8}$ E_h in energy, $1x10^{-7}$ E_h in the density change, and $5x10^{-7}$ in the maximum element of the DIIS error vector). In all cases the geometries were considered converged after the energy change was less than $1x10^{-6}$ E_h, the gradient norm and maximum gradient element were smaller than $3x10^{-4}$ E_h-$Bohr^{-1}$ and $1x10^{-4}$ E_h-$Bohr^{-1}$, respectively, and the root-mean square and maximum displacements of all atoms were smaller than $6x10^{-4}$ Bohr and $1x10^{-3}$ Bohr, respectively.

Numerical frequency calculations were used to verify that the calculated structures represented either local minima (ground states) or saddle points (transition states) on the potential energy surface. The reported energies are Gibbs free energies, calculated for 298.15 K and 1.00 atm, as obtained from numerical frequency calculations on the optimized geometries. Electrostatic potential maps (Fig. 7) were generated by calculating the electrostatic potential along the canonical z-axes of the complexes at every 0.1 Bohr radii (0.052 Å) using the orca_vpot utility program.

In order to compare orbital energies across the series of structurally homologous but compositionally unique Cu^{I} complexes, a normalization of the orbital energies was required. The Cu 1s orbital energy was deemed the most reliable due to its energetic and spatial isolation. This choice was supported by literature reports describing experimental K-edge X-ray absorption near-edge spectroscopy (XANES), which has been used to show that Cu 1s orbital energies depend on oxidation states and coordination geometries,[13] with very little impact by the strength of the ligand field.[14] Orbital energies were thus normalized by calculating differences in energy from the computed Cu 1s orbitals.

Redox Potential Calculations

For the redox potential calculations, the change in free energies for the redox processes ($DG_{red/ox}$) were calculated by taking the differences between the calculated free energies for the reduced (Cu^{I}) and oxidized (Cu^{II}) complexes.[15] For species predicted to coordinate solvent upon oxidation, the calculated free energy for acetonitrile was included in the $DG_{red/ox}$ calculations. To calculate the redox potentials as referenced to NHE, a value of -4.28 eV was subtracted from $DG_{red/ox}$, and the conversion value of -0.630 V was subtracted from this value to give the *E*° values as referenced to Fc/Fc^{+}.[15,16] Relevant free energies for the complexes used to calculate redox potentials are shown below.

MeCN: -132.6248337 E_h
1$^{\mathbf{PMe3}}$: -3478.227854 E_h
2$^{\mathbf{PMe3}}$: -3478.079713 E_h
$^{Me3}P_3$tren-Cu^{II} (C_{3v}-constrained): -3478.070168 E_h
1$^{\mathbf{PMe2Ph}}$: -4052.508296 E_h
2$^{\mathbf{PMe2Ph}}$: -4052.34872 E_h
1$^{\mathbf{PMePh2}}$: -4626.787167 E_h
2$^{\mathbf{PMePh2}}$: -4626.629827 E_h
1$^{\mathbf{PPh3}}$: -5201.07596 E_h
2$^{\mathbf{PPh3}}$: -5200.919534 E_h
1$^{\mathbf{PMe2(NEt2)}}$: -3997.314891 E_h
2$^{\mathbf{PMe2(NEt2)}}$: -3997.164239 E_h
^{H}TMPA-Cu^{I}-MeCN: -2688.352206 E_h
^{H}TMPA-Cu^{II}-MeCN: -2688.179884 E_h
^{tBu}TMPA-Cu^{I}-MeCN: -3159.190533 E_h
^{tBu}TMPA-Cu^{II}-MeCN: -3159.020821 E_h
^{OMe}TMPA-Cu^{I}-MeCN: -3031.408327 E_h
^{OMe}TMPA-Cu^{II}-MeCN: -3031.238915 E_h
^{NMe2}TMPA-Cu^{I}-MeCN: -3089.739079 E_h
^{NMe2}TMPA-Cu^{II}-MeCN: -3089.580913 E_h

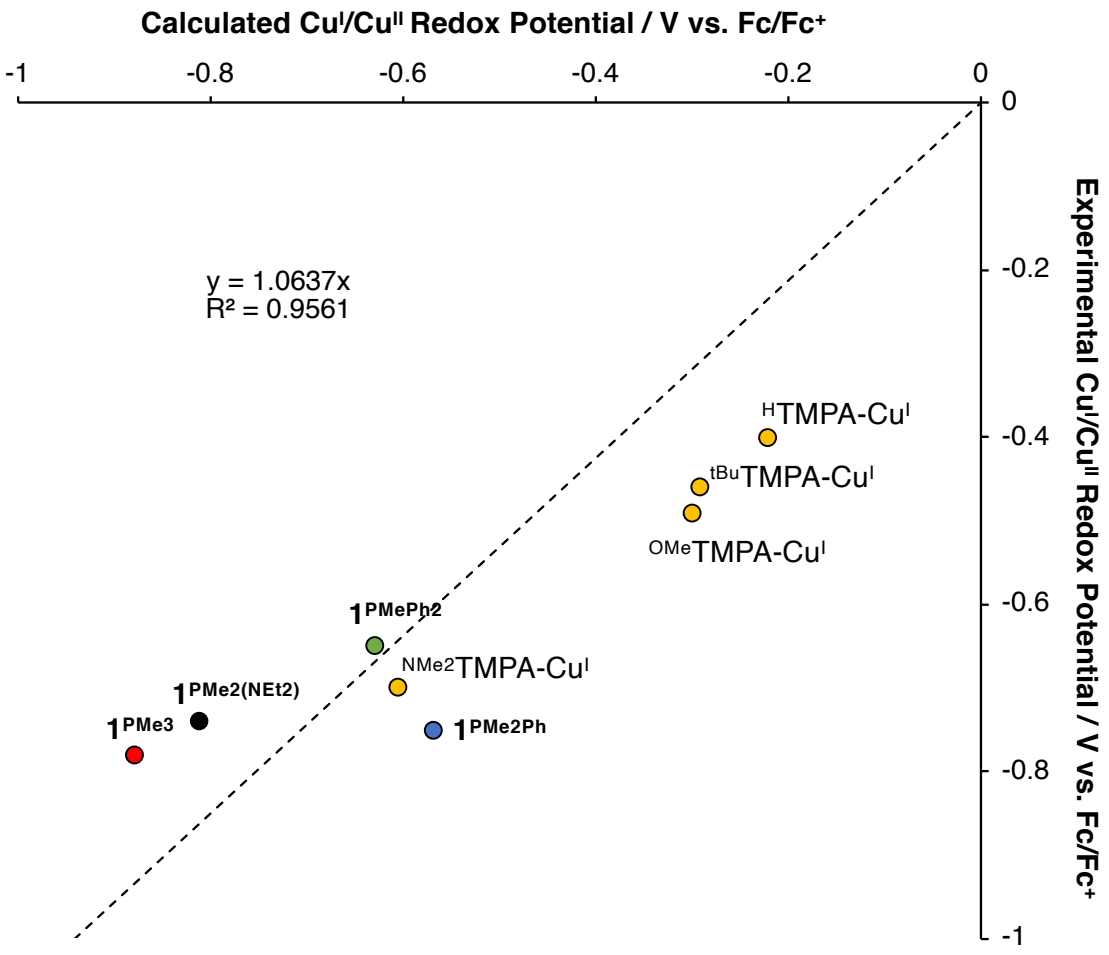


Fig S46. Comparison between calculated and experimental Cu^{I}/Cu^{II} redox potentials for **1**^{PR3} and ^{X}TMPA-Cu^{I} complexes.

Optimized Cartesian Coordinates for Copper Complexes

Optimized Cartesian Coordinates for **1**^{PMe3} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
P	-0.3969802176	2.9522317079	-0.6550983397
P	2.7405726813	-1.1553406567	-0.6685337455
P	-2.3675825242	-1.8216567443	-0.6508560138
N	0.5677437627	1.9817787408	0.1681992453
N	1.4303018316	-1.4958566263	0.1767687061
N	-2.0067629622	-0.5085616919	0.1813685069
N	-0.0000000000	0.0000000000	2.2441195625
C	0.0353928715	1.4290260037	2.5698830222
H	0.4021071775	1.6061809006	3.6070711601
H	-0.9966850873	1.8118764489	2.5250714884
C	0.9043462204	2.2254974018	1.5732352227
H	0.8442113269	3.2961809631	1.8564680074
H	1.9630698916	1.9370842949	1.7235862496
C	0.0409273613	4.7138021984	-0.5473791524
H	-0.0611808320	5.0609627548	0.4945094704
H	-0.6293428936	5.3112887546	-1.1871402873
H	1.0849747166	4.8505066436	-0.8732298738
C	-0.2790672965	2.4982975029	-2.3982694033
H	0.7741923394	2.5471783580	-2.7160520547
H	-0.8882413548	3.1807841957	-3.0135623907
H	-0.6480795893	1.4670725380	-2.5152752540
C	-2.1708260315	2.8790004914	-0.2612426076
H	-2.4878668602	1.8267256455	-0.3717603563
H	-2.7530872964	3.5322607962	-0.9329667881
H	-2.3228001070	3.2016429968	0.7818473746
C	1.2219146453	-0.7408026786	2.5719854294
H	1.1994087368	-1.1386353630	3.6129694962
H	2.0667615236	-0.0360346285	2.5177206412
C	1.4832223727	-1.8979113935	1.5841210280
H	2.4475521856	-2.3668619950	1.8688425345
H	0.7153111421	-2.6802091638	1.7451598302
C	2.2565739469	-1.0184960290	-2.4024252872
H	1.7457343525	-1.9449383474	-2.7097377063
H	3.1445303978	-0.8505150399	-3.0333722406
H	1.5649229363	-0.1668030743	-2.5065923027
C	4.0378053005	-2.4273997341	-0.5917496214
H	4.4071300135	-2.5187110364	0.4430278704
H	4.8827355476	-2.1538101835	-1.2453430305
H	3.6173724766	-3.3951825576	-0.9115136223
C	3.5882086552	0.4067205147	-0.2827757380
H	2.8434541952	1.2171542472	-0.3759023901
H	4.4367605465	0.5809530815	-0.9658848096
H	3.9591590427	0.3691556956	0.7544306665
C	-1.2525461034	-0.6849532595	2.5796728167

H	-1.5863601210	-0.4515262369	3.6167729118
H	-1.0650456926	-1.7701753105	2.5401798960
C	-2.3832070490	-0.3422169833	1.5864142142
H	-3.2731760430	-0.9392301069	1.8739431296
H	-2.6745301025	0.7154834186	1.7371442831
C	-2.0113683526	-1.4870942603	-2.3887534997
H	-2.5881038574	-0.6069940716	-2.7149241072
H	-2.2782431794	-2.3586370563	-3.0081192090
H	-0.9343749055	-1.2765442117	-2.4896238418
C	-4.1166928858	-2.3088146814	-0.5654365887
H	-4.3820982008	-2.5612399611	0.4745178121
H	-4.3017344342	-3.1903554701	-1.2013839423
H	-4.7457910080	-1.4691220164	-0.9039067290
C	-1.4340011838	-3.3311261557	-0.2535641717
H	-0.3596810403	-3.0847060415	-0.3374641818
H	-1.6984599767	-4.1531485624	-0.9397105566
H	-1.6623771000	-3.6354574217	0.7812573083

Optimized Cartesian Coordinates for **1**^{PMe2Ph} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
P	-1.1229370404	2.8337731261	-0.9740433709
P	3.0254950498	-0.4725084662	-0.9598797504
P	-1.8978827248	-2.4058972342	-0.9587656781
N	-1.0609027448	1.7624908517	0.2029612641
N	2.0596064604	0.0217695108	0.2065438288
N	-0.9981055399	-1.8082920174	0.2119473950
N	-0.0000000000	0.0000000000	2.2243326893
C	-0.9786140149	1.0403840769	2.5597864300
H	-0.8537885205	1.4074415400	3.6027205445
H	-1.9821507759	0.5919630709	2.4875781447
C	-0.9150690989	2.2286681439	1.5872862857
H	-1.7196300037	2.9357566439	1.8786489410
H	0.0411424213	2.7738697547	1.7388620429
C	-2.4904025452	4.0232082479	-0.8424303229
H	-3.4280153990	3.4516063751	-0.7459567655
H	-2.5541113684	4.6658911801	-1.7349295370
H	-2.3555911169	4.6549964321	0.0500735996
C	-1.3653123977	1.9668097756	-2.5373096910
H	-0.4976368409	1.3147963467	-2.7175591669
H	-1.4490115413	2.6982873784	-3.3572903924
H	-2.2819053562	1.3586653386	-2.4814044175
C	0.3927774390	3.8294168157	-1.1707598023
C	0.3998600950	5.1016433599	-1.7804366522
H	-0.5275753219	5.5446150332	-2.1587309662
C	1.6021063614	5.8127765902	-1.9140979118
H	1.6001715218	6.7996120182	-2.3919055112
C	2.8036674808	5.2631402419	-1.4364892354

H	3.7415820393	5.8216025074	-1.5397663699
C	2.7995573017	3.9985891368	-0.8247406231
H	3.7352418105	3.5689412673	-0.4469114537
C	1.6018730430	3.2809108042	-0.6904674516
H	1.6068270084	2.2846804676	-0.2288476053
C	1.3894574414	0.3288059581	2.5613382867
H	1.6427470822	0.0424001619	3.6062867136
H	1.5031393733	1.4216943137	2.4842202719
C	2.3891374473	-0.3251201464	1.5948064802
H	3.4023634797	0.0233374257	1.8849352664
H	2.3871697026	-1.4246460508	1.7553950117
C	2.4104636859	0.1562511501	-2.5348940144
H	1.4116034411	-0.2661143555	-2.7196273252
H	3.0914477893	-0.1496496935	-3.3455244046
H	2.3474432603	1.2550181462	-2.4929845089
C	4.7401961882	0.1141005432	-0.8222293804
H	4.7171365117	1.2128762691	-0.7367075424
H	5.3329983315	-0.1630573445	-1.7084732980
H	5.2126553086	-0.3119311342	0.0772472807
C	3.1290537825	-2.2850786377	-1.1378839485
C	2.0506218117	-3.0527783933	-0.6467877701
H	1.1861478298	-2.5543262847	-0.1887766849
C	2.0734501362	-4.4502301681	-0.7665462019
H	1.2348777030	-5.0419721705	-0.3798253318
C	3.1649254200	-5.0922034079	-1.3748466662
H	3.1796334807	-6.1847141900	-1.4667210434
C	4.2400746884	-4.3313448674	-1.8637372373
H	5.0941648518	-4.8278020357	-2.3393473412
C	4.2255195808	-2.9332197502	-1.7442232491
H	5.0715582480	-2.3551522224	-2.1309826915
C	-0.4101184401	-1.3662883004	2.5661966857
H	-0.7884745136	-1.4378566034	3.6101323823
H	0.4802336105	-2.0108027910	2.4953314088
C	-1.4712900077	-1.9116578884	1.5978638240
H	-1.6763672581	-2.9618253633	1.8934476641
H	-2.4237319373	-1.3599141155	1.7504584644
C	-1.0294190569	-2.1995919422	-2.5263306571
H	-0.8944708945	-1.1244609373	-2.7162184432
H	-1.6262684950	-2.6416821985	-3.3404090461
H	-0.0465738592	-2.6935240047	-2.4708028679
C	-2.2514573585	-4.1824853213	-0.8112119393
H	-1.2905178698	-4.7141450367	-0.7158246977
H	-2.7836065111	-4.5621196159	-1.6980064568
H	-2.8629149727	-4.3702693367	0.0858407195
C	-3.5163921087	-1.5890753010	-1.1606355007
C	-3.6507653784	-0.2743791254	-0.6638079417
H	-2.7944288978	0.2222708621	-0.1892643826
C	-4.8701186161	0.4054519926	-0.8005366497
H	-4.9700930327	1.4248795218	-0.4086391532

C	-5.9606595011	-0.2147707641	-1.4323884995
H	-6.9124864139	0.3192369270	-1.5377072676
C	-5.8303491434	-1.5229899586	-1.9279756059
H	-6.6785846467	-2.0110238415	-2.4224176282
C	-4.6147162029	-2.2104872282	-1.7910145845
H	-4.5302826570	-3.2296084288	-2.1832991772

Optimized Cartesian Coordinates for **1**^{PMePh2} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
P	-2.7229736675	-1.2945927513	-0.5690411177
P	2.4734759856	-1.6997511046	-0.5840387927
P	0.1982884735	3.0175377557	-0.5584009624
N	-2.0487146318	-0.0654556427	0.1846615802
N	1.0718103692	-1.7384169861	0.1708836376
N	0.9388402078	1.8161128136	0.1787545154
N	-0.0000000000	0.0000000000	2.2671730019
C	-1.3915623339	-0.3188768608	2.5973094603
H	-1.6655320810	0.0262153630	3.6199219830
H	-1.4964919234	-1.4145760313	2.5886853132
C	-2.3761501974	0.2787604774	1.5723310434
H	-3.4007438406	-0.0295729440	1.8639787549
H	-2.3569144384	1.3815457432	1.6514504433
C	-2.3947141142	-2.9627377544	0.0812729595
C	-1.4950078636	-3.8496853783	-0.5414527418
H	-1.0156810035	-3.5822704360	-1.4868777872
C	-1.1985564422	-5.0848116867	0.0551165333
H	-0.5139221714	-5.7799818100	-0.4442914634
C	-1.7776056655	-5.4342448159	1.2850382870
H	-1.5365876786	-6.3965393107	1.7515348531
C	-2.6746680968	-4.5526873795	1.9124158315
H	-3.1358767427	-4.8240748537	2.8690854531
C	-2.9882560939	-3.3279961103	1.3093594535
H	-3.7025705472	-2.6531182562	1.7949464477
C	-4.5383604061	-1.1784923837	-0.6332406237
C	-5.1249347242	0.0943221651	-0.4863688930
H	-4.4794710135	0.9581017844	-0.3017222782
C	-6.5165063912	0.2438715183	-0.5703088774
H	-6.9683824429	1.2356684421	-0.4493067889
C	-7.3296287183	-0.8771823810	-0.8070601953
H	-8.4179353470	-0.7614099857	-0.8720090438
C	-6.7487849331	-2.1481340073	-0.9583374427
H	-7.3825680341	-3.0233578633	-1.1433598430
C	-5.3573417899	-2.3014189708	-0.8692756035
H	-4.9093228076	-3.2949995250	-0.9813106667
C	-2.1558682755	-1.2692262457	-2.2798921639
H	-2.4560317246	-0.3044008685	-2.7175706857
H	-2.6173919465	-2.0903893777	-2.8506609167

H	-1.0579351933	-1.3537548248	-2.3022795633
C	0.9731521908	-1.0475898146	2.5866353552
H	0.8186692059	-1.4611847119	3.6090642147
H	1.9740881894	-0.5901144476	2.5723964382
C	0.9393729721	-2.1960168026	1.5583023802
H	1.7148486946	-2.9351378285	1.8448879797
H	-0.0290388624	-2.7234297199	1.6389631038
C	3.7467491399	-0.5739588163	0.0652466576
C	4.0562273440	0.6506068820	-0.5580871471
H	3.5822269846	0.9287149490	-1.5031226132
C	4.9728294393	1.5309027462	0.0371342430
H	5.2262820197	2.4726016120	-0.4630631599
C	5.5686216546	1.2082046022	1.2662576283
H	6.2778695299	1.9026383448	1.7314954244
C	5.2619961510	-0.0111502527	1.8945855654
H	5.7302647338	-0.2714528198	2.8508965835
C	4.3631793876	-0.9011141474	1.2930040590
H	4.1415313409	-1.8578866919	1.7797156426
C	3.2877187110	-3.3262409793	-0.6496312751
C	4.6718492846	-3.4691306723	-0.8753799378
H	5.3066211081	-2.5821924266	-0.9792761295
C	5.2392207143	-4.7488038108	-0.9650610973
H	6.3158908730	-4.8561683766	-1.1416298143
C	4.4312892338	-5.8903499849	-0.8250748958
H	4.8786951050	-6.8891338501	-0.8905109471
C	3.0515161478	-5.7516933800	-0.5992055913
H	2.4199593977	-6.6411500025	-0.4874398351
C	2.4808367023	-4.4737914793	-0.5143683613
H	1.4080171694	-4.3510119855	-0.3382032184
C	2.1634385500	-1.2234703933	-2.2949631803
H	1.4777503275	-1.9670314135	-2.7301566842
H	3.1042641251	-1.2131517092	-2.8678073173
H	1.6873277096	-0.2305626865	-2.3188842351
C	0.4216941892	1.3639937567	2.5963664179
H	0.8694068242	1.4265623974	3.6140305337
H	-0.4759943014	2.0008324590	2.6006190380
C	1.4179678547	1.9246496876	1.5612365901
H	1.6630411647	2.9660477965	1.8535476108
H	2.3662507420	1.3594364553	1.6265494832
C	-1.4023857042	3.5590490358	0.1169949191
C	-2.6275915307	3.2292118039	-0.4945188814
H	-2.6463502753	2.6904871438	-1.4455204441
C	-3.8383907198	3.5826827007	0.1206093649
H	-4.7885420250	3.3416952429	-0.3698191993
C	-3.8369422968	4.2460717588	1.3574689323
H	-4.7852772991	4.5128694869	1.8382710519
C	-2.6176371347	4.5766805916	1.9736161888
H	-2.6108627994	5.1017034639	2.9358349664
C	-1.4074196458	4.2429732997	1.3525426298

H	-0.4599778505	4.5192222272	1.8296218397
C	1.2020510026	4.5340057099	-0.6301324427
C	2.6008221175	4.4066961574	-0.5157356746
H	3.0313115419	3.4146798581	-0.3501243995
C	3.4222847696	5.5392040340	-0.6075129739
H	4.5097395953	5.4355030746	-0.5117065913
C	2.8509031620	6.8050303326	-0.8198852466
H	3.4923193948	7.6913494068	-0.8909371516
C	1.4565879037	6.9363440331	-0.9390155010
H	1.0099011104	7.9236941122	-1.1049211417
C	0.6319803646	5.8057823634	-0.8419221870
H	-0.4548077021	5.9139312611	-0.9289784515
C	-0.0872702474	2.5195732691	-2.2670987483
H	0.8914666857	2.2891024790	-2.7158924989
H	-0.5674307776	3.3350435376	-2.8306713862
H	-0.7175496738	1.6167789717	-2.2837422509

Optimized Cartesian Coordinates for **1**$^{PMe2(NEt2)}$ (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
P	-0.7824382473	2.8856478615	-0.8510158264
P	3.0979393239	-0.2913192475	-0.9198685652
P	-2.0371243788	-2.3339772815	-0.9082142693
N	-1.1252717047	1.7966038624	0.2522986581
N	2.0596486871	0.1898121375	0.1885819818
N	-1.0276898716	-1.7822776912	0.1877470100
N	0.0000000000	0.0000000000	2.2188931928
C	-1.0552870479	0.9535260927	2.5731228992
H	-0.9872163011	1.2746116349	3.6373206888
H	-2.0235932420	0.4449878949	2.4465676818
C	-1.0424673956	2.1895116316	1.6620726601
H	-1.8988121942	2.8288974493	1.9590300228
H	-0.1317607896	2.7868787120	1.8834019006
C	-0.9624354817	2.0795270484	-2.4632101172
H	-0.2502598385	1.2464058950	-2.5512849377
H	-0.7806844863	2.8080308934	-3.2686369394
H	-1.9867032308	1.6863700470	-2.5529086136
C	0.9080946954	3.5415310591	-0.7877110976
H	1.0337252269	4.1927918506	0.0916084356
H	1.1842732438	4.0951455995	-1.6985024128
H	1.5606561624	2.6592778902	-0.6644963404
N	-1.7865807440	4.2313311660	-0.7809984784
C	1.3577167964	0.4350579426	2.5566721905
H	1.6366697860	0.1579814911	3.5983460818
H	1.3819202522	1.5341724664	2.4939432889
C	2.4072913076	-0.1221905093	1.5845900675
H	3.3866083924	0.3093277302	1.8816865870
H	2.5020145550	-1.2174297178	1.7406470770

C	2.4030880716	0.1346443967	-2.5342245748
H	1.4586906452	-0.4140422843	-2.6725899075
H	3.1117331725	-0.1570136022	-3.3259087296
H	2.2083292927	1.2164519248	-2.5981022563
C	4.7029828742	0.5527126479	-0.8469574955
H	4.4925815289	1.6329911382	-0.9121767034
H	5.3706112821	0.2711910612	-1.6753863979
H	5.2020665145	0.3457908144	0.1129831965
N	3.4628692978	-1.9237846633	-0.8577924938
C	-0.2979591507	-1.4005684255	2.5282589154
H	-0.6147046797	-1.5363905190	3.5874752359
H	0.6300055444	-1.9774346756	2.3880248468
C	-1.3755432995	-1.9848326250	1.6015086257
H	-1.4760206435	-3.0603506614	1.8586503898
H	-2.3543984499	-1.5242336243	1.8478671623
C	-1.3489032380	-1.9661447719	-2.5380378370
H	-1.2652344836	-0.8746401143	-2.6470246645
H	-2.0217612603	-2.3586638858	-3.3185278854
H	-0.3544413311	-2.4218115586	-2.6508874364
C	-2.2644774372	-4.1341217859	-0.8592227537
H	-1.2721953231	-4.5926220202	-1.0019226719
H	-2.9409022778	-4.5003295998	-1.6463991343
H	-2.6571997247	-4.4320067630	0.1253794601
N	-3.5897096992	-1.6982483967	-0.7965097119
C	2.3468761205	-2.8637771769	-0.6620829719
C	4.7915350048	-2.4892171892	-1.1368259941
C	5.1885692372	-2.5412946633	-2.6160179381
H	4.7959600721	-3.5095027012	-0.7118499342
H	5.5540401480	-1.9282216382	-0.5685006109
H	4.4638442115	-3.1209452160	-3.2109883137
H	6.1828971729	-3.0116206467	-2.7265799064
H	5.2500571984	-1.5291376468	-3.0538812642
C	2.0303252854	-3.7486429224	-1.8693420303
H	1.4528456216	-2.2744891312	-0.3918291362
H	2.5762846838	-3.5026843296	0.2150534459
H	1.8203968860	-3.1405499710	-2.7670900110
H	1.1420768044	-4.3698056209	-1.6546438785
H	2.8603944697	-4.4346666804	-2.1116852046
C	-4.7359439401	-2.3386176417	-1.4708813332
C	-3.6919934051	-0.2442576821	-0.5768888374
C	-4.7183671146	0.1402595418	0.4877241618
C	-5.6289546496	-3.1518560292	-0.5318993211
C	-1.3801241825	5.5712147879	-1.2350682696
C	-3.2348777326	3.9511948695	-0.8193738985
C	-3.9964406600	4.5698450682	0.3529863196
C	-1.3333743410	5.7574733709	-2.7553679659
H	-2.0917818863	6.2922525417	-0.7946863449
H	-0.4000769062	5.8149997157	-0.7932885643
H	-2.2906296426	5.4702087970	-3.2255367678

H	-0.5330293917	5.1510595694	-3.2147857711
H	-1.1373169788	6.8157416450	-3.0057965053
H	-5.3269707033	-1.5395451567	-1.9558748776
H	-4.3807102541	-2.9799491528	-2.2987602771
H	-6.4839691821	-3.5787121236	-1.0880808217
H	-6.0251724168	-2.5223401777	0.2828588356
H	-5.0702290018	-3.9852436069	-0.0727686036
H	-3.9421467047	0.2585479940	-1.5361644899
H	-2.7015695216	0.1345680696	-0.2750569019
H	-5.7494093693	-0.1207181712	0.1897035639
H	-4.6855384080	1.2311329922	0.6619250755
H	-4.4987357401	-0.3662919657	1.4441789506
H	-3.3668091120	2.8565152151	-0.7953803974
H	-3.6603079659	4.2996857726	-1.7817387822
H	-3.6188642721	4.1774264039	1.3129449366
H	-5.0725849880	4.3298014042	0.2770584673
H	-3.8995211839	5.6699588847	0.3701214528

Optimized Cartesian Coordinates for **2**^{PMe3} (Å):

Cu	-0.0484702502	0.0236801048	0.3280766944
P	-0.7066689459	3.0778897711	-0.4089887984
P	3.1081065776	0.3340461134	-0.2817817299
P	-0.6807024380	-2.6877282671	-0.9675192382
N	-0.3213663368	1.9148776048	0.6464442420
N	1.9197207742	-0.5226630239	0.3814400846
N	-0.9246421804	-1.7152716988	0.3208444607
N	-0.0748131609	-0.1736241221	2.5324463627
C	-0.5235095026	1.1589220701	2.9748989413
H	-0.2172640091	1.3733078161	4.0182341214
H	-1.6233520065	1.1732949975	2.9321055477
C	0.0116448671	2.2516552706	2.0385865130
H	-0.4188915558	3.2210277803	2.3512926321
H	1.1071751944	2.3486537861	2.1667871144
C	-2.0588398232	4.1149890763	0.1862798773
H	-2.9256393124	3.4767205305	0.4205875046
H	-2.3294610120	4.8416718626	-0.5973564901
H	-1.7473698835	4.6638757253	1.0891620889
C	-1.2588754521	2.2894320402	-1.9265200090
H	-0.4447442478	1.6947444161	-2.3678574066
H	-1.5611381691	3.0641905689	-2.6492098041
H	-2.1172104046	1.6369145681	-1.7023825523
C	0.6382789439	4.2120390955	-0.8315635549
H	1.0218017259	4.6744497333	0.0928676663
H	0.2700405087	5.0028730174	-1.5058483330
H	1.4518540903	3.6635676408	-1.3312001748
C	1.3355168346	-0.4676259108	2.8394459753
H	1.4141874116	-1.0927931733	3.7511743023

H	1.8366969755	0.4885231190	3.0554767877
C	2.1036962260	-1.1626400702	1.6871825432
H	3.1663804800	-1.1904513390	1.9956612817
H	1.7888552605	-2.2174313146	1.6126340478
C	2.6048247116	0.7695072624	-1.9512646102
H	2.4283750216	-0.1500735431	-2.5302341048
H	3.3946011190	1.3640958678	-2.4370851022
H	1.6794839091	1.3618253733	-1.9151683053
C	4.6426684504	-0.6107630488	-0.4207451028
H	5.0204992674	-0.8653194439	0.5825277376
H	5.4012192636	-0.0070878856	-0.9457890858
H	4.4468457759	-1.5370814797	-0.9846012208
C	3.5640749989	1.8740445163	0.5580643315
H	2.6908587257	2.5424657791	0.5964049909
H	4.3896212880	2.3759148373	0.0269776555
H	3.8848657545	1.6407919116	1.5867483132
C	-1.0328513911	-1.2724864452	2.7459015029
H	-2.0412513925	-0.8317128348	2.7105824536
H	-0.9014528810	-1.7446640153	3.7405847377
C	-0.9354471518	-2.3458448743	1.6553588629
H	-0.0381266858	-2.9710421895	1.8240253152
H	-1.8059412110	-3.0228283106	1.7612890754
C	-0.7981348075	-1.6710477086	-2.4436760321
H	-1.7700512623	-1.1541043865	-2.4580468879
H	-0.7029694095	-2.3093874653	-3.3365708452
H	0.0188490685	-0.9324873536	-2.4460084723
C	-1.9258843094	-3.9863589402	-1.0728375905
H	-1.8406693127	-4.6531009099	-0.1998544638
H	-1.7616461594	-4.5738278158	-1.9911813213
H	-2.9286131550	-3.5303165491	-1.0954229890
C	0.9345366166	-3.4932282319	-0.9938449440
H	1.7054789726	-2.7078521537	-0.9274855212
H	1.0502708105	-4.0695580469	-1.9262541887
H	1.0256781956	-4.1750997044	-0.1334048868

Optimized Cartesian Coordinates for **2**$^{\mathbf{PMe3}}$ (N_{eq} – Cu – N_{eq} angle constrained to 120°) (Å):

Cu	-0.0776187509	-0.3492889701	-0.2387053344
P	2.9684999945	0.3198050762	0.5392973725
P	-1.3201515489	2.3590919992	0.8004944184
P	-1.6465128434	-2.9699511141	0.5370384107
N	1.7533839992	0.2563700676	-0.5299032728
N	-1.5351817722	0.9800074934	-0.0121497315
N	-0.5044217029	-2.2454519082	-0.3650900605
N	-0.3104499396	-0.2322479440	-2.4090914477
C	1.0617291003	0.0056165222	-2.8828882861
H	1.0752501411	0.5044456166	-3.8730348954
H	1.5526125353	-0.9735995735	-2.9951456828

C	1.8754816825	0.8381398937	-1.8730428878
H	2.9243195239	0.8777625341	-2.2220571409
H	1.5135885945	1.8853897297	-1.8776218966
C	3.3217759217	1.9632932406	1.2062428662
H	3.5536213468	2.6496790885	0.3753869870
H	4.1860442961	1.9143604962	1.8894472557
H	2.4473573896	2.3379282993	1.7611866239
C	2.5276298307	-0.7509086768	1.9136946863
H	1.6027144857	-0.3865134828	2.3870675663
H	3.3385583713	-0.7500287368	2.6593702806
H	2.3662063830	-1.7715495005	1.5326514071
C	4.5155189157	-0.2872474725	-0.1638394336
H	4.3583909734	-1.3020627986	-0.5631050769
H	5.2846086211	-0.3112132523	0.6258408503
H	4.8520777051	0.3821475039	-0.9715313806
C	-1.2335711213	0.9060674313	-2.5284056142
H	-1.8219169402	0.8605174536	-3.4678890816
H	-0.6301955535	1.8271907552	-2.5681178871
C	-2.2060844831	0.9920459658	-1.3262216543
H	-2.8315895016	1.8926320199	-1.4742676368
H	-2.8979011643	0.1298813360	-1.3616765708
C	-0.6704498178	1.9416767200	2.4236459700
H	-1.3869081746	1.2878768367	2.9445469188
H	-0.5157832331	2.8622197808	3.0088423319
H	0.2889859928	1.4144996263	2.3190943962
C	-2.8700694650	3.2504634256	1.0559261036
H	-3.2794259427	3.5762401072	0.0862302311
H	-2.6813999992	4.1393403495	1.6802665836
H	-3.5927855155	2.5868870132	1.5573559999
C	-0.1828821837	3.5620738591	0.0628720028
H	0.8106659016	3.1037292136	-0.0522314961
H	-0.1037106313	4.4584876302	0.6999399956
H	-0.5627916698	3.8550848373	-0.9294757538
C	-0.8761733402	-1.5561103263	-2.7386134978
H	-0.6686445346	-1.8385089524	-3.7910197055
H	-1.9702121254	-1.4930301445	-2.6284035820
C	-0.3459898541	-2.6423218872	-1.7835500196
H	-0.8525915653	-3.5959203228	-2.0257611542
H	0.7326108562	-2.8062861966	-1.9686894021
C	-1.6924648828	-2.1255926973	2.1199591486
H	-0.6935555757	-2.1628324422	2.5820371364
H	-2.4253738922	-2.6146909964	2.7811192465
H	-1.9854857962	-1.0777794755	1.9458469864
C	-1.2786685664	-4.7132614207	0.8244965771
H	-1.2487032662	-5.2479987181	-0.1388086262
H	-2.0599357154	-5.1589896654	1.4622965295
H	-0.2978875826	-4.7960852883	1.3201223992
C	-3.3106474666	-2.8999503185	-0.1675876660
H	-3.6162727211	-1.8463410695	-0.2697199364

H	-4.0203444100	-3.4253279189	0.4929113598
H	-3.3154093130	-3.3837806518	-1.1578028298

Optimized Cartesian Coordinates for $^{Me3}P_3$tren-Cu^{II}-MeCN (Å):

Cu	-0.0330565712	-0.0544296985	0.0826521129
P	3.2019237923	0.2931609877	0.4561905504
P	-2.0974584479	2.2669481846	0.9041370530
P	-1.3308593724	-3.0455317013	0.4195205148
N	1.8455554014	0.7765180382	-0.2422254763
N	-1.8735781896	0.9636760842	-0.0070483736
N	-0.1524606369	-2.1731575461	-0.2279508880
N	-0.1482619848	0.0515866373	-2.0592935481
C	1.1737090729	0.5306316263	-2.5506226584
H	1.0439847782	1.0057647929	-3.5419077513
H	1.8311449554	-0.3432472322	-2.6705867847
C	1.7947469369	1.4693566857	-1.5237292034
H	2.7835610088	1.7972806222	-1.8922672206
H	1.1847204967	2.3894325446	-1.4332583118
C	4.6651859606	0.4587961292	-0.5950401586
H	4.5229420326	-0.1100821344	-1.5279541739
H	5.5358726461	0.0556506362	-0.0521829832
H	4.8514121917	1.5187137225	-0.8303210545
C	3.5938078638	1.2179386447	1.9655076485
H	3.7490320063	2.2764661047	1.6985708906
H	4.5032371167	0.8189934240	2.4448639767
H	2.7502727031	1.1529544459	2.6688016595
C	3.1238110486	-1.4474803106	0.9343012880
H	2.2035539587	-1.6390139032	1.5032104912
H	4.0051237930	-1.7154371160	1.5393414237
H	3.0962652384	-2.0602046817	0.0197884565
C	-1.2345734714	1.0192159984	-2.3679222703
H	-1.5667860166	0.8742337425	-3.4145288433
H	-0.8166054173	2.0337872168	-2.2788128988
C	-2.3780747070	0.8628631012	-1.3742166216
H	-3.1544046387	1.6113325636	-1.6146478688
H	-2.8616725266	-0.1212445950	-1.5153368936
C	-2.7227455458	1.8140789741	2.5383418301
H	-3.7197702637	1.3597747932	2.4174342296
H	-2.7943831103	2.7049601514	3.1837616968
H	-2.0509853697	1.0779571418	3.0016506413
C	-3.2949944059	3.4415870239	0.2280219309
H	-2.9333789384	3.8468118294	-0.7305554032
H	-3.4145040117	4.2699875159	0.9453925546
H	-4.2688268283	2.9478313463	0.0802336276
C	-0.5844116816	3.2244637136	1.1848338907
H	0.2051309968	2.5626789550	1.5712840807
H	-0.7678987504	4.0441765059	1.8987514376

H	-0.2525272171	3.6412865474	0.2202317167
C	-0.4565219136	-1.3275107453	-2.5250600345
H	-0.1525880155	-1.4296428192	-3.5848945515
H	-1.5452643945	-1.4709925291	-2.4723702926
C	0.2298318855	-2.3561137232	-1.6282442102
H	0.0036462118	-3.3649020926	-2.0229920093
H	1.3274189655	-2.2390430566	-1.7121287327
C	-1.1841500066	-3.0303477734	2.2179329541
H	-0.1444858107	-3.2472242152	2.5080353569
H	-1.8562138038	-3.7954544972	2.6388218286
H	-1.4860580534	-2.0463996721	2.6032554376
C	-1.3043879039	-4.7850041007	-0.0894295892
H	-1.5107905184	-4.8704569817	-1.1683169956
H	-2.0827909575	-5.3362340294	0.4631176163
H	-0.3156306008	-5.2194845032	0.1307274782
C	-3.0293570415	-2.4804150312	0.1058988577
H	-3.0981854633	-1.4226485487	0.4117527460
H	-3.7527648614	-3.0832320378	0.6802621116
H	-3.2582710573	-2.5683103703	-0.9685397125
N	0.1726918123	-0.0650980556	2.0803023529
C	0.3750226800	-0.1144815498	3.2184271227
C	0.6136742425	-0.1946069850	4.6437346256
H	0.5274639368	-1.2438897334	4.9755487652
H	-0.1303536780	0.4182458925	5.1814349918
H	1.6257684504	0.1774596461	4.8790495664

Optimized Cartesian Coordinates for **2**^{PMe2Ph} (Å):

Cu	-0.0823813737	0.4028147951	-0.1812367265
P	-1.0865999327	3.1832205542	-0.6458326821
P	2.8404819335	-0.2780772201	-1.2517477212
P	-2.0011391614	-2.0244092639	-1.1278498012
N	-1.5217358356	1.7320671276	-0.0620921943
N	1.8383802135	0.2504197604	-0.0812394456
N	-1.0407872037	-1.4010486156	0.0127478771
N	-0.0600764468	0.4355336975	2.0258406916
C	-1.0910281916	1.4246189970	2.3949540899
H	-0.5834641482	2.3815963607	2.5830204722
H	-1.6002217962	1.1329587880	3.3339017670
C	-2.1318427193	1.6156880847	1.2737870051
H	-2.8251841357	0.7592544293	1.2451162998
H	-2.7565444698	2.4958398401	1.5162739335
C	-2.4157566384	4.3944619376	-0.5159302497
H	-3.3067499004	3.9890917193	-1.0225799546
H	-2.0985010518	5.3280305169	-1.0081672980
H	-2.6632946876	4.6082880383	0.5346366491
C	-0.7375776737	2.9646931911	-2.3945013905
H	0.0481070036	2.2112233718	-2.5454395182

H	-0.4099378893	3.9200314172	-2.8335416320
H	-1.6606262720	2.6232508413	-2.8890103955
C	0.3812774166	3.8841844294	0.1498498380
C	0.2483958587	4.5720357709	1.3760932017
H	-0.7423722879	4.8161096249	1.7737685259
C	1.3871474746	4.9368546998	2.1071507788
H	1.2736996427	5.4642127342	3.0609007854
C	2.6676660394	4.6256886422	1.6190559198
H	3.5571498339	4.9080022211	2.1935091923
C	2.8068846834	3.9598414709	0.3908775752
H	3.8051400818	3.7315556053	0.0009563609
C	1.6705622765	3.5866552035	-0.3399119805
H	1.7956316214	3.0601512066	-1.2889345566
C	1.3367174710	0.8335429975	2.2725644060
H	1.6538758299	0.6346127596	3.3162128101
H	1.4022623532	1.9180397425	2.0961962805
C	2.3011676242	0.1236873143	1.3134447344
H	3.3051077683	0.5689089830	1.4479429585
H	2.3994389482	-0.9440457951	1.5937360544
C	2.2042419243	0.2775629257	-2.8381800934
H	1.1669065352	-0.0642647781	-2.9685517694
H	2.8216162262	-0.1553112537	-3.6415431201
H	2.2549310668	1.3762103728	-2.8949538050
C	4.5072595007	0.3909292588	-1.0857510661
H	4.4343105922	1.4836133063	-0.9663631082
H	5.0911337040	0.1683363295	-1.9929223854
H	5.0101819020	-0.0491310127	-0.2111087952
C	2.9685624732	-2.0801979163	-1.2992862414
C	1.9374422387	-2.8509945446	-0.7211069329
H	1.0740174586	-2.3573571629	-0.2594998285
C	2.0125083660	-4.2509420387	-0.7609049813
H	1.2199244430	-4.8523268291	-0.3007668357
C	3.1032770042	-4.8839002945	-1.3791655029
H	3.1578708546	-5.9782422360	-1.4070764425
C	4.1266795238	-4.1158045458	-1.9595768657
H	4.9787573244	-4.6076283396	-2.4423111112
C	4.0654777368	-2.7156291851	-1.9188545827
H	4.8719598627	-2.1287998706	-2.3708755587
C	-0.3820068001	-0.9588655169	2.3612843148
H	-0.7495233430	-1.0385995741	3.4037942474
H	0.5457498357	-1.5467800970	2.2943912678
C	-1.4241346839	-1.5853245221	1.4163208844
H	-1.4731534297	-2.6619220145	1.6761565301
H	-2.4309605077	-1.1734694723	1.6298992313
C	-1.3452835020	-1.5119983137	-2.7219518806
H	-1.3873022750	-0.4155132551	-2.8102604686
H	-1.9449518352	-1.9618657806	-3.5287233860
H	-0.3036233286	-1.8622125194	-2.8020982288
C	-1.9886204316	-3.8307431130	-1.1223993011

H	-0.9529734813	-4.1593992366	-1.3020594934
H	-2.6362207643	-4.2213860327	-1.9236445766
H	-2.3287373706	-4.2187889136	-0.1495086755
C	-3.7272438281	-1.4896343792	-1.0275354903
C	-3.9905271899	-0.1047839719	-1.1164854260
H	-3.1626707074	0.6031682217	-1.2440051452
C	-5.3029487306	0.3691397916	-0.9971114919
H	-5.5016621948	1.4453206042	-1.0655060394
C	-6.3607762205	-0.5316775791	-0.7835034284
H	-7.3873659538	-0.1592690348	-0.6879574247
C	-6.1021169207	-1.9083171753	-0.6874454620
H	-6.9243805583	-2.6125383875	-0.5165415488
C	-4.7895424879	-2.3905982419	-0.8085831221
H	-4.6061742867	-3.4663096509	-0.7300195210

Optimized Cartesian Coordinates for **2**^{PMePh2} (Å):

Cu	3.6155958609	4.0459803876	5.5981674321
P	1.5755633923	1.6015035112	5.5563971609
P	6.6700047173	4.1722671029	5.0683030767
P	3.0903877193	4.9145216570	8.6718186770
N	1.8944133638	3.1824754898	5.4902924880
N	5.1695306630	4.5553316904	4.5615172690
N	3.7863460777	5.2305445002	7.2534110037
N	2.6193894329	5.7420756522	4.5706815870
C	1.2846970607	5.2117000920	4.2400813421
H	1.3531549959	4.7248064163	3.2559081574
H	0.5308752249	6.0193791001	4.1616945475
C	0.8261107591	4.1695621324	5.2728882220
H	0.5671789178	4.6640522550	6.2266286407
H	-0.1043570969	3.7000036316	4.9033892170
C	0.7510472244	1.0494257683	4.0463276255
C	1.1359075733	1.6539285810	2.8300693289
H	1.8807387267	2.4569682345	2.8315369206
C	0.5704826102	1.2209460130	1.6237402764
H	0.8687513588	1.6947538765	0.6817616919
C	-0.3754538487	0.1814641013	1.6253515591
H	-0.8199785184	-0.1543062410	0.6813492331
C	-0.7496009998	-0.4308416953	2.8327744000
H	-1.4824025839	-1.2456203197	2.8332963826
C	-0.1886019684	-0.0015470671	4.0445148927
H	-0.4807109567	-0.4856453983	4.9816032485
C	0.5559073965	1.0755851625	6.9502591681
C	1.1244260717	0.4280626934	8.0676545389
H	2.1797129788	0.1397130745	8.0731974838
C	0.3333900402	0.1421118476	9.1901121335
H	0.7826689616	-0.3551377001	10.0569116210
C	-1.0291532171	0.4813834293	9.1969500518

H	-1.6465672792	0.2514589999	10.0726184595
C	-1.6030045991	1.1104659097	8.0793385178
H	-2.6680823495	1.3672790070	8.0783330884
C	-0.8145139733	1.4181813045	6.9639628286
H	-1.2689757793	1.9211155044	6.1040699260
C	3.1537749476	0.7420296589	5.6433390773
C	3.5138652256	5.9711926776	3.4229697729
H	3.3590674886	6.9729892198	2.9738442230
H	3.2666159876	5.2141344358	2.6623631941
C	4.9845546930	5.8105583176	3.8125757119
H	5.5992718213	5.8156519268	2.8913537885
H	5.3085642781	6.6867720171	4.4031932377
C	7.7605009833	3.9384513152	3.6509832294
C	9.1415009375	4.2106392320	3.7268981776
H	9.5751903496	4.6202741378	4.6451467010
C	9.9605434689	3.9561653858	2.6174405430
H	11.0340116217	4.1688135390	2.6749580877
C	9.4061730382	3.4341744534	1.4368720310
H	10.0494636252	3.2405512235	0.5706938061
C	8.0297075596	3.1600821832	1.3619252458
H	7.5979520244	2.7533013908	0.4404859179
C	7.2044293411	3.4082387173	2.4666754341
H	6.1302181105	3.1973988093	2.4151696839
C	7.4407506817	5.3840721363	6.1571049419
C	7.6436525950	5.1146847727	7.5261890409
H	7.3778457770	4.1437487544	7.9528161690
C	8.1990508808	6.0976099224	8.3577380084
H	8.3645424831	5.8772269769	9.4177787612
C	8.5303047661	7.3584086091	7.8373425917
H	8.9560960371	8.1268764853	8.4925886386
C	8.3260498558	7.6331380475	6.4744072441
H	8.5935942190	8.6127688411	6.0630782315
C	7.7930590105	6.6486649132	5.6320841356
H	7.6741121538	6.8594865999	4.5643113619
C	6.5507512565	2.6049969635	5.9394126987
C	2.6289214060	6.7769131397	5.6197001821
H	1.6520800946	6.7502856136	6.1254655756
H	2.7413625791	7.7828036881	5.1699483310
C	3.7314712104	6.5856315872	6.6963579045
H	4.7227651598	6.8215758555	6.2745671914
H	3.5464369011	7.3512495238	7.4728639513
C	1.3098215375	5.2255795820	8.8043767229
C	0.3607754150	4.1858157474	8.8672367468
H	0.6767409136	3.1402673934	8.9108472353
C	-1.0094352126	4.4881756993	8.8711243776
H	-1.7407369813	3.6763844084	8.9275799280
C	-1.4414356591	5.8209598661	8.8002449187
H	-2.5132486379	6.0498442974	8.7965040647
C	-0.4992730592	6.8626510203	8.7451101621

H	-0.8312266556	7.9061087742	8.7015674771
C	0.8691896646	6.5682405315	8.7581669442
H	1.5959154923	7.3876266326	8.7399348190
C	3.8290844323	5.8982239839	9.9991908534
C	3.1708391021	6.0284564398	11.2400193608
H	2.1866452080	5.5722783096	11.3946355177
C	3.7774190128	6.7500010154	12.2775248779
H	3.2665198016	6.8487317958	13.2421066933
C	5.0326272316	7.3508341207	12.0783492844
H	5.5005950816	7.9210647273	12.8891955557
C	5.6862332428	7.2245135893	10.8416505449
H	6.6630256912	7.6959491237	10.6843954009
C	5.0888943294	6.4960587308	9.8032219865
H	5.5974034481	6.3884959932	8.8416527471
C	3.3797959013	3.1795715174	9.0385062063
H	3.7157751565	0.9786605958	4.7262326559
H	2.9787579878	-0.3443178721	5.6838379627
H	3.7336608261	1.0529081680	6.5252818515
H	7.5530599555	2.2820410517	6.2607561813
H	6.1411180009	1.8593583640	5.2414169939
H	5.8930140983	2.7018591590	6.8175769324
H	2.8771238939	2.5568989836	8.2862366562
H	2.9927919992	2.9338684697	10.0390956079
H	4.4649782550	2.9978700046	9.0118777121

Optimized Cartesian Coordinates for **2**$^{PMe2(NEt2)}$ (Å):

Cu	0.0758510021	-0.1311141432	0.0766203337
P	-0.6592576803	2.8246356804	-1.0112748080
P	3.0914318513	-0.3122159713	-0.8686691323
P	-2.1508919735	-2.2162992763	-0.9019549860
N	-0.8980318385	1.7035944930	0.1213972515
N	2.0217570335	0.0832585762	0.2727864434
N	-1.1706326856	-1.6177067463	0.2473594407
N	0.0075624666	-0.0511891860	2.2580171705
C	-0.9659430042	1.0207453273	2.5081608674
H	-0.8798968884	1.4076482568	3.5432854901
H	-1.9771843260	0.6021539059	2.3952067263
C	-0.7931424077	2.1751049803	1.5134394421
H	-1.5815102630	2.9182466511	1.7337582879
H	0.1711483132	2.6863043594	1.7094116039
C	-0.8752330892	2.0217948918	-2.6130383393
H	-0.1385837094	1.2226625062	-2.7670474075
H	-0.7550335025	2.7731370634	-3.4087819014
H	-1.8905939458	1.6012182347	-2.6718963369
C	0.9902345144	3.5635008266	-0.9858583852
H	1.1097321244	4.2008074598	-0.0964590180
H	1.2014752868	4.1492635836	-1.8929861591

H	1.7046251253	2.7287574889	-0.9046044024
N	-1.7369589956	4.0822477323	-0.8594129116
C	1.3924544984	0.2741423416	2.6514326921
H	1.6116632530	-0.0861227284	3.6758560401
H	1.4936656289	1.3690379978	2.6541809207
C	2.3903339804	-0.3110472676	1.6569647025
H	3.4000366445	0.0521295371	1.9266060068
H	2.4176068900	-1.4139269129	1.7591477287
C	2.3839662315	0.1478957356	-2.4619671447
H	1.4522338084	-0.4121640388	-2.6339607141
H	3.1009674739	-0.1185038527	-3.2541715232
H	2.1862988529	1.2289085483	-2.5074583214
C	4.6377593923	0.6018370719	-0.7132827657
H	4.3772381271	1.6726053680	-0.7253950014
H	5.3235013138	0.3919805884	-1.5474377815
H	5.1331207557	0.3642052653	0.2406252562
N	3.4961315208	-1.9247656175	-0.8377928216
C	-0.4434010699	-1.4094942965	2.5951350236
H	-0.7936600406	-1.4788218985	3.6448770731
H	0.4197783943	-2.0840195033	2.4820735869
C	-1.5589458408	-1.8606254059	1.6475767550
H	-1.7641259291	-2.9321745242	1.8318874048
H	-2.4978972057	-1.3274997728	1.8897130125
C	-1.4064412171	-1.8069708879	-2.4888224791
H	-1.3285500847	-0.7152303959	-2.5869139049
H	-2.0558193098	-2.1871021128	-3.2941308161
H	-0.4106698959	-2.2652070464	-2.5839964811
C	-2.2516714728	-4.0119283431	-0.8236495320
H	-1.2253008440	-4.4030282888	-0.9151464253
H	-2.8612710333	-4.4117523887	-1.6482324833
H	-2.6766271050	-4.3313956686	0.1392561291
N	-3.6913615063	-1.6193203885	-0.7747066769
C	2.4079051513	-2.9120415529	-0.7284327772
C	4.8539914744	-2.4336349193	-1.1140124195
C	5.2771546382	-2.3995382115	-2.5848698823
H	4.8789464415	-3.4706953709	-0.7358401268
H	5.5795084861	-1.8726041458	-0.5006756527
H	4.5831744410	-2.9710034992	-3.2224234381
H	6.2863163786	-2.8357174116	-2.6946030300
H	5.3198623745	-1.3662344306	-2.9723272028
C	2.0739933215	-3.6602934166	-2.0200948480
H	1.5105330301	-2.3802077230	-0.3666265339
H	2.6790421216	-3.6333225244	0.0658187906
H	1.8353638753	-2.9627097811	-2.8419617597
H	1.2023285545	-4.3190565449	-1.8555138887
H	2.9102532878	-4.2991089227	-2.3503673956
C	-4.8472455310	-2.3319638615	-1.3682781152
C	-3.8272708172	-0.1573171698	-0.5982685929
C	-4.8364140411	0.2258074582	0.4814879989

C	-5.6514829396	-3.1412265274	-0.3522452930
C	-1.3983441114	5.4787048236	-1.1974987005
C	-3.1738609042	3.7361994711	-0.9075473655
C	-3.9535157357	4.2295920877	0.3098701277
C	-1.3737810404	5.7817065661	-2.6971306069
H	-2.1445167183	6.1180928218	-0.6953742933
H	-0.4316031944	5.7343425168	-0.7358585716
H	-2.3266151200	5.5031845462	-3.1805189504
H	-0.5596637573	5.2390735822	-3.2091586505
H	-1.2130780014	6.8617865911	-2.8634254068
H	-5.4871411757	-1.5697956753	-1.8470329026
H	-4.5039141819	-2.9846121263	-2.1911007351
H	-6.5212948755	-3.6104757140	-0.8463523531
H	-6.0205415860	-2.4993022692	0.4650385300
H	-5.0410501682	-3.9436016224	0.0954461491
H	-4.1130984745	0.3000253382	-1.5674143853
H	-2.8370902691	0.2515203963	-0.3323926969
H	-5.8604977732	-0.0900278071	0.2191206974
H	-4.8489967460	1.3222607264	0.6089191743
H	-4.5711335954	-0.2313051470	1.4505570547
H	-3.2589334333	2.6399134417	-0.9719640349
H	-3.6161025058	4.1386767047	-1.8388249887
H	-3.5789623904	3.7642189868	1.2374744614
H	-5.0223318603	3.9736728460	0.1999625547
H	-3.8834362863	5.3253949778	0.4227126201

Optimized Cartesian Coordinates for **3**^{PMe3} (Å):

Cu	0.0421707362	0.1902666936	-0.1916120421
Cl	0.0006971938	0.2562934857	-2.5757412067
P	0.6860868752	3.3322509370	-0.6398129533
P	2.4214361669	-1.9247194840	-0.8170388888
P	-3.0009675900	-0.8265122052	-0.7088450327
N	-0.1779996119	2.2491363073	0.1533252359
N	1.9502559569	-0.6647649234	0.0419903379
N	-1.6357686607	-1.0496644720	0.0865417186
N	0.0758044796	0.1261948334	2.0075781276
C	0.1239625306	1.5373702885	2.4631760027
H	1.1753039817	1.8641333432	2.4524562163
H	-0.2454652160	1.6060724738	3.5062686137
C	-0.6702477948	2.4273381444	1.5089936745
H	-1.7435508468	2.1530049604	1.5552950044
H	-0.6101297870	3.4702794613	1.8737651188
C	0.9912564310	4.8578708497	0.2919783863
H	0.0380648765	5.3533235936	0.5378301833
H	1.5980280860	5.5374641066	-0.3288770530
H	1.5401169892	4.6316430542	1.2206416530
C	2.3168766961	2.7089614735	-1.1156398026

H	2.9013123497	2.5182802201	-0.2016413027
H	2.8422911495	3.4395483904	-1.7527989532
H	2.1794656952	1.7596803300	-1.6555120678
C	-0.1084319725	3.8504678375	-2.1810868239
H	-0.2849848770	2.9484692154	-2.7887002929
H	0.5315443038	4.5591992947	-2.7331292314
H	-1.0733837771	4.3268229793	-1.9407471275
C	1.2925844518	-0.6338773137	2.3864194192
H	1.0472845504	-1.7067376660	2.3578940315
H	1.5854214336	-0.3767857647	3.4243843268
C	2.4153527149	-0.3671344714	1.3858652607
H	2.7208555731	0.6969791947	1.4488926508
H	3.3024355476	-0.9529682016	1.6930910737
C	3.6432777917	-2.9731557270	0.0179224758
H	4.5559353712	-2.3961576231	0.2384522219
H	3.9032065381	-3.8134511726	-0.6468322239
H	3.2232404130	-3.3723752171	0.9554687855
C	3.1826056415	-1.4397851746	-2.3858149441
H	2.4569696688	-0.8169859170	-2.9331288153
H	3.4471463787	-2.3276164669	-2.9844414019
H	4.0886016912	-0.8483681010	-2.1732659003
C	1.0496734981	-3.0198201994	-1.2572037076
H	0.6524020782	-3.4747319039	-0.3359051706
H	1.3869857092	-3.8084659195	-1.9500517107
H	0.2600300595	-2.4120237107	-1.7247577768
C	-1.1718784647	-0.5601264695	2.4244722111
H	-1.9798694881	0.1871488074	2.4502872019
H	-1.0488752336	-0.9688480518	3.4477152178
C	-1.5451580524	-1.6400452477	1.4107596326
H	-0.7719185091	-2.4347547771	1.4151575971
H	-2.4789203467	-2.1276041062	1.7494246694
C	-4.4764994888	-1.3840706408	0.1866386804
H	-4.4193989584	-2.4671917859	0.3818547967
H	-5.3659233921	-1.1784307748	-0.4315170579
H	-4.5679515631	-0.8412056987	1.1414699434
C	-3.0305846742	-1.7038946960	-2.2919779856
H	-2.1608817365	-1.3692641776	-2.8797681483
H	-3.9630908000	-1.4904278371	-2.8410603238
H	-2.9496520791	-2.7865828266	-2.0993482813
C	-3.2932841280	0.9140806619	-1.1081237081
H	-3.4402970880	1.4707401921	-0.1689823133
H	-4.1819160921	1.0223177918	-1.7518838688
H	-2.4005473979	1.3048437266	-1.6200019633

Optimized Cartesian Coordinates for ^{H}TMPA-Cu^{I}-MeCN (Å):

Cu	-0.1651443012	0.0155098571	-0.1076789835
N	0.2320441049	-0.0328767818	2.3461574612

N	-0.9619948840	1.8444778754	0.6475481982
N	1.9445046388	-0.1327868348	0.1341875792
N	-1.2030785943	-1.7020252497	0.6161580296
C	0.3064881993	1.3775148235	2.6888963386
C	1.4836425138	-0.7632138020	2.4554300325
C	-0.9401211195	-0.7310876901	2.8474088844
C	-1.8258297418	2.5773958470	-0.0793173071
C	-0.7233908579	2.1959331364	1.9308536575
C	2.7804948407	0.1593664891	-0.8797172362
C	2.4606900377	-0.3732161750	1.3602502051
C	-1.5906169924	-2.6819463103	-0.2212115811
C	-1.3291845066	-1.8912088696	1.9487908037
H	1.3072918747	1.7422252911	2.3929815364
H	0.2099775567	1.5692157205	3.7785499922
H	1.2573042478	-1.8384725819	2.3336467587
H	1.9707620391	-0.6535535588	3.4474656642
H	-1.7816620822	-0.0142123965	2.8492566535
H	-0.8252919348	-1.0872209742	3.8930627969
C	-2.4991229147	3.6911782168	0.4336841836
H	-1.9806921595	2.2497423364	-1.1138935340
C	-1.3661076868	3.2922275062	2.5244690576
C	4.1687919761	0.2325736497	-0.7247344545
C	3.8406935403	-0.3078094848	1.6022584523
C	-2.1161286868	-3.8998411908	0.2233843108
H	-1.4688957684	-2.4750531039	-1.2908471460
C	-1.8357405374	-3.0878424887	2.4765869251
C	-2.2659796225	4.0548578299	1.7676225620
H	-3.1940226810	4.2523912258	-0.1998105087
H	-1.1592171288	3.5396196654	3.5715649986
C	4.7108539466	-0.0033393699	0.5467060396
H	4.2230548018	-0.4940863001	2.6119904795
C	-2.2381718014	-4.1085674487	1.6044922648
H	-2.4146830740	-4.6658277107	-0.5000239822
H	-1.9105872669	-3.2123783569	3.5625379473
H	-2.7795322654	4.9140738418	2.2136504845
H	5.7921020699	0.0537136158	0.7156395250
H	-2.6351414341	-5.0515186432	1.9971537853
H	4.8047601310	0.4761773178	-1.5822725386
H	2.3092981933	0.3431384132	-1.8522869289
N	-0.4938318993	0.0586398788	-2.0609691750
C	-0.6830128489	0.0834279355	-3.2070826217
C	-0.9206224192	0.1150059102	-4.6397234986
H	-1.6049841704	0.9442523045	-4.8897299058
H	-1.3745947307	-0.8362575723	-4.9675032495
H	0.0325593984	0.2617642065	-5.1767029566

Optimized Cartesian Coordinates for ^{H}TMPA-Cu^{I} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	0.0000000000	-0.0000000000	2.2383165214
N	-0.8726921066	1.8062782575	0.2638755770
N	2.0047226797	-0.1399878644	0.2710834182
N	-1.1148514818	-1.6694527241	0.2674393148
C	-0.0362169798	1.4272603076	2.5475732949
C	1.2536914798	-0.6812723720	2.5508240012
C	-1.2182123574	-0.7457680825	2.5453279703
C	-1.5576228477	2.5190418588	-0.6537201508
C	-0.8917743156	2.2087456075	1.5615432449
C	2.9655301219	0.1056467508	-0.6429187474
C	2.3601963200	-0.3243899073	1.5693443210
C	-1.3715334520	-2.6286123340	-0.6452621367
C	-1.4517099254	-1.8864133889	1.5660035197
H	0.9977133181	1.8088279024	2.4628298046
H	-0.3682428553	1.6382876839	3.5837277884
H	1.0708441644	-1.7679720074	2.4635371349
H	1.5986481999	-0.5009316942	3.5885261325
H	-2.0681812054	-0.0456624847	2.4485371661
H	-1.2406597439	-1.1310509921	3.5844248406
C	-2.2983262824	3.6591486193	-0.3270341400
H	-1.5094419749	2.1529002591	-1.6847426376
C	-1.6239309603	3.3322684203	1.9653206387
C	4.3217281882	0.1864538055	-0.3117058821
C	3.6972771733	-0.2433063179	1.9778652435
C	-1.9661845408	-3.8496988417	-0.3124321668
H	-1.0833213683	-2.4033648716	-1.6774470167
C	-2.0372228989	-3.0906116703	1.9756893312
C	-2.3369501889	4.0725031665	1.0114988330
H	-2.8380797402	4.2018320341	-1.1098394544
H	-1.6304204208	3.6210716658	3.0218874561
C	4.6960168528	0.0127950198	1.0276241594
H	3.9486099001	-0.3826368679	3.0348291021
C	-2.3023781951	-4.0885049386	1.0269307335
H	-2.1522667887	-4.5962652953	-1.0913693895
H	-2.2828669565	-3.2394812302	3.0325217310
H	-2.9155968570	4.9534074242	1.3109167352
H	5.7468331719	0.0790653623	1.3302133860
H	-2.7596138499	-5.0366220311	1.3309778467
H	5.0627251989	0.3888663837	-1.0918616516
H	2.6269563629	0.2446854803	-1.6750765751

Optimized Cartesian Coordinates for ^{H}TMPA-Cu^{II}-MeCN (Å):

Cu	-0.1293692752	0.0088675687	0.1316781633
N	0.2077813213	-0.0322523898	2.1840488671
N	-1.0435105115	1.8121140637	0.6511761757
N	1.9581711882	-0.0475159266	0.1215959119

N	-1.1399937892	-1.7589611544	0.5973220670
C	0.3075933665	1.3873410073	2.6068276964
C	1.4768354876	-0.7792949582	2.3718001267
C	-0.9632233827	-0.7281731578	2.7738874652
C	-1.9261361599	2.5096303450	-0.0816480668
C	-0.7369558360	2.2148012770	1.9051902692
C	2.7692451730	0.2809988162	-0.8966543074
C	2.4809834720	-0.3720375978	1.3257374830
C	-1.4954718527	-2.7339518800	-0.2545711086
C	-1.3488144741	-1.9107401537	1.9247261544
H	1.3090192514	1.7517200688	2.3213536513
H	0.2272646176	1.4648496024	3.7047611281
H	1.2530365916	-1.8536948109	2.2587277763
H	1.8613099641	-0.6272138617	3.3950292844
H	-1.8017075609	-0.0115010008	2.7975901981
H	-0.7480172926	-1.0204585253	3.8161096583
C	-2.5469621608	3.6620607350	0.4100232748
H	-2.1371143792	2.1289564458	-1.0856882629
C	-1.3256465881	3.3487053619	2.4731798909
C	4.1606159636	0.2942715358	-0.7578041944
C	3.8613111270	-0.3684420616	1.5482277814
C	-2.0907516049	-3.9196630631	0.1870450354
H	-1.2941470441	-2.5540563294	-1.3150497949
C	-1.9259856101	-3.0727295104	2.4457677865
C	-2.2422274824	4.0865214417	1.7104857731
H	-3.2589859655	4.2070107609	-0.2172288257
H	-1.0686137741	3.6454635121	3.4947281415
C	4.7146148233	-0.0341222227	0.4869656471
H	4.2572039590	-0.6232642696	2.5361605193
C	-2.3073022834	-4.0915125383	1.5610122775
H	-2.3703615469	-4.6912875715	-0.5367057092
H	-2.0724180996	-3.1744477512	3.5255270902
H	-2.7171038659	4.9793365310	2.1311656059
H	5.7999115870	-0.0245921429	0.6340760372
H	-2.7625609416	-5.0115911470	1.9428399198
H	4.7906687939	0.5640266428	-1.6108341956
H	2.2851548958	0.5398776222	-1.8433252411
N	-0.4484407893	0.0463575320	-1.8066678432
C	-0.6336977063	0.0712351173	-2.9474686055
C	-0.8650853657	0.1031605826	-4.3749605154
H	-1.2939121178	-0.8597894041	-4.7009445945
H	0.0900267122	0.2754988582	-4.8998216466
H	-1.5684308343	0.9182480005	-4.6165039451

Optimized Cartesian Coordinates for ^{H}TMPA-Cu^{II} (Å):

Cu	-0.0323163202	-0.0217410555	0.2565753581
N	0.3319453826	-0.0393528636	2.2807658105

N	-0.9204696469	1.7518377550	0.6328912024
N	1.9818386491	-0.0929157388	0.0953771795
N	-1.0428777367	-1.7313878743	0.6258809185
C	0.3974422447	1.3991103924	2.6374630963
C	1.6208650571	-0.7640108179	2.3977348676
C	-0.8363537312	-0.7625418422	2.8393729914
C	-1.7909156774	2.4249542299	-0.1393899439
C	-0.6447574071	2.1898276829	1.8864197619
C	2.7427924711	0.2078324292	-0.9712555155
C	2.5643201849	-0.3716040325	1.2878846117
C	-1.4158649104	-2.6825518121	-0.2478230062
C	-1.2265387557	-1.9214869627	1.9560776053
H	1.4017626995	1.7650147749	2.3655044734
H	0.2876584158	1.5081097392	3.7303314744
H	1.4048065206	-1.8435578842	2.3310684216
H	2.0567253775	-0.5728526387	3.3937229974
H	-1.6745918823	-0.0480745002	2.8992736999
H	-0.6041459946	-1.0899625072	3.8677003511
C	-2.4261418741	3.5868288334	0.3088375274
H	-1.9769772536	2.0173561953	-1.1381568972
C	-1.2537093604	3.3327666611	2.4090663903
C	4.1385330029	0.2345983070	-0.8954008971
C	3.9518412150	-0.3473865973	1.4447004925
C	-2.0059101533	-3.8779016776	0.1734394095
H	-1.2346959247	-2.4734557410	-1.3069528656
C	-1.7933921683	-3.0971729351	2.4526988372
C	-2.1548879392	4.0456651157	1.6046009837
H	-3.1235038764	4.1128893089	-0.3498930098
H	-1.0238436033	3.6576335039	3.4283191160
C	4.7518295182	-0.0447055122	0.3330190601
H	4.3959989807	-0.5632128776	2.4211240880
C	-2.1947463546	-4.0889482901	1.5456439265
H	-2.3035385329	-4.6267091131	-0.5666178103
H	-1.9183616296	-3.2311090897	3.5314496482
H	-2.6438702704	4.9463262452	1.9905088313
H	5.8424237451	-0.0214788251	0.4294018194
H	-2.6439899290	-5.0188913992	1.9097877554
H	4.7261406708	0.4765171873	-1.7860070725
H	2.2139567967	0.4304042265	-1.9035156885

Optimized Cartesian Coordinates for ^{tBu}TMPA-Cu^{I}-MeCN (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-0.0000000000	0.0000000000	2.5011703824
N	-1.0689086968	-1.7503142230	0.5907354318
N	-0.9873306797	1.7899316447	0.5846002852
N	2.0456200117	-0.0559050696	0.5876452952
C	-1.2024309206	-0.7499302500	2.8214751227

C	-0.0486691148	1.4178428352	2.8144071441
C	1.2504727178	-0.6662586836	2.8210465124
C	-1.2774398307	-2.7670554200	-0.2619405513
C	-1.3871118378	-1.9367828143	1.8922057357
C	-1.7700385992	2.4706526100	-0.2687002953
C	-0.9902502973	2.1630622558	1.8851074693
C	3.0300734286	0.2596620697	-0.2702386410
C	2.3700570407	-0.2404012622	1.8877518357
H	-2.0664385321	-0.0748137046	2.6810537157
H	-1.2370197602	-1.0922946041	3.8776855091
H	0.9665651265	1.8292070784	2.6654576339
H	-0.3234020116	1.6243551295	3.8707504997
H	1.0953864451	-1.7521631376	2.6834676364
H	1.5671106956	-0.5231921959	3.8763211400
C	-1.7971356205	-4.0060580337	0.1285803715
H	-1.0108196321	-2.5785092548	-1.3087919559
C	-1.8981051951	-3.1511447533	2.3593328929
C	-2.5914704385	3.5342856180	0.1202023748
H	-1.7397166112	2.1432448615	-1.3147722632
C	-1.7930005081	3.2086052908	2.3502475580
C	4.3670068847	0.4096533354	0.1132035735
H	2.7300328788	0.4003843966	-1.3154507756
C	3.6814390857	-0.0909402934	2.3486743995
C	-2.1211593968	-4.2316269038	1.4796506198
H	-1.9335036043	-4.7781258598	-0.6323873026
H	-2.1196128849	-3.2438931773	3.4275790827
C	-2.6257806534	3.9318751793	1.4700144124
H	-1.7618861307	3.4510548341	3.4176370527
C	4.7292023324	0.2373872684	1.4625551361
H	5.1037451469	0.6677417234	-0.6513407802
H	3.8745778451	-0.2359316090	3.4166207607
H	-3.1989210088	4.0292624981	-0.6410888448
C	-3.5136775557	5.0677695221	1.9979979149
C	6.1641610436	0.4030015434	1.9821612518
C	-2.6782601659	-5.5606591535	2.0085399628
C	-2.8402120141	-6.6058738654	0.8888868401
C	-4.0631746128	-5.3014436922	2.6519661807
C	-1.7044567736	-6.1205821232	3.0745281412
H	-4.7709754795	-4.8934176015	1.9082578229
H	-3.9979924135	-4.5885067139	3.4918149225
H	-4.4798631501	-6.2469626181	3.0431856685
H	-3.5436540374	-6.2635019036	0.1095628411
H	-3.2400619478	-7.5428849973	1.3141260506
H	-1.8747937769	-6.8415913135	0.4072185257
H	-0.7051987890	-6.2993085064	2.6383292850
H	-2.0869722269	-7.0804336726	3.4659986425
H	-1.5890306440	-5.4298309052	3.9274397527
C	7.1594400711	0.6997635141	0.8445849440
C	6.6008012076	-0.9034999489	2.6894468338

C	6.1919054376	1.5791910356	2.9895334470
H	6.5661021827	-1.7584087803	1.9904170134
H	5.9573933590	-1.1405628694	3.5539579407
H	7.6372790712	-0.8025905653	3.0586105315
H	5.8685439724	2.5179972493	2.5050632123
H	7.2182690859	1.7237346708	3.3724291741
H	5.5303484497	1.3940252864	3.8535092959
H	7.1784432226	-0.1154593855	0.0998768035
H	8.1766352251	0.7997313085	1.2617145025
H	6.9178625340	1.6420058007	0.3217329070
C	-4.3209231400	5.7411368917	0.8725504397
C	-2.6176572001	6.1332239117	2.6756505119
C	-4.5023327535	4.4808583468	3.0365831432
H	-5.1357975018	3.7008848867	2.5774955577
H	-5.1619754484	5.2794502512	3.4211351612
H	-3.9753318394	4.0334412282	3.8970198976
H	-1.8986860574	6.5603040141	1.9536161950
H	-2.0467975509	5.7100798888	3.5197861106
H	-3.2416357502	6.9556779276	3.0691851154
H	-3.6614537395	6.1849177549	0.1058554472
H	-4.9380868567	6.5531077844	1.2949302652
H	-5.0008697809	5.0274569125	0.3745487973
N	-0.0023809566	0.0011462608	-1.9772135352
C	-0.0069428061	0.0542449178	-3.1380233919
C	-0.0129636423	0.1214417449	-4.5895136388
H	0.8384616841	0.7297058392	-4.9419302402
H	-0.9529818901	0.5813744163	-4.9414760285
H	0.0706943161	-0.8943655358	-5.0139235116

Optimized Cartesian Coordinates for ^{tBu}TMPA-Cu^{I} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	0.0000000000	-0.0000000000	2.2402570035
N	-1.0542255117	-1.7097195367	0.2698938104
N	-0.9533641566	1.7666071570	0.2707673491
N	2.0075226533	-0.0621334440	0.2702784704
C	-1.1850953122	-0.7965953211	2.5496809208
C	-0.1003425904	1.4238167832	2.5516216793
C	1.2817458364	-0.6281486752	2.5514241017
C	-1.2770403351	-2.6901784450	-0.6247900482
C	-1.3684860195	-1.9472183553	1.5714179373
C	-1.6930499861	2.4462950249	-0.6248268781
C	-1.0068085801	2.1556991755	1.5726753899
C	2.9684859566	0.2286380242	-0.6259698768
C	2.3707812125	-0.2168680083	1.5714335717
H	-2.0629245303	-0.1318158532	2.4526924725
H	-1.1901184886	-1.1800782196	3.5897171737
H	0.9127041578	1.8560709940	2.4575878554

H	-0.4333358053	1.6173197307	3.5911036717
H	1.1437583009	-1.7209101493	2.4577037724
H	1.6172677297	-0.4383579330	3.5908563995
C	-1.8048198514	-3.9380546330	-0.2782685661
H	-1.0157618565	-2.4651673506	-1.6645328403
C	-1.8834246713	-3.1757183950	1.9870956465
C	-2.5183827037	3.5206687851	-0.2785584616
H	-1.6237961523	2.1096948930	-1.6649704963
C	-1.8214230577	3.2099617426	1.9880512568
C	4.3147780854	0.3851007613	-0.2818266635
H	2.6420187321	0.3444555058	-1.6651941424
C	3.6940221065	-0.0572149342	1.9850906993
C	-2.1209510122	-4.2174418677	1.0639815405
H	-1.9526719929	-4.6761108321	-1.0699425127
H	-2.1000188778	-3.3113967610	3.0514221301
C	-2.6092461706	3.9310076168	1.0640992922
H	-1.8347279716	3.4647171861	3.0526358536
C	4.7159705378	0.2482281473	1.0598647363
H	5.0285069081	0.6208266300	-1.0745587422
H	3.9208772752	-0.1770041236	3.0491929154
H	-3.0863475662	4.0137084900	-1.0706799711
C	-3.5103667154	5.0775999072	1.5417598053
C	6.1648456948	0.4234002882	1.5338792094
C	-2.6873087739	-5.5614001502	1.5409287242
C	-2.8572141744	-6.5606680529	0.3813947026
C	-4.0696989734	-5.3154171323	2.1952296467
C	-1.7169748489	-6.1691545863	2.5839485660
H	-4.7732220195	-4.8679082865	1.4705135051
H	-3.9967294759	-4.6409265284	3.0657294139
H	-4.4962477286	-6.2726079679	2.5451248025
H	-3.5603893899	-6.1848106107	-0.3826869784
H	-3.2614107654	-7.5113613078	0.7703273987
H	-1.8938340867	-6.7826169007	-0.1108314349
H	-0.7184390991	-6.3358793000	2.1416131982
H	-2.1052948725	-7.1414747732	2.9367232918
H	-1.5992597678	-5.5137963267	3.4639253778
C	7.1230809433	0.7142879742	0.3635500123
C	6.6258101926	-0.8772185919	2.2367865663
C	6.2197110157	1.6071521049	2.5314358540
H	6.5735160036	-1.7366739418	1.5445371389
H	6.0085776905	-1.1103777093	3.1214426072
H	7.6723079894	-0.7706291321	2.5746668952
H	5.8765558760	2.5409523901	2.0510269538
H	7.2575797171	1.7587433798	2.8786240889
H	5.5885833733	1.4251793567	3.4184801684
H	7.1229620253	-0.1075168848	-0.3740694277
H	8.1522478246	0.8220019743	0.7478256148
H	6.8607706166	1.6509306332	-0.1593676545
C	-4.2561962931	5.7505007371	0.3743016325

C	-2.6388078077	6.1394940398	2.2556054904
C	-4.5543738030	4.5049241793	2.5332618174
H	-5.1738500001	3.7312904550	2.0453690920
H	-5.2224934789	5.3126054119	2.8824405288
H	-4.0756983622	4.0542350254	3.4199395678
H	-1.8828454454	6.5558870998	1.5659349919
H	-2.1128817307	5.7176049612	3.1290293843
H	-3.2740199147	6.9694095038	2.6137059561
H	-3.5569870814	6.1879958137	-0.3601946304
H	-4.8895994938	6.5670814740	0.7623358121
H	-4.9147111295	5.0382932087	-0.1536101148

Optimized Cartesian Coordinates for ^{tBu}TMPA-Cu^{II}-MeCN (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-0.0000000000	0.0000000000	2.0849711297
N	-0.9519386976	-1.8255300684	0.3298564690
N	-1.1101601892	1.7346928871	0.3316802328
N	2.0553770626	0.0958389174	0.3320973708
C	-1.2004257073	-0.7738135503	2.4892048406
C	-0.0704171798	1.4259514165	2.4895915579
C	1.2703265504	-0.6531507636	2.4889600891
C	-1.1016506321	-2.8406225139	-0.5326774804
C	-1.3550462886	-1.9886217403	1.6117262721
C	-1.9164114661	2.3713271973	-0.5294208489
C	-1.0452912861	2.1677872435	1.6125588072
C	3.0077276283	0.4788451355	-0.5299231497
C	2.3997775093	-0.1782726608	1.6123033519
H	-2.0788036018	-0.1188464291	2.3607224694
H	-1.1383415145	-1.0405870814	3.5584497096
H	0.9356299248	1.8610876758	2.3633239484
H	-0.3336217909	1.5054130135	3.5586596756
H	1.1423613533	-1.7414159623	2.3604792996
H	1.4696766947	-0.4669963196	3.5584571864
C	-1.6663677248	-4.0635584637	-0.1581085029
H	-0.7561207192	-2.6677372781	-1.5568721541
C	-1.9108419651	-3.1849741599	2.0596219474
C	-2.6908446711	3.4733372077	-0.1545949173
H	-1.9436678556	1.9833630760	-1.5526320463
C	-1.7990945600	3.2504865630	2.0602817792
C	4.3495085027	0.5989244045	-0.1567575536
H	2.6837357036	0.6977339769	-1.5523388125
C	3.7151677491	-0.0668042501	2.0581967578
C	-2.0878251427	-4.2678587519	1.1696729310
H	-1.7599934705	-4.8427015380	-0.9173121450
H	-2.2038978832	-3.2637003100	3.1102841443
C	-2.6506796064	3.9442252237	1.1716924001
H	-1.7157841258	3.5474161762	3.1096928019

C	4.7397326021	0.3256089032	1.1681585296
H	5.0705297320	0.9133929679	-0.9141394102
H	3.9326312424	-0.2904629112	3.1064513746
H	-3.3211995702	3.9427353765	-0.9125395480
C	-3.4730003946	5.1391422982	1.6688340670
C	6.1865394755	0.4449171636	1.6614772719
C	-2.6983135590	-5.5828994505	1.6688375888
C	-2.8192455622	-6.6276355147	0.5437509008
C	-4.1107675435	-5.2933987385	2.2358639591
C	-1.7903239522	-6.1534185489	2.7868562674
H	-4.7684990791	-4.8717371466	1.4550191895
H	-4.0797490460	-4.5845001572	3.0809779005
H	-4.5645523813	-6.2319319850	2.6005704174
H	-3.4705343559	-6.2727762546	-0.2742571725
H	-3.2629073723	-7.5531158110	0.9491897966
H	-1.8338502282	-6.8872286449	0.1184976699
H	-0.7729144571	-6.3500682785	2.4042692108
H	-2.2099779278	-7.1055270997	3.1575791809
H	-1.7093385620	-5.4630936303	3.6441219741
C	7.1477429513	0.8636033383	0.5333120216
C	6.6380268225	-0.9282997414	2.2178837873
C	6.2394869934	1.5104724631	2.7847963976
H	6.5822361405	-1.7066920818	1.4360930294
H	6.0195655990	-1.2523177774	3.0726878741
H	7.6844464351	-0.8619038297	2.5650406849
H	5.9087674717	2.4948180787	2.4081564676
H	7.2758616349	1.6115221732	3.1529779483
H	5.6014066918	1.2373478295	3.6426603587
H	7.1530639056	0.1302929599	-0.2923253864
H	8.1748355422	0.9282812298	0.9317519164
H	6.8857679941	1.8533118105	0.1199176782
C	-4.3533758256	5.7391537223	0.5570418347
C	-2.4972662438	6.2292821117	2.1789057297
C	-4.3846278005	4.6684179391	2.8295376069
H	-5.0732758791	3.8735162335	2.4916938449
H	-4.9891437234	5.5175102439	3.1948196190
H	-3.8001963892	4.2801684182	3.6810742870
H	-1.8336020069	6.5740844902	1.3661158735
H	-1.8663247876	5.8611601926	3.0062266275
H	-3.0706871269	7.0972469547	2.5498977397
H	-3.7482480095	6.1134400684	-0.2872883824
H	-4.9254311392	6.5913850826	0.9621974879
H	-5.0782428912	5.0030390482	0.1670732770
N	0.0025298346	0.0025312002	-1.9679590432
C	0.0003154501	0.0484687923	-3.1231067842
C	-0.0028365126	0.1011612107	-4.5690002591
H	0.8292468444	0.7363470482	-4.9178186009
H	-0.9588888849	0.5246554389	-4.9212126363
H	0.1184278541	-0.9171523965	-4.9762265562

Optimized Cartesian Coordinates for ^{tBu}TMPA-Cu^{II} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-0.0000000000	-0.0000000000	2.0613932332
N	-0.9452908024	-1.7737577111	0.2009824463
N	-1.0677887265	1.7022385157	0.2025791902
N	2.0068316977	0.0642486035	0.2022496824
C	-1.1986694991	-0.8014312448	2.4086168403
C	-0.0966395085	1.4381697111	2.4094110964
C	1.2929648888	-0.6370713994	2.4112707611
C	-1.0980086301	-2.7587059572	-0.6977701751
C	-1.3437230580	-1.9834686219	1.4815545790
C	-1.8499762472	2.3220151454	-0.6948107025
C	-1.0506495624	2.1522370868	1.4833075492
C	2.9348586962	0.4201495886	-0.6995948056
C	2.3894583313	-0.1760072622	1.4823194481
H	-2.0788853173	-0.1443170237	2.3087548308
H	-1.1334242434	-1.1136443219	3.4654353210
H	0.9112123061	1.8756124618	2.3108293030
H	-0.4003681081	1.5368371973	3.4662140705
H	1.1632925088	-1.7283233121	2.3162217195
H	1.5310925079	-0.4209828898	3.4673632545
C	-1.6660113477	-3.9913410047	-0.3639779268
H	-0.7552849296	-2.5504820796	-1.7166028853
C	-1.8981620484	-3.1939938673	1.8863792655
C	-2.6422226887	3.4233412543	-0.3588499422
H	-1.8393763224	1.9219043731	-1.7139647701
C	-1.8278605188	3.2327764224	1.8894821898
C	4.2873955529	0.5397112272	-0.3693912819
H	2.5811535962	0.6128190875	-1.7177379174
C	3.7167737833	-0.0558584624	1.8834979951
C	-2.0836170486	-4.2425080858	0.9568201186
H	-1.7660993199	-4.7410877356	-1.1511737715
H	-2.1866918017	-3.3111511021	2.9346018296
C	-2.6523529580	3.9098967172	0.9621212900
H	-1.7847372180	3.5427489517	2.9373905089
C	4.7161292958	0.3026067618	0.9504509302
H	4.9867110334	0.8248754756	-1.1578125914
H	3.9663194681	-0.2484595478	2.9306435796
H	-3.2469796781	3.8801281065	-1.1446119317
C	-3.4982507236	5.1049533946	1.4145726098
C	6.1774034702	0.4259444659	1.3952114890
C	-2.7035940533	-5.5695934241	1.4074887540
C	-2.8200839408	-6.5753442989	0.2472272348
C	-4.1194129013	-5.2874504690	1.9707175525
C	-1.8095904183	-6.1815218659	2.5148746985
H	-4.7656891220	-4.8326283043	1.1990955420

H	-4.0906724867	-4.6096948652	2.8411946361
H	-4.5843542809	-6.2345798667	2.2969520347
H	-3.4632920332	-6.1906307024	-0.5636164866
H	-3.2711632046	-7.5116144359	0.6178562110
H	-1.8323058944	-6.8252160587	-0.1784183741
H	-0.7897395574	-6.3720803013	2.1359796806
H	-2.2392110999	-7.1422531046	2.8496966923
H	-1.7336399874	-5.5204951850	3.3952440491
C	7.1079779653	0.7823285846	0.2208709354
C	6.6310075874	-0.9270584695	1.9975953375
C	6.2732222161	1.5400054088	2.4677413875
H	6.5440960357	-1.7376131521	1.2522502225
H	6.0363299517	-1.2074287379	2.8840642565
H	7.6880752874	-0.8570057585	2.3096288174
H	5.9412813975	2.5099341464	2.0565950667
H	7.3211677186	1.6456836264	2.7999209076
H	5.6581537895	1.3128274372	3.3554570099
H	7.0760367208	0.0137685197	-0.5712852714
H	8.1477915388	0.8478853487	0.5843228860
H	6.8473606817	1.7574423568	-0.2264727669
C	-4.3543484257	5.6747651925	0.2686712276
C	-2.5438819079	6.2122752595	1.9287469354
C	-4.4353586720	4.6478954340	2.5604686911
H	-5.1071204077	3.8391353284	2.2217474701
H	-5.0574868513	5.4983535711	2.8910588558
H	-3.8703253577	4.2843669738	3.4356437733
H	-1.8647640340	6.5498468331	1.1258621713
H	-1.9293326663	5.8632404708	2.7764183162
H	-3.1336726929	7.0804951590	2.2721443535
H	-3.7312662278	6.0431270766	-0.5651147630
H	-4.9482494361	6.5259875443	0.6432700537
H	-5.0590459799	4.9228776229	-0.1281571527

Optimized Cartesian Coordinates for ^{OMe}TMPA-Cu^{I}-MeCN (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	0.0000000000	0.0000000000	2.5100949190
N	-1.1335855689	-1.7139025618	0.6042069664
N	-0.9206568037	1.8302301879	0.5949547916
N	2.0502355271	-0.1125342448	0.6019144679
C	-1.2266422541	-0.7063290914	2.8358364084
C	0.0034961870	1.4181780756	2.8258257345
C	1.2268698939	-0.7096188705	2.8292009839
C	-1.3841042487	-2.7218851470	-0.2484077192
C	-1.4580357151	-1.8871681979	1.9090518234
C	-1.6746803551	2.5436756375	-0.2584178757
C	-0.9102985679	2.2006990385	1.8994135803
C	3.0448704162	0.1950192764	-0.2475976510

C	2.3628060112	-0.3028650128	1.9075367061
H	-2.0666958114	-0.0016275729	2.6958037306
H	-1.2700534720	-1.0450749724	3.8928381443
H	1.0323282739	1.7918143194	2.6724692630
H	-0.2596598435	1.6334900676	3.8831890317
H	1.0399952044	-1.7879632236	2.6738618139
H	1.5409081607	-0.5901805902	3.8880813330
C	-1.9542047348	-3.9414691032	0.1261947166
H	-1.1104812661	-2.5445154016	-1.2954942621
C	-2.0176234688	-3.0719442485	2.3842782802
C	-2.4539651111	3.6418551974	0.1147910778
H	-1.6565169641	2.2163278151	-1.3048724460
C	-1.6640409715	3.2730722620	2.3728486043
C	4.3825241494	0.3371987779	0.1310674362
H	2.7546438900	0.3389912944	-1.2952723833
C	3.6649677600	-0.1716299329	2.3862888607
C	-2.2814000104	-4.1299829994	1.4857236291
H	-2.1245113310	-4.7099505968	-0.6311704043
H	-2.2573930274	-3.1927844121	3.4457357082
C	-2.4549362223	4.0227609559	1.4733339191
H	-1.6496533700	3.5434193904	3.4337286577
C	4.7093357609	0.1517235196	1.4910301230
H	5.1306172107	0.5915211621	-0.6232336165
H	3.8893659754	-0.3158765600	3.4481463229
H	-3.0400894633	4.1668065220	-0.6427809025
O	-3.1572213556	5.0476784897	1.9893514313
O	5.9443865248	0.2637473806	2.0128031643
O	-2.8246032237	-5.2466347970	2.0037609860
C	-3.1076979358	-6.3487667356	1.1331483570
H	-3.5439831809	-7.1337110011	1.7685171651
H	-3.8331929401	-6.0587704021	0.3510628228
H	-2.1831958764	-6.7265993349	0.6591588473
C	-3.9753629532	5.8371818594	1.1173871400
H	-4.4404477067	6.6065216000	1.7514113083
H	-3.3649977567	6.3216092833	0.3332682765
H	-4.7620869005	5.2199258731	0.6460559459
C	7.0350547613	0.6044931821	1.1484647979
H	7.9289588243	0.6439897306	1.7884203393
H	7.1739522843	-0.1626227312	0.3646265022
H	6.8724012490	1.5908450389	0.6764381951
N	0.0043736477	0.0011222128	-1.9678991671
C	0.0127842567	0.0872267149	-3.1272792365
C	0.0228566599	0.1939466034	-4.5763752125
H	0.9413018841	0.7078514619	-4.9100107591
H	-0.8548941032	0.7698479646	-4.9182669147
H	-0.0100847565	-0.8125763158	-5.0287645659

Optimized Cartesian Coordinates for ^{OMe}TMPA-Cu^{I} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-0.0000000000	0.0000000000	2.2447850037
N	-1.1154764733	-1.6779513061	0.2751142366
N	-0.8936371606	1.8042823858	0.2754021965
N	2.0116097090	-0.1248556134	0.2760182072
C	-1.2096135536	-0.7574175441	2.5556807979
C	-0.0526857085	1.4255510087	2.5579013711
C	1.2606231901	-0.6690329303	2.5557371974
C	-1.3709451084	-2.6530340183	-0.6173337247
C	-1.4292005659	-1.9057097729	1.5820287511
C	-1.6067100701	2.5147514741	-0.6186666816
C	-0.9332075878	2.1920482088	1.5816630781
C	2.9830930574	0.1501514886	-0.6145508569
C	2.3646589856	-0.2800035303	1.5836676351
H	-2.0659279782	-0.0659879510	2.4534371311
H	-1.2283936599	-1.1363823364	3.5972833735
H	0.9739341194	1.8237007076	2.4617622000
H	-0.3770046970	1.6290379852	3.5982321554
H	1.0912036365	-1.7562231388	2.4500472861
H	1.5974531312	-0.4985666236	3.5981279537
C	-1.9313011205	-3.8880016003	-0.2830199902
H	-1.1101114034	-2.4359062436	-1.6589048259
C	-1.9749641901	-3.1117175260	2.0098293127
C	-2.3895240008	3.6228460937	-0.2870386818
H	-1.5508672493	2.1775952386	-1.6594754757
C	-1.6990343727	3.2729322889	2.0068855037
C	4.3309416265	0.2947681920	-0.2776515387
H	2.6655165896	0.2647014513	-1.6567225709
C	3.6799896269	-0.1385964000	2.0137347326
C	-2.2417186147	-4.1345286991	1.0706447669
H	-2.1068324800	-4.6249615300	-1.0696685248
H	-2.2055100940	-3.2783446745	3.0668153245
C	-2.4451793656	4.0189742304	1.0655584974
H	-1.7268685519	3.5578617194	3.0633958039
C	4.6982206140	0.1519687830	1.0766485823
H	5.0566498353	0.5193765869	-1.0623588361
H	3.9386176996	-0.2519622087	3.0712915399
H	-2.9369837531	4.1442090889	-1.0750874471
O	-3.1578516788	5.0547708592	1.5402950018
O	5.9472246626	0.2748179181	1.5573859158
O	-2.7718993369	-5.2732715181	1.5485883623
C	-3.0578981072	-6.3419900453	0.6370721675
H	-3.4809098680	-7.1547157934	1.2456892445
H	-3.7948720609	-6.0252722465	-0.1234172729
H	-2.1361709444	-6.6926977938	0.1378301709
C	-3.9279270512	5.8455547798	0.6256408962
H	-4.4082715185	6.6280769902	1.2313115542
H	-3.2776213173	6.3122643014	-0.1366083408

H	-4.7021811667	5.2328512749	0.1287170369
C	7.0138111940	0.5809436786	0.6500532834
H	7.9259481690	0.6372523123	1.2622121444
H	7.1258159384	-0.2132392100	-0.1105899359
H	6.8404992175	1.5516620143	0.1505450238

Optimized Cartesian Coordinates for ^{OMe}TMPA-Cu^{II}-MeCN (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	0.0000000000	0.0000000000	2.0866788770
N	-1.0465876607	-1.7706574974	0.3282026485
N	-1.0255810875	1.7871986499	0.3329649842
N	2.0558223978	0.0030820271	0.3304401507
C	-1.2340739553	-0.7159798669	2.4943102787
C	-0.0022904278	1.4275708794	2.4917128458
C	1.2386444590	-0.7114513361	2.4882532753
C	-1.2513970316	-2.7756312861	-0.5379560989
C	-1.4517364221	-1.9202405669	1.6151241835
C	-1.8030828385	2.4624526765	-0.5280622121
C	-0.9466900406	2.2136131366	1.6192688704
C	3.0253811000	0.3499595882	-0.5306914332
C	2.3889797540	-0.2798586165	1.6158698948
H	-2.0806071747	-0.0199487263	2.3684068207
H	-1.1827464370	-0.9875675972	3.5628125679
H	1.0212805579	1.8154665773	2.3547023800
H	-0.2532342548	1.5210380471	3.5624612881
H	1.0642399636	-1.7917483361	2.3478036631
H	1.4455704565	-0.5440774931	3.5592932788
C	-1.8719121764	-3.9727756097	-0.1824567392
H	-0.9027218406	-2.6149896276	-1.5630657968
C	-2.0631115199	-3.0810768955	2.0686028946
C	-2.5332504939	3.5946924444	-0.1679091548
H	-1.8434974478	2.0794148223	-1.5527950543
C	-1.6489884874	3.3199170212	2.0774273527
C	4.3705488347	0.4277633599	-0.1712564174
H	2.7107100228	0.5765502675	-1.5544423402
C	3.6982476279	-0.2158164463	2.0724401267
C	-2.2921013370	-4.1399453380	1.1565075887
H	-2.0105299969	-4.7458443203	-0.9408421746
H	-2.3712169710	-3.1867828136	3.1127288770
C	-2.4607025991	4.0435268756	1.1701792717
H	-1.5810853369	3.6400842327	3.1210975211
C	4.7266334850	0.1391179836	1.1655948781
H	5.1072105640	0.7135777184	-0.9247657744
H	3.9448766321	-0.4364217575	3.1149425930
H	-3.1420234731	4.0974479885	-0.9219162280
O	-3.1085044379	5.1058961576	1.6600325663
O	5.9702371144	0.1801672848	1.6551643501

O	-2.8905517954	-5.2322271842	1.6431542045
C	-3.1462517869	-6.3428389489	0.7684774640
H	-3.6389508088	-7.1059399101	1.3879875547
H	-3.8154095525	-6.0437088133	-0.0580586254
H	-2.2016772699	-6.7453758094	0.3609553183
C	-3.9476512283	5.8809559765	0.7887537224
H	-4.3573621758	6.6912804551	1.4087504257
H	-3.3589471210	6.3072642040	-0.0430903201
H	-4.7717252237	5.2637179943	0.3884643310
C	7.0561779497	0.5442381447	0.7878110349
H	7.9626061630	0.5063082869	1.4089303147
H	7.1455985800	-0.1717987783	-0.0486789778
H	6.9155367121	1.5665846706	0.3935849813
N	0.0003158630	0.0023279234	-1.9686954847
C	-0.0056191157	0.0037453277	-3.1247322143
C	-0.0118264288	0.0050830946	-4.5717560423
H	0.8665987720	0.5591824302	-4.9447314580
H	-0.9330736933	0.4903918632	-4.9371417017
H	0.0262535684	-1.0335916950	-4.9425123585

Optimized Cartesian Coordinates for ^{OMe}TMPA-Cu^{II} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-0.0000000000	0.0000000000	2.0598401826
N	-1.0396015793	-1.7210874145	0.2014452799
N	-0.9706066345	1.7616612618	0.2014216192
N	2.0106209245	-0.0328110361	0.2018031091
C	-1.2367193220	-0.7392014957	2.4115735989
C	-0.0221642668	1.4405932987	2.4117740276
C	1.2592172070	-0.7016226323	2.4091756907
C	-1.2367343727	-2.7024956940	-0.6959416979
C	-1.4377916307	-1.9163941361	1.4887238063
C	-1.7206525277	2.4245361640	-0.6960115419
C	-0.9408771422	2.2038824934	1.4888613077
C	2.9572971221	0.2995178140	-0.6929810895
C	2.3787878712	-0.2780627483	1.4896379226
H	-2.0830741120	-0.0401147555	2.3047302430
H	-1.1895445561	-1.0486387424	3.4699252990
H	1.0059369043	1.8255499124	2.3056612667
H	-0.3146393154	1.5543478911	3.4699269092
H	1.0797945955	-1.7840028255	2.2957500469
H	1.5025215205	-0.5119997222	3.4689035918
C	-1.8471742073	-3.9135575920	-0.3745979887
H	-0.8926427459	-2.5074625849	-1.7169778272
C	-2.0346901132	-3.0959332560	1.9061237804
C	-2.4620609878	3.5601926011	-0.3748621317
H	-1.7244744366	2.0290409713	-1.7170802161
C	-1.6622135073	3.3117573130	1.9062111208

C	4.3095498386	0.3921978707	-0.3684085878
H	2.6162860208	0.4979072428	-1.7144358093
C	3.6970109499	-0.1916910106	1.9098329067
C	-2.2600820294	-4.1271387188	0.9603487112
H	-1.9843665019	-4.6622579736	-1.1571438585
H	-2.3369254232	-3.2384119407	2.9474124676
C	-2.4396239047	4.0249836437	0.9598467575
H	-1.6341341790	3.6446772311	2.9475546455
C	4.7008073219	0.1430239682	0.9668287537
H	5.0254847971	0.6589723361	-1.1482891751
H	3.9720106961	-0.3805408972	2.9513304012
H	-3.0406744488	4.0543080592	-1.1575815158
O	-3.1036560340	5.0906218344	1.4127163108
O	5.9534623619	0.2047787680	1.4234518914
O	-2.8464071958	-5.2370541925	1.4141222358
C	-3.1014157808	-6.3224379039	0.5062958697
H	-3.5850142248	-7.1069055651	1.1056623733
H	-3.7780817201	-6.0006795276	-0.3052179108
H	-2.1566725310	-6.7050686837	0.0810221023
C	-3.9080170609	5.8604592322	0.5029555830
H	-4.3359258088	6.6783748252	1.0999669405
H	-3.2867948919	6.2752301919	-0.3106122251
H	-4.7191385145	5.2413420081	0.0803640829
C	7.0179729533	0.5483418572	0.5201353090
H	7.9380938505	0.5324890137	1.1214506917
H	7.0908665996	-0.1920947429	-0.2962078513
H	6.8617508866	1.5579742900	0.1005000293

Optimized Cartesian Coordinates for ^{NMe2}TMPA-Cu^{I}-MeCN (Å):

Cu	-0.0017552662	-0.0185624185	-0.3531653253
N	0.0065208619	-0.0122021504	2.1750982713
N	-1.1536266653	-1.7121444255	0.2692203952
N	-0.8989597833	1.8307472336	0.2654089717
N	2.0456537462	-0.1505158103	0.2566868895
C	-1.2270019006	-0.7059949750	2.4973224297
C	0.0271862256	1.4052630453	2.4881738057
C	1.2270136193	-0.7354353680	2.4837848997
C	-1.4113951915	-2.7371026371	-0.5693449575
C	-1.4602018335	-1.8926063452	1.5766217736
C	-1.6622340599	2.5623208211	-0.5723319899
C	-0.8887991821	2.1970140120	1.5696272527
C	3.0533361024	0.1617538759	-0.5842251465
C	2.3639136339	-0.3279128191	1.5617302386
H	-2.0584034965	0.0068686895	2.3465175021
H	-1.2801573309	-1.0354999220	3.5579034724
H	1.0595223873	1.7646841691	2.3238306705
H	-0.2211009138	1.6240320025	3.5495710152

H	1.0272232246	-1.8101963753	2.3193984844
H	1.5441815341	-0.6291151994	3.5442892836
C	-1.9587331447	-3.9537290419	-0.1790874761
H	-1.1569554605	-2.5661659268	-1.6228839010
C	-1.9976478563	-3.0785749806	2.0724439911
C	-2.4314695573	3.6534095389	-0.1846983879
H	-1.6532182077	2.2465452055	-1.6231285011
C	-1.6347246823	3.2654388079	2.0628551730
C	4.3797869772	0.3167070422	-0.1984232048
H	2.7712758969	0.2984221971	-1.6356834339
C	3.6596216089	-0.1839728925	2.0528060327
C	-2.2746445399	-4.1686797009	1.1952467736
H	-2.1280698282	-4.7222827166	-0.9359985487
H	-2.2011417386	-3.1476046747	3.1434190710
C	-2.4413755672	4.0492881668	1.1856941155
H	-1.5818658126	3.4850757409	3.1315866375
C	4.7329540921	0.1452360188	1.1729580505
H	5.1224524931	0.5744664553	-0.9563039945
H	3.8269881039	-0.3285813379	3.1225073329
H	-3.0175202600	4.1802921270	-0.9404130223
N	-3.1772994706	5.1060510998	1.6308129189
N	6.0124290502	0.2932817995	1.6170745016
N	-2.8016813015	-5.3422254448	1.6442218028
C	-3.0492353413	-6.4385649229	0.7129850296
H	-3.4843804483	-7.2852089470	1.2615854537
H	-3.7583821189	-6.1390751834	-0.0813150959
H	-2.1136355136	-6.7807138526	0.2308033090
C	-3.0830423985	-5.5255619630	3.0645582911
H	-3.5044369663	-6.5280512114	3.2216176336
H	-2.1639223079	-5.4348466873	3.6742569395
H	-3.8148552012	-4.7807697072	3.4298919270
C	-3.9919025460	5.8773979374	0.6970701097
H	-4.4891773502	6.6917431555	1.2418427664
H	-3.3728351089	6.3230195065	-0.1041098011
H	-4.7705877501	5.2493303175	0.2240756034
C	-3.1629740191	5.4686691173	3.0443978928
H	-3.8156432896	6.3390054297	3.1986096383
H	-3.5328626468	4.6407613993	3.6785215567
H	-2.1436281483	5.7343979368	3.3828026035
C	7.0749407918	0.6566683043	0.6846327781
H	8.0261133218	0.7212065158	1.2308070676
H	7.1856594989	-0.0992926623	-0.1154225300
H	6.8789728510	1.6367898999	0.2094859148
C	6.3238871684	0.1229793669	3.0327650236
H	7.4010901293	0.2770699983	3.1843757082
H	5.7767272478	0.8528823740	3.6593367642
H	6.0667470298	-0.8944260331	3.3828726544
N	-0.0059499822	-0.0122933415	-2.3118797960
C	0.0034022523	-0.0105041953	-3.4751540666

C	0.0152058141	-0.0087870591	-4.9280385905
H	0.4991702768	-0.9269947412	-5.3044094291
H	0.5731866971	0.8674167377	-5.3021458872
H	-1.0176284485	0.0343496243	-5.3158733361

Optimized Cartesian Coordinates for ^{NMe2}TMPA-Cu^{I} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-0.0000000000	-0.0000000000	2.2503366206
N	-1.1389197148	-1.6647704985	0.2823857662
N	-0.8717685756	1.8171310632	0.2826119491
N	2.0121363142	-0.1515382355	0.2848331375
C	-1.2187193013	-0.7428584301	2.5575387642
C	-0.0355470070	1.4262550482	2.5594655474
C	1.2520196584	-0.6835555542	2.5595752169
C	-1.4033110181	-2.6566575568	-0.5969765778
C	-1.4414296753	-1.8970293406	1.5898356373
C	-1.5948997654	2.5437935810	-0.5984577644
C	-0.9188371557	2.1991365081	1.5888985051
C	3.0037864362	0.1207934962	-0.5924608706
C	2.3632760000	-0.2975159853	1.5926687654
H	-2.0658205608	-0.0415668203	2.4448305566
H	-1.2478257752	-1.1130048066	3.6029876583
H	0.9952328551	1.8108728444	2.4520918477
H	-0.3472958326	1.6347815056	3.6035660291
H	1.0693442031	-1.7679482734	2.4458755728
H	1.5866874236	-0.5239262398	3.6053276696
C	-1.9487622717	-3.8859703010	-0.2485131580
H	-1.1575817245	-2.4472502829	-1.6443570560
C	-1.9734183903	-3.1017456714	2.0372954237
C	-2.3775739907	3.6383877311	-0.2531108143
H	-1.5398865161	2.2222720667	-1.6448112157
C	-1.6866525785	3.2704621316	2.0332512481
C	4.3401163266	0.2679652352	-0.2417909488
H	2.7007661439	0.2279903659	-1.6402991668
C	3.6715264743	-0.1527051378	2.0419626932
C	-2.2527937890	-4.1575047652	1.1181655258
H	-2.1257664202	-4.6223549952	-1.0347943983
H	-2.1749980996	-3.2128420257	3.1047706403
C	-2.4551327533	4.0438137509	1.1119749455
H	-1.6807832852	3.5025589443	3.1002901818
C	4.7255990561	0.1404557996	1.1254034829
H	5.0668505724	0.4869038035	-1.0265396583
H	3.8668764393	-0.2725875467	3.1096498073
H	-2.9229210088	4.1615372861	-1.0408600002
N	-3.2161187009	5.0986022006	1.5140255534
N	6.0151521156	0.2931785241	1.5340950597
N	-2.7718168939	-5.3488504231	1.5238464454
C	-3.0438570511	-6.4002414634	0.5482299658

H	-3.4582161599	-7.2747315558	1.0683084770
H	-3.7772138360	-6.0667016492	-0.2099327526
H	-2.1211856419	-6.7129767317	0.0238064641
C	-3.0579445209	-5.5842488892	2.9358529554
H	-3.4592731529	-6.5997776898	3.0570644757
H	-2.1432601870	-5.4966282920	3.5518439972
H	-3.8062537527	-4.8667740593	3.3223855240
C	-3.9729334124	5.8724118474	0.5340841432
H	-4.5279648369	6.6653051650	1.0540164029
H	-3.3057670263	6.3455877707	-0.2113456881
H	-4.6996065562	5.2364962359	-0.0051064601
C	-3.2431150726	5.4932226926	2.9193238786
H	-3.9210621805	6.3494615648	3.0386675344
H	-3.6093326137	4.6705980767	3.5614603017
H	-2.2386951241	5.7911292966	3.2756811246
C	7.0647421242	0.5713398471	0.5582398583
H	8.0238249633	0.6802125543	1.0828539412
H	7.1621569937	-0.2495648445	-0.1776087901
H	6.8620872413	1.5087354957	0.0075071273
C	6.3656739555	0.1284461139	2.9417230396
H	7.4423746897	0.3074690110	3.0668907048
H	5.8191012942	0.8480142653	3.5792851453
H	6.1388811075	-0.8940256242	3.2992532871

Optimized Cartesian Coordinates for ^{NMe2}TMPA-Cu^{II}-MeCN (Å):

Cu	0.0031113277	0.0077995004	-0.0452366948
N	0.0123979723	-0.0005775312	2.0438290302
N	-1.0557005367	-1.7523689799	0.2806733925
N	-0.9969585740	1.8032894947	0.2967868237
N	2.0578807590	-0.0134195559	0.2767420707
C	-1.2229746288	-0.7142207555	2.4509322282
C	0.0171915035	1.4258409766	2.4521513340
C	1.2507886245	-0.7174831795	2.4359309084
C	-1.2585716964	-2.7737122091	-0.5765020989
C	-1.4375350197	-1.9207968853	1.5719930414
C	-1.7896871129	2.4938232399	-0.5479779238
C	-0.9331684121	2.2160134839	1.5879882318
C	3.0376929679	0.3510408820	-0.5752185391
C	2.3989541410	-0.2742896013	1.5643105953
H	-2.0661051189	-0.0146734813	2.3210398562
H	-1.1735118348	-0.9823597265	3.5208071902
H	1.0421210689	1.8070615480	2.3065445150
H	-0.2236612299	1.5169072752	3.5258268478
H	1.0716000347	-1.7953790362	2.2833007702
H	1.4585025403	-0.5620209246	3.5090252623
C	-1.8450380535	-3.9751692852	-0.2087540741
H	-0.9321633764	-2.6105991628	-1.6090076192

C	-2.0172175768	-3.0895893682	2.0426095263
C	-2.5274257946	3.6049831237	-0.1682227636
H	-1.8280928461	2.1311369493	-1.5806273059
C	-1.6452281668	3.3039484826	2.0706449284
C	4.3697190419	0.4608948400	-0.2058497849
H	2.7294713584	0.5635760588	-1.6043866537
C	3.6996692170	-0.1789247952	2.0360059841
C	-2.2544123891	-4.1779921056	1.1457245640
H	-1.9777924351	-4.7456434155	-0.9700000528
H	-2.2856060963	-3.1524774585	3.0984290691
C	-2.4775404368	4.0591265483	1.1862431290
H	-1.5481537644	3.5661548709	3.1254982390
C	4.7546059155	0.1926203537	1.1444865752
H	5.0981480821	0.7580945355	-0.9621524507
H	3.8920164725	-0.3942058018	3.0883886105
H	-3.1382674538	4.1076039968	-0.9198489893
N	-3.1802704694	5.1372488490	1.6115192739
N	6.0405463159	0.2921147958	1.5607123916
N	-2.8270129295	-5.3343925239	1.5602178793
C	-3.0346216297	-6.4325378425	0.6174447573
H	-3.5027414153	-7.2737072583	1.1459424112
H	-3.6995254589	-6.1275876683	-0.2115420389
H	-2.0761554867	-6.7793931600	0.1893937803
C	-3.2289990941	-5.5001635162	2.9560183994
H	-3.6909158440	-6.4887877832	3.0804000281
H	-2.3591778862	-5.4334252232	3.6355930964
H	-3.9659569412	-4.7315824613	3.2525454527
C	-4.0172342690	5.8866089878	0.6756499321
H	-4.4825048909	6.7277069963	1.2068516454
H	-3.4174289869	6.2901996361	-0.1605791101
H	-4.8194299400	5.2509306576	0.2574869097
C	-3.1070428603	5.5619318530	3.0085815941
H	-3.7496114569	6.4413744579	3.1491420191
H	-3.4560592105	4.7632329119	3.6885597455
H	-2.0734332511	5.8355411111	3.2901487601
C	7.0892439767	0.6922516335	0.6236157359
H	8.0530471818	0.7055803866	1.1497688750
H	7.1625023814	-0.0173258959	-0.2209027783
H	6.8986454122	1.7026158849	0.2169822498
C	6.3885734887	0.0206217488	2.9544882770
H	7.4711767885	0.1511947820	3.0844471684
H	5.8679374901	0.7142256824	3.6402362475
H	6.1267775493	-1.0153938117	3.2379129394
N	-0.0050519706	0.0175862680	-2.0180490007
C	-0.0092410216	0.0260540188	-3.1742799340
C	-0.0144738743	0.0370233554	-4.6220694272
H	-0.9572701940	-0.4005835032	-4.9922591991
H	0.8362968522	-0.5552393544	-5.0000258367
H	0.0734031709	1.0753430838	-4.9848400170

Optimized Cartesian Coordinates for ^{NMe2}TMPA-Cu^{II} (Å):

Cu	0.3558017326	-0.4007941490	0.2144160767
N	0.3393568791	-0.2631828905	2.3674847048
N	-0.9710130887	-1.8048132353	0.4673023712
N	-0.6193059465	1.4337063707	0.3293680759
N	2.2714087907	-0.1226848071	0.4267774195
C	-0.8364097719	-1.0387301856	2.8002840692
C	0.2374803017	1.1852628038	2.6128665946
C	1.6553994306	-0.8567336958	2.6684208339
C	-1.4922219533	-2.6068215262	-0.4916655313
C	-1.3006070790	-2.0490656756	1.7676698745
C	-1.3778223661	2.0644346000	-0.5923393776
C	-0.6886283305	1.8647317836	1.6128446203
C	3.1435288949	0.3892365007	-0.4720847238
C	2.6941349088	-0.3021024042	1.7161697038
H	-1.6639694623	-0.3242060572	2.9520344284
H	-0.6547742087	-1.5270144225	3.7747026755
H	1.2467413217	1.6170596880	2.5025673571
H	-0.0939416597	1.3917863372	3.6465331669
H	1.5680639154	-1.9467374474	2.5148920524
H	1.9517951089	-0.6900013645	3.7204822826
C	-2.3144131611	-3.6846253058	-0.2166064315
H	-1.2171960851	-2.3671710460	-1.5239351732
C	-2.1006761488	-3.1204242637	2.1345250409
C	-2.2190643023	3.1268131407	-0.2966591501
H	-1.3038194098	1.6903208645	-1.6193410569
C	-1.5136191176	2.9084928891	2.0110527972
C	4.4585896061	0.6899436894	-0.1642043329
H	2.7583213051	0.5469118784	-1.4844202505
C	3.9868939845	-0.0125356089	2.1145808291
C	-2.6438608074	-3.9920211644	1.1405789735
H	-2.6812458485	-4.2850507010	-1.0501680825
H	-2.3020574869	-3.2752960318	3.1957486740
C	-2.3206406212	3.5931496673	1.0498876731
H	-1.5228818615	3.1904635020	3.0655752740
C	4.9382333030	0.4838931096	1.1672387006
H	5.1021532071	1.0790843555	-0.9542902316
H	4.2574485194	-0.1777055666	3.1584051908
H	-2.7951762505	3.5775603613	-1.1064117927
N	-3.1369702435	4.6178030856	1.3996313426
N	6.2158626354	0.7569176144	1.5174987598
N	-3.4268530777	-5.0470927800	1.4677760977
C	-3.9651119311	-5.9198547319	0.4238725010
H	-4.5247102720	-6.7381248640	0.8955835458
H	-4.6478753300	-5.3662647854	-0.2464720037
H	-3.1513002000	-6.3556773224	-0.1825169535

C	-3.7778497940	-5.3034234097	2.8647756268
H	-4.4099008362	-6.1994817180	2.9157005785
H	-2.8728566534	-5.4774567264	3.4742866489
H	-4.3363555143	-4.4532530489	3.2967121017
C	-3.9489757078	5.2905151983	0.3867697731
H	-4.5356086278	6.0844597336	0.8680974541
H	-3.3148956586	5.7487856726	-0.3944545577
H	-4.6483083970	4.5850470925	-0.0986743818
C	-3.2101910223	5.0607116489	2.7908167294
H	-3.9248435950	5.8912741517	2.8651779567
H	-3.5542315586	4.2452284749	3.4534571505
H	-2.2263365057	5.4137156268	3.1512845695
C	7.1557319156	1.2916585993	0.5308895794
H	8.1450459731	1.3870785406	0.9962621643
H	7.2393789092	0.6145036114	-0.3371684162
H	6.8338180482	2.2872351071	0.1751763426
C	6.6608911940	0.5769758383	2.9003253699
H	7.7317569481	0.8094975455	2.9642961053
H	6.1111376933	1.2485059654	3.5843685051
H	6.5077053660	-0.4662281128	3.2282240842

Optimized Cartesian Coordinates for $TMG_3tren\text{-}Cu^{I}$ (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	0.0000000000	0.0000000000	2.2562715051
N	-2.0413320948	0.0149884078	0.2208344102
N	-4.1826567515	0.6771304870	-0.5993721255
N	-2.8274034862	-0.7834037024	-1.8241541447
C	-1.4053064955	-0.2574769162	2.5839841221
C	-2.3532099229	0.4279328691	1.5884165537
C	-2.9829052647	-0.0086092231	-0.6889430689
C	-4.2438516866	2.0500487057	-0.1220402042
C	-5.4387736030	0.1213197731	-1.0831196995
C	-1.8657171704	-1.8708921755	-1.8262412211
C	-3.1525856959	-0.2467664248	-3.1429247157
H	-1.6581049682	0.0670831431	3.6175220786
H	-2.2499114457	1.5238571144	1.7033415666
H	-3.3982943013	0.1817651541	1.8594125064
H	-5.8044370415	0.6422187106	-1.9909273348
H	-3.2306271712	2.4612645503	-0.0204229583
H	-1.5738972496	-1.3448049710	2.5338534044
H	-6.2137632881	0.2219124481	-0.2989038818
H	-4.7901981941	2.6715602385	-0.8578451006
H	-4.7633728708	2.1354686426	0.8522289345
H	-5.3103854181	-0.9456452906	-1.3155961636
H	-1.8500387378	-2.3540199075	-0.8398916126
H	-0.8361222977	-1.5165111039	-2.0401027874
H	-3.6768692345	0.7136943821	-3.0440592466

H	-3.7916193342	-0.9466818870	-3.7124245967
H	-2.1553439957	-2.6059628631	-2.5970702424
H	-2.2259402533	-0.0721597392	-3.7259071361
N	1.0196702297	-1.7674615701	0.2158461637
C	0.8181808850	-2.2491961865	1.5818404880
C	0.9271302881	-1.0876548615	2.5816128410
C	0.4797007027	1.3460241884	2.5840498970
C	1.5426268497	1.8297374712	1.5859375327
N	1.0274301547	1.7675169388	0.2188590883
C	1.4736350118	2.5976784894	-0.6898970690
N	2.6565087584	3.3122295842	-0.5929525162
C	3.8858781757	2.6937215697	-0.1220955247
H	3.7511074194	1.6083129950	-0.0218912751
H	4.6924537816	2.8676139765	-0.8608338748
H	4.2185522527	3.1032056166	0.8515774471
C	2.7819206461	4.6813501491	-1.0728420525
H	3.4129521419	4.7511345307	-1.9820402371
H	3.2483457444	5.3068549969	-0.2874481294
H	1.7868751106	5.0889616727	-1.3025739914
N	0.7303376875	2.8364743176	-1.8328762722
C	-0.6815152745	2.4990130240	-1.8497434794
H	-1.1358395244	2.7485933678	-0.8811578254
H	-0.8476474419	1.4154703881	-2.0254817712
H	-1.1787633225	3.0707085948	-2.6519026844
C	1.3731957306	2.8498876446	-3.1448820875
H	2.4660363094	2.8590522621	-3.0319989787
H	1.0663769926	3.7359628494	-3.7304835859
H	1.0962388627	1.9424523555	-3.7186848584
H	2.4425617116	1.1946926144	1.6959172847
H	1.8489285504	2.8581904024	1.8587687341
H	0.8923331544	1.4004257221	3.6156562401
H	-0.3789436063	2.0346581257	2.5413714739
H	0.7708991469	-1.4732422882	3.6132376167
H	1.9516992214	-0.6857179423	2.5360601814
H	-0.1772877205	-2.7207196237	1.6906948001
H	1.5621722790	-3.0236092372	1.8520774262
C	1.5225224562	-2.5635465551	-0.6940696383
N	1.5492326990	-3.9452806266	-0.6048015401
C	0.3976427933	-4.7027911733	-0.1404326171
H	-0.4708732658	-4.0404536328	-0.0261402704
H	0.1389152911	-5.4773821748	-0.8885370237
H	0.5881492609	-5.2097613255	0.8255562807
C	2.6739214752	-4.7366532231	-1.0833902290
H	2.4219759292	-5.3164908050	-1.9944424081
H	2.9805616987	-5.4546470850	-0.2985029247
H	3.5244699020	-4.0774498429	-1.3094409904
N	2.1121908158	-2.0319878481	-1.8275960808
C	2.5326904101	-0.6426067548	-1.8261118652
H	2.9692479649	-0.3866475720	-0.8510268050

H	1.6814095850	0.0488338043	-1.9982477960
H	3.2826540387	-0.4911546865	-2.6212262536
C	1.8049230579	-2.5787325648	-3.1472100901
H	1.2619278740	-3.5286883553	-3.0482523740
H	2.7270405651	-2.7522316774	-3.7317492615
H	1.1619905669	-1.8759051074	-3.7147217194

Optimized Cartesian Coordinates for $TMG_3tren\text{-}Cu^{II}$-MeCN (Å):

Cu	0.0193099639	-0.0079769823	0.0350911808
N	0.0303626521	0.0098251289	2.1896072043
N	2.0973053110	-0.1295813691	0.3066672392
N	4.2223587523	-0.7735166930	-0.5367706709
N	3.0042373341	0.9411780470	-1.5472427613
N	-1.1401866006	-1.7429723783	0.3392628793
N	-2.7680435799	-3.2749736189	-0.4690384095
N	-0.6882675754	-3.0795767947	-1.5084059831
N	-0.9325010187	1.8520918881	0.3079332981
N	-1.4630546494	4.0057115569	-0.5467332750
N	-2.3393320735	2.0785304470	-1.5279571124
N	0.0121151700	-0.0213889519	-1.9491881816
C	1.4525022068	0.1450507484	2.5989541955
H	1.5697618717	-0.1936206972	3.6455837752
H	1.7208315256	1.2101119693	2.5486611876
C	2.3552358391	-0.6338356092	1.6505195625
H	3.4083244511	-0.4902392641	1.9526351439
H	2.1411778537	-1.7162094083	1.7369971636
C	3.0796121168	-0.0100884500	-0.5635250602
C	5.5381295165	-0.2184138629	-0.8393384858
H	5.4778322490	0.8770148043	-0.9043259441
H	5.9462500191	-0.6164371795	-1.7877631051
H	6.2376651935	-0.4834484345	-0.0250510215
C	4.2051067707	-2.1814991441	-0.1644685387
H	3.1723865478	-2.5481891496	-0.1303243958
H	4.6812486036	-2.3580609059	0.8182260920
H	4.7551479903	-2.7657346990	-0.9251350620
C	2.3216884982	2.2057494680	-1.3272480634
H	2.1123917755	2.3190948322	-0.2557417929
H	1.3668850182	2.2601837852	-1.8795748761
H	2.9676891861	3.0361765239	-1.6670084089
C	3.5230576536	0.7218814502	-2.8901760220
H	3.7957177051	-0.3346110279	-3.0232288074
H	4.4064002463	1.3531232858	-3.1027616357
H	2.7432450322	0.9783364288	-3.6311947693
C	-0.5609937672	-1.2830530235	2.6211685402
H	-0.9053401194	-1.1998986438	3.6692352298
H	0.2270254359	-2.0488479667	2.5764687497
C	-1.6937681123	-1.6913050038	1.6873237947

H	-2.0935873123	-2.6692958076	2.0110831359
H	-2.5241493196	-0.9641202061	1.7673357829
C	-1.5377357946	-2.6631851730	-0.5151672666
C	-2.9436698517	-4.6946780439	-0.7604553611
H	-1.9640648911	-5.1857902765	-0.8431887606
H	-3.5120616252	-4.8556761896	-1.6960650685
H	-3.5030364817	-5.1672905998	0.0681722050
C	-3.9772543594	-2.5630878737	-0.0785630500
H	-3.7889718488	-1.4835924004	-0.0543533365
H	-4.3467197711	-2.8853219494	0.9130664155
H	-4.7709749982	-2.7594697610	-0.8228872178
C	0.7492721826	-3.1323907403	-1.3024950527
H	0.9638178028	-2.9636849945	-0.2394328846
H	1.2795012323	-2.3643630582	-1.8933041136
H	1.1304243117	-4.1257165752	-1.6045502626
C	-1.1556250407	-3.4263857895	-2.8429995853
H	-2.2079899577	-3.1321696648	-2.9627178818
H	-1.0568631163	-4.5084835222	-3.0516722804
H	-0.5527865409	-2.8845373584	-3.5954756812
C	-0.7916506477	1.1762775361	2.6043353844
H	-0.5350515755	1.4583286857	3.6428049698
H	-1.8482584159	0.8719886214	2.5814342725
C	-0.5953021821	2.3402627462	1.6400499363
H	-1.2424303223	3.1800224625	1.9523210559
H	0.4492342817	2.7024920365	1.6960179154
C	-1.5425960980	2.6332689200	-0.5597784874
C	-2.6090019576	4.8562773172	-0.8529214810
H	-3.5249598772	4.2508587797	-0.9004054322
H	-2.4795545896	5.3949041568	-1.8108420489
H	-2.7268165987	5.6068917127	-0.0494470720
C	-0.2356200706	4.7088903881	-0.2001776851
H	0.6019897297	4.0032506610	-0.1551462023
H	-0.3177599613	5.2313496937	0.7713119244
H	-0.0145584879	5.4612847831	-0.9798860462
C	-2.4179371406	2.6149233539	-2.8793740151
H	-1.6446459068	3.3817803620	-3.0288773779
H	-3.4100379143	3.0542110279	-3.0956844195
H	-2.2472317499	1.8006652233	-3.6078950711
C	-3.0782606068	0.8510195887	-1.2849101623
H	-3.0740572023	0.6376723713	-0.2082776383
H	-2.6352197095	-0.0106927803	-1.8149897852
H	-4.1203356776	0.9746418308	-1.6327622231
C	0.0122189954	-0.0275806326	-3.1047006210
C	0.0064795020	-0.0350857614	-4.5540629801
H	0.8139505843	-0.6860988911	-4.9300166131
H	0.1627149035	0.9881653572	-4.9357338998
H	-0.9614709175	-0.4133606722	-4.9240887862

Optimized Cartesian Coordinates for tren-Cu^{I}-MeCN (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-1.1782309766	1.7202841105	0.6663668782
N	2.0777448485	0.1623508715	0.6655534174
N	-0.8966195739	-1.8788278323	0.6631743707
N	0.0000000000	0.0000000000	2.7286093668
C	-0.8804327306	1.1163927300	3.0474330584
H	-0.6759060581	1.5450256698	4.0550198651
H	-1.9189091678	0.7427147914	3.0755556988
C	-0.8027708749	2.2312353475	2.0019035584
H	-1.4471032893	3.0717924089	2.3281739454
H	0.2284604004	2.6191702032	1.9327365242
C	1.4070764424	0.2037474321	3.0473230161
H	1.6765023156	-0.1895692608	4.0540686871
H	1.6031115859	1.2898067516	3.0781529835
C	2.3336548805	-0.4189948922	2.0005611009
H	3.3838139875	-0.2806538705	2.3262902056
H	2.1550997275	-1.5061052723	1.9306619827
C	-0.5272689231	-1.3208039286	3.0456600364
H	-1.0033729683	-1.3583422791	4.0519905648
H	0.3151926814	-2.0336571526	3.0766660152
C	-1.5289307100	-1.8116474883	1.9979711800
H	-1.9328651818	-2.7912612342	2.3225145104
H	-2.3822287498	-1.1147721611	1.9280490114
H	-2.1670483992	1.4702922949	0.6637096196
H	-1.0841618717	2.4620991797	-0.0245397833
H	-1.5840650720	-2.1703463966	-0.0289091185
H	-0.1836784049	-2.6082777357	0.6614450347
H	2.6726175991	-0.2894051416	-0.0261192277
H	2.3553749448	1.1437443550	0.6631039437
N	-0.0005339543	-0.0148043232	-1.9497009425
C	-0.0008346002	-0.0623458605	-3.1129356562
C	0.0002219605	-0.1242215687	-4.5650060243
H	0.6202331399	-0.9713235904	-4.9075003722
H	0.4107987203	0.8110964749	-4.9844571956
H	-1.0294346972	-0.2615338973	-4.9397654486

Optimized Cartesian Coordinates for tren-Cu^{I} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-1.1317124134	1.7468293462	0.2196741974
N	2.0801943137	0.1015872983	0.2214603659
N	-0.9473797701	-1.8552247820	0.2218408158
N	0.0000000000	0.0000000000	2.2759728150
C	-0.9111716294	1.1014454156	2.6133094999
H	-0.7182139104	1.5068363855	3.6294054105
H	-1.9403121594	0.7046743281	2.6222988159

C	-0.8370892781	2.2407367419	1.5915334160
H	-1.5318248919	3.0452332268	1.8999119903
H	0.1775640890	2.6735083315	1.5736068159
C	1.4090528446	0.2383745941	2.6142820474
H	1.6626411532	-0.1293418444	3.6314066758
H	1.5804781495	1.3279606800	2.6206678637
C	2.3597029842	-0.3976252382	1.5945853144
H	3.4034072348	-0.1971983467	1.9035512254
H	2.2278197576	-1.4928387655	1.5786471721
C	-0.4989571992	-1.3391070737	2.6146503439
H	-0.9465640360	-1.3733537227	3.6307806740
H	0.3584822830	-2.0328540880	2.6241241935
C	-1.5230999356	-1.8447988380	1.5932401249
H	-1.8737883487	-2.8478486959	1.9029263056
H	-2.4043335552	-1.1813006846	1.5739456084
H	-2.1298289567	1.5583697405	0.1307606430
H	-0.9312896556	2.4813994512	-0.4563033194
H	-1.6828909508	-2.0510508116	-0.4544017893
H	-0.2838603048	-2.6245981182	0.1351229717
H	2.6152755390	-0.4419268308	-0.4531050784
H	2.4180984745	1.0592724874	0.1302544118

Optimized Cartesian Coordinates for tren-Cu^{II}-MeCN (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-1.0796960871	1.8193349916	0.2311617485
N	2.1116885273	0.0363808177	0.2311532946
N	-1.0452319905	-1.8358002369	0.2284098309
N	-0.0000000000	-0.0000000000	2.1108927480
C	-0.9579407913	1.0629366704	2.5392835135
H	-0.7612807895	1.3326403058	3.5925951165
H	-1.9740224355	0.6435268711	2.4874810694
C	-0.8655306377	2.2728782959	1.6248504387
H	-1.6048985786	3.0307363236	1.9384210305
H	0.1302522474	2.7401355337	1.6792224094
C	1.3990848927	0.2974016442	2.5409014412
H	1.5348222267	-0.0133038844	3.5925150105
H	1.5428890208	1.3874644742	2.4947615066
C	2.4006796485	-0.3818966010	1.6223690075
H	3.4268730101	-0.1201022502	1.9348251862
H	2.3088226546	-1.4781731426	1.6718321017
C	-0.4425655043	-1.3614142393	2.5363542342
H	-0.7708315684	-1.3291476839	3.5909620505
H	0.4270990546	-2.0333760257	2.4787264713
C	-1.5410819008	-1.8801633902	1.6237453857
H	-1.8297479147	-2.8997269250	1.9342294743
H	-2.4413319591	-1.2486766199	1.6832233354
H	-2.0685761250	1.6368764864	0.0612551977

H	-0.8059430946	2.5389483546	-0.4348453688
H	-1.8080323497	-1.9539376539	-0.4353857243
H	-0.3964049115	-2.6031211888	0.0542301535
H	2.6017890684	-0.5532798516	-0.4385770486
H	2.4409575503	0.9874679171	0.0666432478
N	0.0039069334	0.0066496248	-1.9777819563
C	0.0035831832	0.0011698874	-3.1340458429
C	0.0056844726	-0.0076524299	-4.5818421911
H	0.6660763119	-0.8134437334	-4.9455509680
H	0.3720852444	0.9630529250	-4.9575823098
H	-1.0192468371	-0.1794997470	-4.9527224742

Optimized Cartesian Coordinates for tren-Cu^{II} (Å):

Cu	0.0000000000	0.0000000000	0.0000000000
N	-1.0574904602	1.7676135881	0.1020860928
N	2.0607692314	0.0294173802	0.1027858992
N	-1.0031603940	-1.8004259176	0.1033232887
N	0.0000000000	-0.0000000000	2.0817559821
C	-0.9620832928	1.0789988888	2.4495436507
H	-0.7631673388	1.3874890780	3.4918345254
H	-1.9759386104	0.6542971608	2.4120868518
C	-0.8558619376	2.2573618093	1.4927785463
H	-1.5990203782	3.0224205754	1.7742105346
H	0.1394022591	2.7252146276	1.5448965088
C	1.4152507867	0.2934553794	2.4503156508
H	1.5821834947	-0.0333647031	3.4926635315
H	1.5547979892	1.3837911270	2.4134006086
C	2.3834643215	-0.3878603757	1.4943258125
H	3.4171450838	-0.1253613517	1.7761301040
H	2.2924408931	-1.4837883285	1.5477060509
C	-0.4533676051	-1.3723890918	2.4506528135
H	-0.8198428613	-1.3536474474	3.4930307934
H	0.4211329047	-2.0382398144	2.4133089487
C	-1.5271212007	-1.8705409500	1.4944196179
H	-1.8169995750	-2.8968096717	1.7764975470
H	-2.4307009458	-1.2435299969	1.5471336697
H	-2.0483203229	1.5989227870	-0.0737683029
H	-0.7732574948	2.4788845507	-0.5698904950
H	-1.7619825424	-1.9095865058	-0.5678816030
H	-0.3624453532	-2.5746144189	-0.0734101297
H	2.5341630768	-0.5741973907	-0.5678703581
H	2.4114415463	0.9709884933	-0.0749351041

Computational Details for Truncated Phosphinimines

All density functional theory (DFT) calculations were performed with the ORCA program package, v3.0.3.[6] Geometry optimizations were carried out at the unrestricted B97-D3 level of density functional theory, and the def2-TZVP basis sets and the def2-TZVP/J auxiliary basis sets were used for all atoms.[8–12] The Conductor-like Screening Model (COSMO; dipole moment corresponding to acetonitrile) was used for all calculations.

The SCF calculations were tightly converged ($1x10^{-8}$ E_h in energy, $1x10^{-7}$ E_h in the density change, and $5x10^{-7}$ in the maximum element of the DIIS error vector). In all cases the geometries were considered converged after the energy change was less than $1x10^{-6}$ E_h, the gradient norm and maximum gradient element were smaller than $3x10^{-4}$ E_h-Bohr^{-1} and $1x10^{-4}$ E_h-Bohr^{-1}, respectively, and the root-mean square and maximum displacements of all atoms were smaller than $6x10^{-4}$ Bohr and $1x10^{-3}$ Bohr, respectively.

Numerical frequency calculations were used to verify that the calculated structures represented either local minima (ground states) or saddle points (transition states) on the potential energy surface. The natural bond orbital (NBO) analysis was carried out using the NBO 7.0 program,[17] which was run through Orca 3.0.

Optimized Cartesian Coordinates for Truncated Phosphinimines

Optimized cartesian coordinates for $HN=PH_3$ (Å):

N	-0.0044101046	-0.0113990753	-0.0102447061
H	0.7701242821	0.4710930781	-0.4579021470
P	0.0031430525	-0.0019097114	1.5545420656
H	-1.1231602222	-0.7034563960	2.0215855867
H	1.0465667792	-0.6199119912	2.3200177923
H	-0.0955093361	1.2103532854	2.3143239972

Optimized cartesian coordinates for $MeN=PMe_3$ (Å):

N	-0.0087153506	-0.0571707560	-0.0250901146
P	-0.0057528476	-0.0261432058	1.5347886226
C	1.0319372894	0.5323131665	-0.8453759047
H	2.0360831284	0.1028504921	-0.6709392549
H	0.7975748610	0.3554685076	-1.9031368854
H	1.1276680473	1.6273579785	-0.7241314008
C	1.3943281281	-0.8499452238	2.4034155982
H	2.3287241430	-0.3456578234	2.1366831130
H	1.2760465964	-0.8213920573	3.4918033496
H	1.4531015336	-1.8898673819	2.0688323946
C	-1.4909690908	-0.8839837962	2.1231183819
H	-1.5343221341	-0.8855820236	3.2165144556
H	-2.3727960665	-0.3800241142	1.7193424610
H	-1.4737046541	-1.9122713711	1.7528818564
C	-0.0499036465	1.6214597280	2.3569848484
H	-0.9218866748	2.1733987328	1.9939013007

H	-0.0984692282	1.5366421173	3.4477802710
H	0.8521882836	2.1794188195	2.0857058532

Optimized cartesian coordinates for MeN=PMe$_2$Ph (Å):

N	-0.0567087782	-0.1131895979	-0.0250838522
P	0.0056245328	-0.0106305676	1.5333422110
C	0.8736734930	0.5826381648	-0.8975001568
H	1.9329767483	0.3236357858	-0.7155681341
H	0.6550427462	0.3136856879	-1.9389404095
H	0.7999572332	1.6834484423	-0.8331683992
C	-1.3646941851	-0.9788228927	2.2219074663
H	-1.3202143968	-0.9857126330	3.3149885364
H	-2.3118790763	-0.5457070781	1.8880553149
H	-1.2869645516	-2.0018816625	1.8458099940
C	-0.1661384210	1.6571960747	2.2883121851
H	-1.0595560201	2.1217431890	1.8601539134
H	-0.2705816833	1.6198749767	3.3767899423
H	0.7063756563	2.2657513531	2.0335246884
C	1.5200893959	-0.7006267257	2.3193761491
C	2.2075249163	-1.6843822442	1.5934919159
C	2.0163706266	-0.3074665777	3.5701027253
C	3.3640874752	-2.2672793256	2.1105590405
H	1.8225312328	-1.9773529374	0.6197021325
C	3.1737477421	-0.8905445613	4.0873911258
H	1.5040968469	0.4555666534	4.1495067413
C	3.8490458844	-1.8712925302	3.3584668459
H	3.8897170325	-3.0275747472	1.5381372769
H	3.5495854988	-0.5783924804	5.0587628185
H	4.7523750290	-2.3227177814	3.7608745041

Optimized cartesian coordinates for MeN=PMePh$_2$ (Å):

N	0.0970262387	-0.0315581829	0.0091949509
P	0.0077075665	-0.0356436641	1.5715555166
C	1.3011460338	0.3499170233	-0.7074102884
H	2.1827323144	-0.2550388488	-0.4300641680
H	1.1369787692	0.2025013207	-1.7822972757
H	1.5851392020	1.4089028055	-0.5670557746
C	-1.5773831976	-0.7714569307	2.0524748400
H	-1.6775792013	-0.7975127201	3.1409087228
H	-2.3682078883	-0.1476028566	1.6282307345
H	-1.6609619128	-1.7782771161	1.6364256743
C	1.3248313523	-0.9445768599	2.4552141743
C	1.1634363133	-2.2788232966	2.8548782214
C	2.5888224296	-0.3467111102	2.5839110882
C	2.2347417310	-2.9925963583	3.3915225172
H	0.1984703581	-2.7664808522	2.7494057937
C	3.6615295517	-1.0635579915	3.1115854456

H	2.7284551364	0.6874372521	2.2796011198
C	3.4859873411	-2.3870310801	3.5202677786
H	2.0928585091	-4.0228339012	3.7083271669
H	4.6347446375	-0.5883997643	3.2058014722
H	4.3210668734	-2.9445329828	3.9364115762
C	0.0066687201	1.6068015143	2.3983643648
C	0.2482758646	1.7754611416	3.7684145321
C	-0.2847588936	2.7255478071	1.6082820360
C	0.1963629682	3.0461907772	4.3399489281
H	0.4883743524	0.9133693544	4.3859093652
C	-0.3321342352	3.9977821566	2.1799347939
H	-0.4747233740	2.5811048835	0.5474550634
C	-0.0922787894	4.1588770064	3.5455141987
H	0.3841227173	3.1707614406	5.4036363692
H	-0.5538998365	4.8628755273	1.5599792224
H	-0.1276115756	5.1497563862	3.9913018177

Optimized cartesian coordinates for $MeN{=}PPh_3$ (Å):

N	-0.0029981904	0.0264120888	-0.0253688928
P	-0.0191848020	-0.0065250730	1.5411469340
C	0.9225095730	0.8521582344	-0.7779893685
H	1.9824936480	0.5802457658	-0.6228725801
H	0.7142523624	0.7353770212	-1.8489287385
H	0.8312991876	1.9285490685	-0.5470386805
C	1.4478580183	-0.7560555676	2.3517963749
C	2.1477074726	-1.7217233123	1.6152796184
C	1.8767206109	-0.4357725427	3.6466153983
C	3.2575509441	-2.3597301661	2.1675157816
H	1.8096440438	-1.9590411855	0.6092714056
C	2.9853113332	-1.0773416102	4.1994713199
H	1.3501377594	0.3230652835	4.2187345445
C	3.6766863514	-2.0397287591	3.4607873765
H	3.7972242620	-3.1054766513	1.5891341197
H	3.3122921619	-0.8234958787	5.2048617565
H	4.5427190165	-2.5364413921	3.8909633723
C	-0.1992482400	1.6077935181	2.3769372923
C	-1.4478262638	2.0621115503	2.8241728690
C	0.8976207572	2.4843606446	2.4094796167
C	-1.5923989393	3.3598271257	3.3137798323
H	-2.3054078925	1.3959686841	2.7923807536
C	0.7493530070	3.7834631235	2.8929534222
H	1.8710291337	2.1447827120	2.0649693146
C	-0.4951190423	4.2226730795	3.3493220162
H	-2.5629470713	3.6980192756	3.6681723994
H	1.6055009441	4.4530966624	2.9144300876
H	-0.6093535624	5.2342710712	3.7302902325
C	-1.4277857121	-1.0230615030	2.0560151229
C	-2.3843016651	-1.3950715980	1.1043284932

C	-1.5798644384	-1.4212938404	3.3902025536
C	-3.4862398132	-2.1587052391	1.4891850464
H	-2.2378836911	-1.0799352490	0.0755857022
C	-2.6856064070	-2.1797428347	3.7715606238
H	-0.8338019350	-1.1432976683	4.1295370311
C	-3.6401756330	-2.5489911703	2.8211314852
H	-4.2265085154	-2.4492835860	0.7479741116
H	-2.7998622953	-2.4870211207	4.8079198413
H	-4.5004826625	-3.1434071885	3.1185742634

Optimized cartesian coordinates for $MeN{=}PMe_2(NEt_2)$ (Å):

N	-1.1403765433	-0.6752400976	1.0083269468
P	-0.1598100213	-0.0539115942	-0.0241859251
C	-1.1369240439	-0.4451174839	2.4366615670
H	-2.1528481242	-0.5840117850	2.8312175574
H	-0.4910177676	-1.1547914850	2.9840321967
H	-0.8166370242	0.5691733487	2.7373204271
C	-0.8609586834	-0.3017130944	-1.6820014265
H	-1.7978259734	0.2555795893	-1.7695977758
H	-0.1666019918	0.0284806257	-2.4607654252
H	-1.0660847419	-1.3680698574	-1.8061911226
N	1.4025465228	-0.7125662868	-0.0457666274
C	0.1143700296	1.7577166761	0.1011571517
H	0.5292887677	1.9803270888	1.0886676211
H	0.7988632004	2.1437779160	-0.6594023388
H	-0.8513836693	2.2619331983	-0.0014758321
C	1.6871834917	-1.8837674084	0.7934166473
C	2.4293981457	-0.3021696660	-0.9988705530
C	2.7364929326	-1.3128287055	-2.1099996687
H	3.3579659373	-0.0761116546	-0.4503140296
H	2.1134396344	0.6410229884	-1.4566018537
H	3.1548099125	-2.2381304126	-1.7026094962
H	3.4711808191	-0.8941737549	-2.8084546374
H	1.8308503191	-1.5675382330	-2.6701815019
C	1.0807785598	-3.2021699898	0.3035273235
H	1.3299048965	-1.6873386834	1.8095254986
H	2.7800965160	-1.9680428464	0.8581683736
H	-0.0103115135	-3.1257984933	0.3041393481
H	1.3697380203	-4.0234932886	0.9713019102
H	1.4162608978	-3.4490902738	-0.7082611972

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