Supporting Information for:

Conformational Dynamicity in a Copper(II) Coordination Complex

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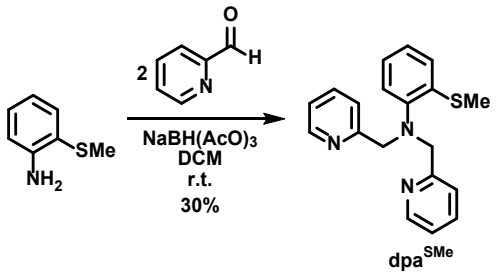
Table of Contents ***Page***

Scheme S1. Synthesis of dpa^{SMe}.



dpa^{SMe}: 2-(methylthio)aniline (1.130 g, 8.12 mmol) was added to a round-bottom flask equipped with a stir bar under N_2 and dissolved in DCM (74 mL, 0.11 M). 2-pyridinecarboxaldehyde (2.610 g, 24.4 mmol) was added to the stirring solution and the reaction mixture was allowed to stir for 30 min. Sodium triacetoxyborohydride (5.160 g, 24.4 mmol) was added in portions and the reaction mixture further permitted to stir overnight. Following extraction with sat. Na_2CO_3 (aq.), the aqueous layer was rinsed with DCM and the organic layers subsequently combined and dried over Na_2SO_4, concentrated under reduced pressure to provide a bright yellow oil. This oil solidified on standing under vacuum overnight to yield a crystalline solid, which was rinsed with 7:3 hexanes/EtOAc and filtered to afford the product as light-yellow crystals (0.794 g, 30%). ^{1}H NMR (CD_2Cl_2, 600MHz): 8.45 (dt, J_1 = 4.72, J_2 = 1.04 Hz, 2H), 7.63 (d, J = 7.74 Hz, 2H), 7.60 (td, J_1 = 7.23 Hz, J_2 = 1.66 Hz, 2H), 7.15-7.04 (m, 5H), 6.96 (td, J_1 = 7.59 Hz, J_2 = 1.43 Hz, 1H), 4.33 (s, 4H), 2.46 (s, 3H). ^{13}C NMR (CD_2Cl_2, 151MHz): 159.4, 149.2, 147.2, 136.7, 136.6, 125.2, 124.6, 124.3, 122.8, 122.7, 122.3, 59.6, 14.4. HRMS: ESI Positive ion mode m/z [M+1] calculated: 322.1378, found: 322.1380.

Table S1. UV-vis Absorption λ_{max} and ε of *d* → *d* features in Spectra of [CuCl(dpa^{SMe})]PF_6.

Solvent	λ_1 (nm)	λ_2 (nm)	ε_1 (M^{-1} cm^{-1})	ε_2 (M^{-1} cm^{-1})	$\varepsilon_1/\varepsilon_2$	$E_T(30)^a$
DCM	728	944	128	206	0.62	40.7
Acetone	725	930	126	182	0.69	42.2
DMF	720	923	147	195	0.75	43.2
MeCN	721	927	122	181	0.67	45.6
MeOH	727	922	115	154	0.75	55.4

[a] $E_T(30)$ indices for solvent polarity from reference 1.

Table S2. Crystal and Structural Refinement Data for $CuCl(dpa^{SMe})•0.5CH_2Cl_2$

Complex	$CuCl(dpa^{SMe})•0.5CH_2Cl_2$
Empirical formula	$C_{19.5}H_{20}Cl_2CuN_3S$
Formula weight	462.88
Temperature/K	100.0
Crystal system	monoclinic
Space group	I2/a
a/Å	16.8518(5)
b/Å	13.7158(4)
c/Å	17.8744(8)
α/°	90
β/°	103.7470(10)
γ/°	90
Volume/$Å^3$	4013.1(2)
Z	8
ρ_{calc}g/cm3	1.532
μ/mm^{-1}	1.468
F(000)	1896.0
Crystal size/mm^3	0.518 × 0.126 × 0.109
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.784 to 61.058
Index ranges	$-24 \leq h \leq 24$, $-19 \leq k \leq 19$, $-24 \leq l \leq 25$
Reflections collected	46699
Independent reflections	6126 [Rint = 0.0272, Rsigma = 0.0167]
Data/restraints/parameters	6126/0/241
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R1 = 0.0218, wR2 = 0.0556
Final R indexes [all data]	R1 = 0.0243, wR2 = 0.0571
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.32

[a] $R = \Sigma| |F_o|-|F_c| | / \Sigma |F_o|$. [b] $wR = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w(Fo^2)^2]\}^{1/2}$. [c] Goodness-of-fit = $\{\Sigma [w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table S3. Crystal and Structural Refinement Data for $[CuCl(dpa^{SMe})]PF_6 \cdot 0.5CH_2Cl_2$ Trigonal Bipyramidal Isomer

Complex	$[CuCl(dpa^{SMe})]PF_6$_TBP
Empirical formula	$C_{19}H_{21}ClCuF_6N_3OPS$
Formula weight	583.41
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.0079(3)
b/Å	18.5616(7)
c/Å	13.3009(5)
α/°	90
β/°	92.2550(10)
γ/°	90
Volume/Å^3	2222.20(14)
Z	4
ρ_{calc}g/cm^3	1.744
μ/mm^{-1}	1.338
F(000)	1180.0
Crystal size/mm^3	0.317 × 0.212 × 0.082
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.388 to 52.96
Index ranges	$-11 \le h \le 11$, $-23 \le k \le 23$, $-16 \le l \le 16$
Reflections collected	60578
Independent reflections	4569 [R_{int} = 0.0548, R_{sigma} = 0.0253]
Data/restraints/parameters	4569/0/302
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0421, wR_2 = 0.1222
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.1258
Largest diff. peak/hole / e Å^{-3}	1.24/-1.30

[a]$R = \Sigma| |F_o|-|F_c| | / \Sigma |F_o|$. [b]$wR = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w(Fo^2)^2]\}^{1/2}$. [c]Goodness-of-fit = $\{\Sigma [w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table S4. Crystal and Structural Refinement Data for [CuCl(dpa^{SMe})]PF_6•2CH_2Cl_2 Square Pyramidal Isomer

Identification code	[CuCl(dpaSMe)]PF6_SP
Empirical formula	$C_{20.75}H_{22}Cl_{4.5}CuF_6N_3PS$
Formula weight	713.51
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	11.4469(5)
b/Å	14.3440(7)
c/Å	19.0859(9)
α/°	69.367(2)
β/°	88.157(2)
γ/°	73.3880(10)
Volume/Å^3	2802.1(2)
Z	4
ρ_{calc}g/cm^3	1.691
μ/mm^{-1}	1.398
F(000)	1432.0
Crystal size/mm^3	0.376 × 0.331 × 0.196
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.124 to 55.224
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -24 ≤ l ≤ 24
Reflections collected	81376
Independent reflections	12905 [R_{int} = 0.0540, R_{sigma} = 0.0337]
Data/restraints/parameters	12905/0/739
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0568, wR_2 = 0.1587
Final R indexes [all data]	R_1 = 0.0633, wR_2 = 0.1679
Largest diff. peak/hole / e Å^{-3}	2.13/-1.28

[a]R = Σ| $|F_o|-|F_c|$ |/ Σ $|F_o|$. [b]*w*R = {Σ [*w*($F_o^2 - F_c^2$)^2]/ Σ*w*(Fo^2)^2]}$^{1/2}$.[c]Goodness-of-fit = {Σ [*w*($F_o^2 - F_c^2$)^2]/(*n*−*p*)}$^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

Table S5. Electrochemical Parameters from Cyclic Voltammetry.

Scan Rate (mV/s)	$E°'$ (V vs $Fc^{0/+}$)	i_a/i_c ($Cu^{II/I}$)	$E_a–E_c$ (V, $Cu^{II/I}$)	i_a/i_c ($Fc^{+/0}$)	$E_a–E_c$ (V, $Fc^{+/0}$)
25	–0.426	0.425	0.085	1.58	0.10692
50	–0.421	0.548	0.095	1.45	0.12199
75	–0.426	0.641	0.099	1.40	0.13693
100	–0.424	0.689	0.105	1.42	0.14696
150	–0.426	0.695	0.115	1.48	0.16204
200	–0.426	0.699	0.125	1.43	0.18226
300	–0.431	0.699	0.140	1.43	0.19708
400	–0.431	0.697	0.150	1.42	0.21698
500	–0.436	0.694	0.155	1.43	0.23238

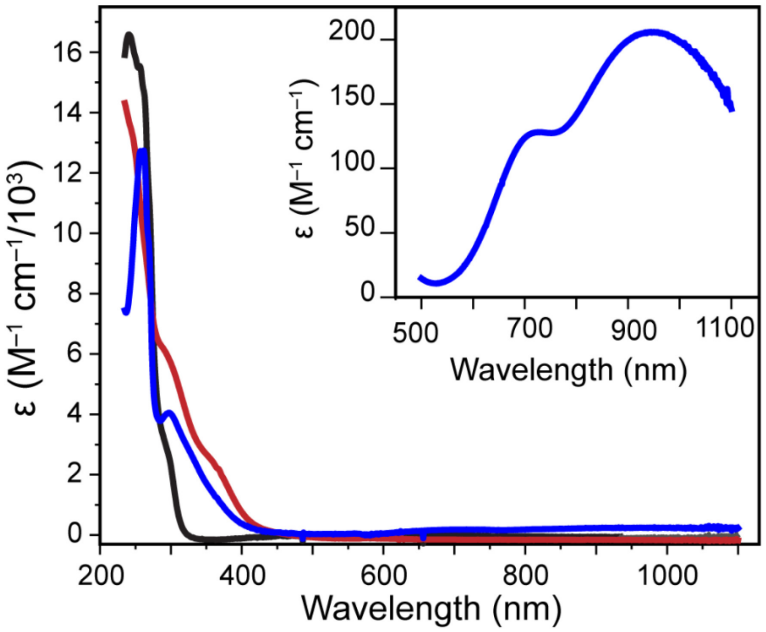


Figure S1. UV-vis absorption spectra of dpa^{SMe} (black), $CuCl(dpa^{SMe})$ (red), and $[CuCl(dpa^{SMe})]PF_6$ (blue) in DCM. Inset is the $d \rightarrow d$ transitions of the latter.

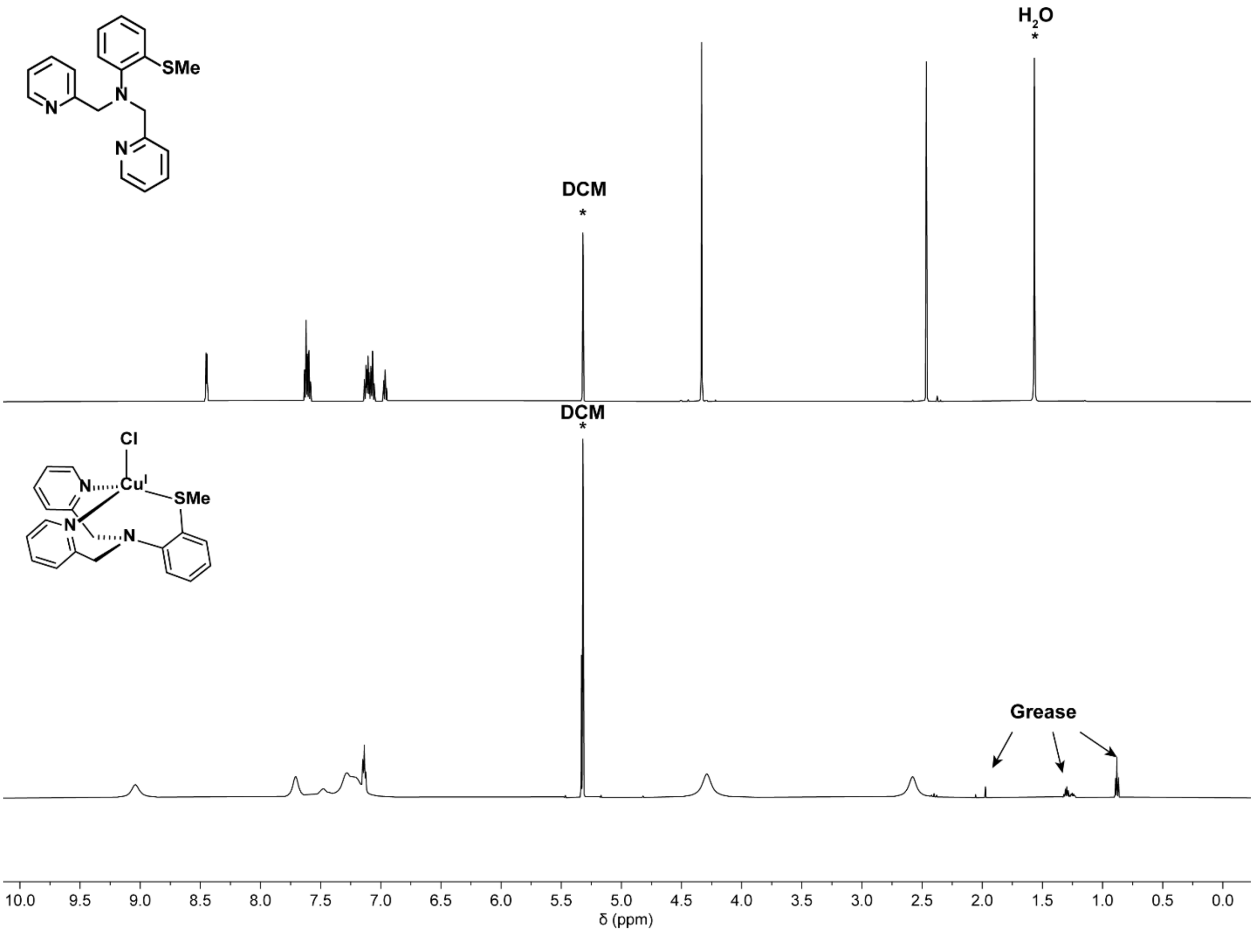


Figure S2. ^{1}H-NMR spectra of dpa^{SMe} (top) and CuCl(dpa^{SMe}) (bottom) collected in CD_2Cl_2 at 600 MHz. The deshielded resonances indicate ligand binding to Cu^{I} in solution.

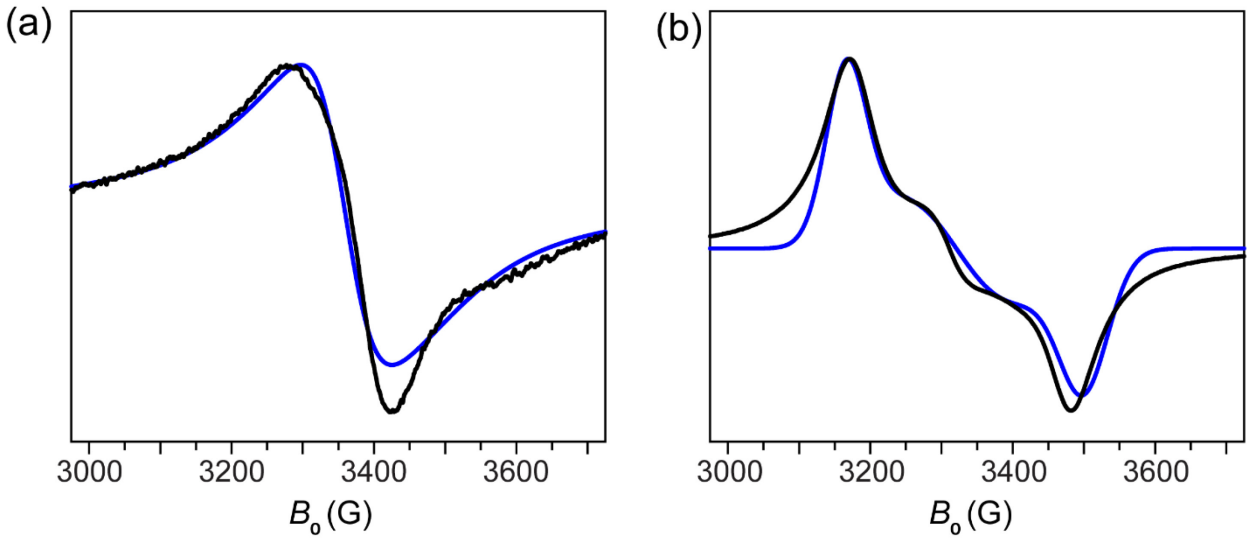


Figure S3. Powder EPR spectra (**–**) and simulations (**–**) for square pyramidal (a), and trigonal bipyramidal (b) $[CuCl(dpa^{SMe})]PF_6$ prepared as 50% v/v mixtures with $[NBu_4]PF_6$ as diluent. $[NBu_4]PF_6$ was recrystallized thrice before use.

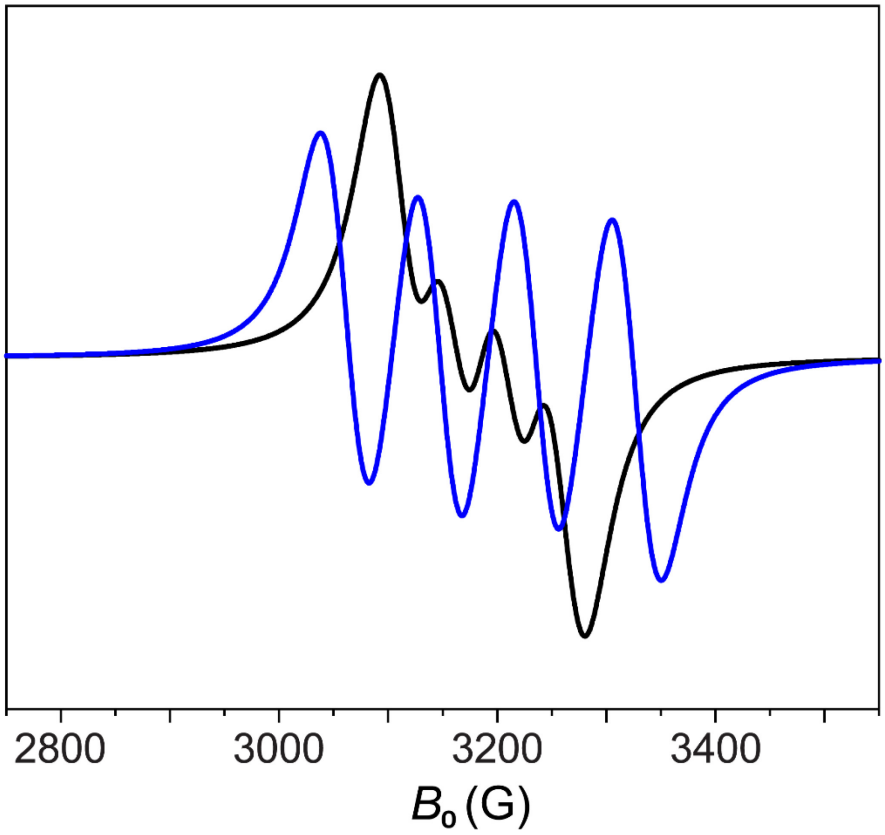


Figure S4. DFT calculated isotropic EPR spectra for trigonal bipyramidal (**–**) and square pyramidal (**–**) [CuCl(dpa^{SMe})]PF_6. Calculated at B3LYP using def-TZVPP basis set on non-H atoms and using the coordinates in Tables S6 and S7.

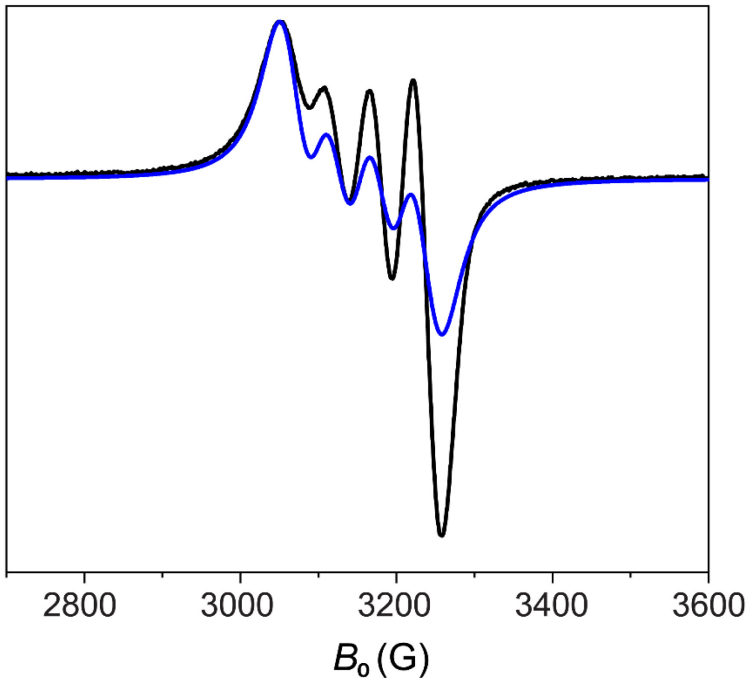


Figure S5. EPR spectrum (**–**), and simulation (**–**) of 3.6 mM [CuCl(dpa^{SMe})]PF_6 in 1:1 DCM:toluene at 280 K.

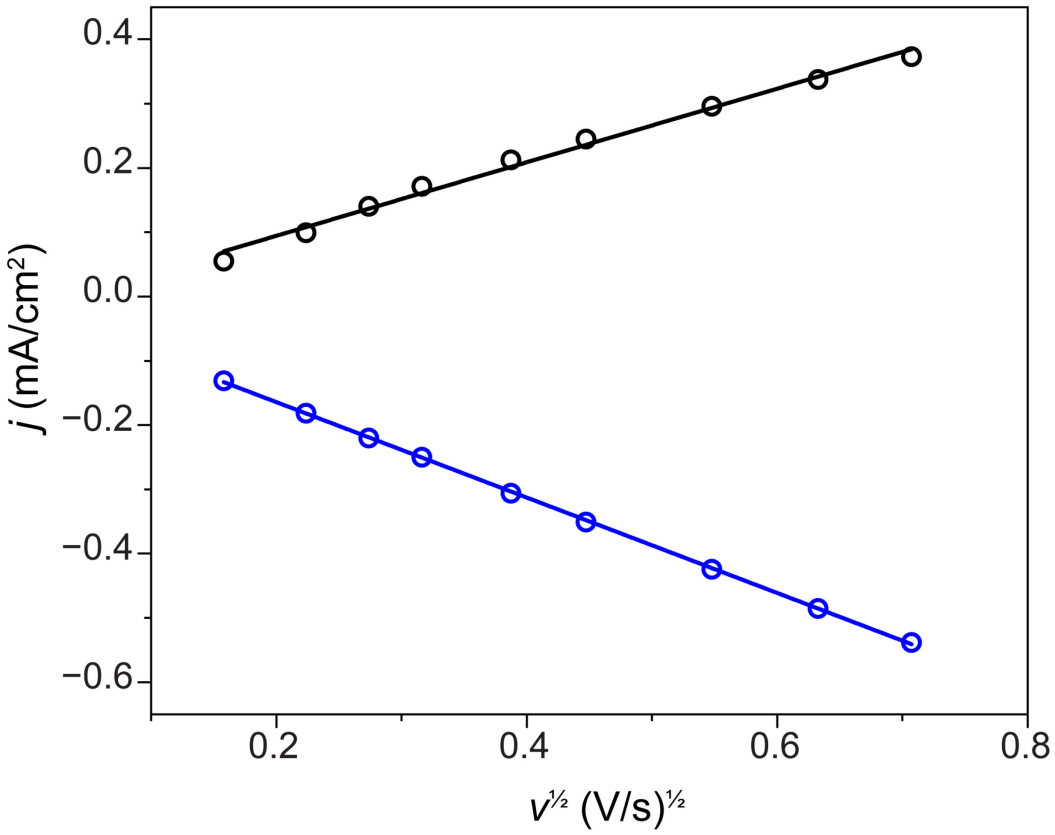


Figure S6. Plot of the current density (*j*, open circles) vs the square root of the scan rate ($v^{½}$) for 1 mM [CuCl(dpa^{SMe})]PF_6 in DCM with 100 mM [NBu_4]PF_6 as supporting electrolyte. Lines are linear fits for anodic (**–**, $R^2 = 0.999$) and cathodic (**–**, $R^2 = 0.999$) current densities.

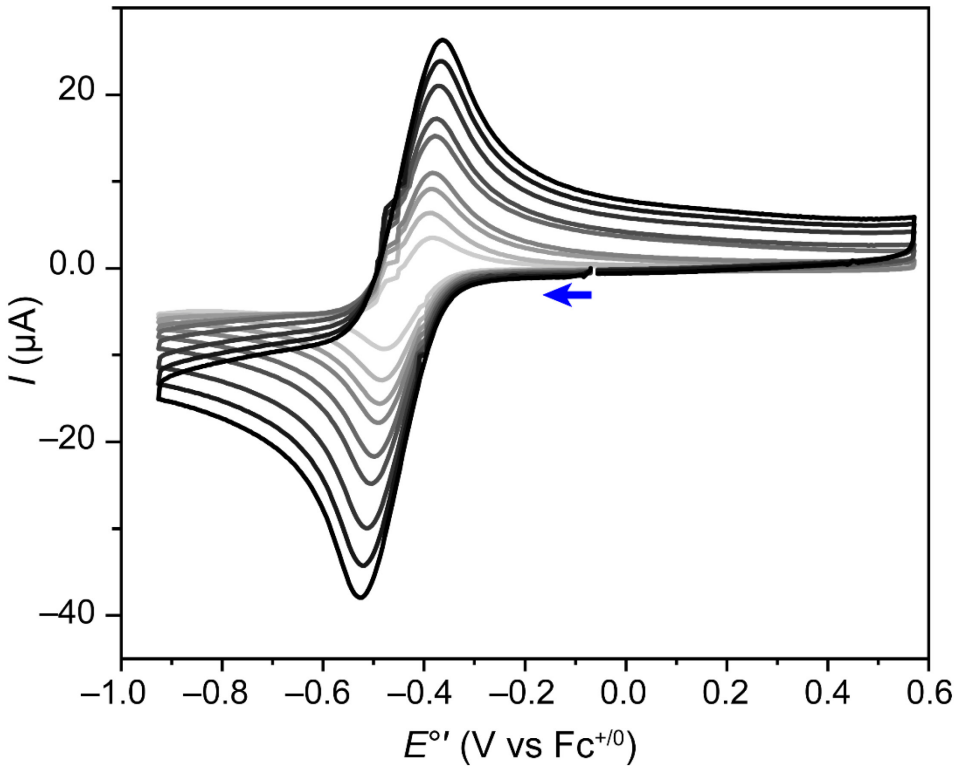


Figure S7. Cyclic voltammograms of 1 mM [CuCl(dpa^{SMe})]PF_6 in DCM with 100 mM [NBu_4]PF_6 as supporting electrolyte and scan rates from 25 mV/s – 500 mV/s (light to dark). All scans were initiated from OCP, as indicated by the arrowhead.

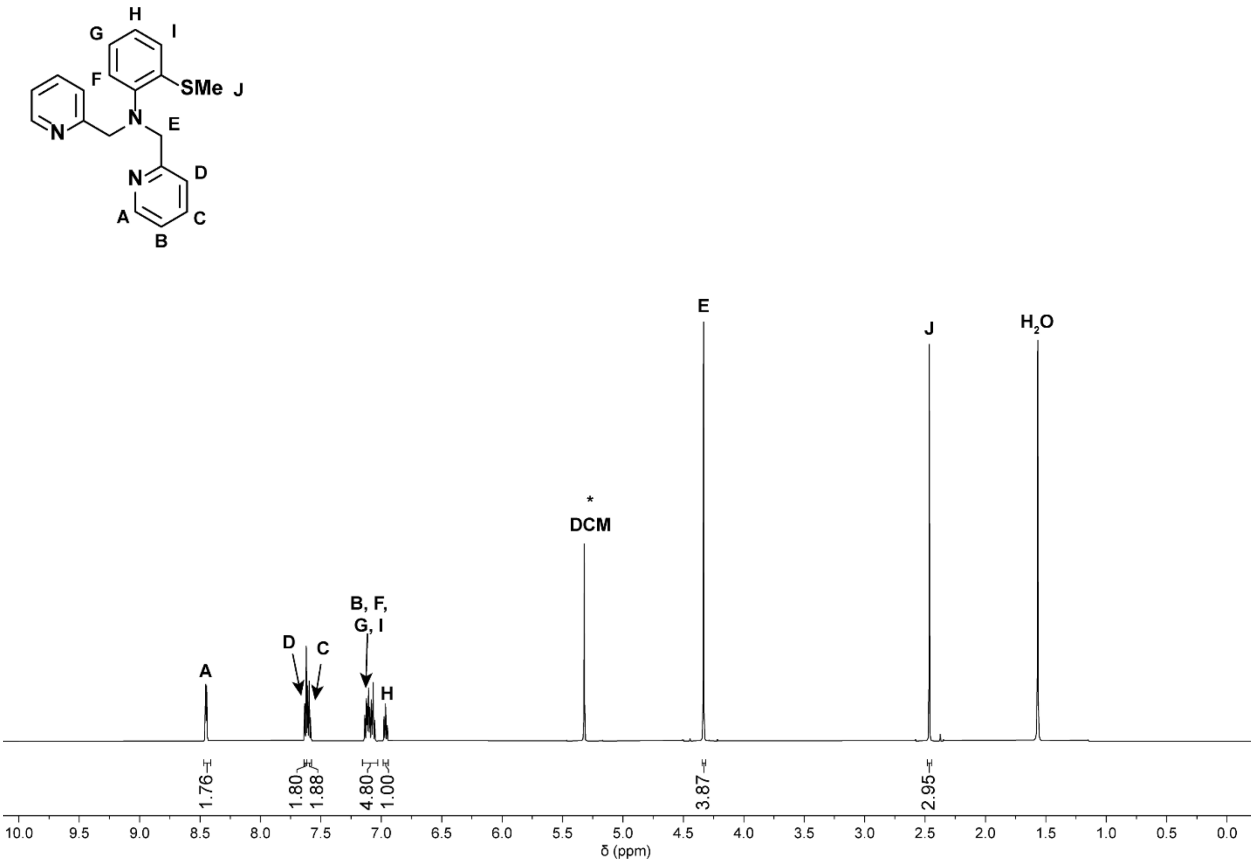


Figure S8. ^{1}H-NMR spectrum of dpa^{SMe} in CD_2Cl_2 measured at 600 MHz.

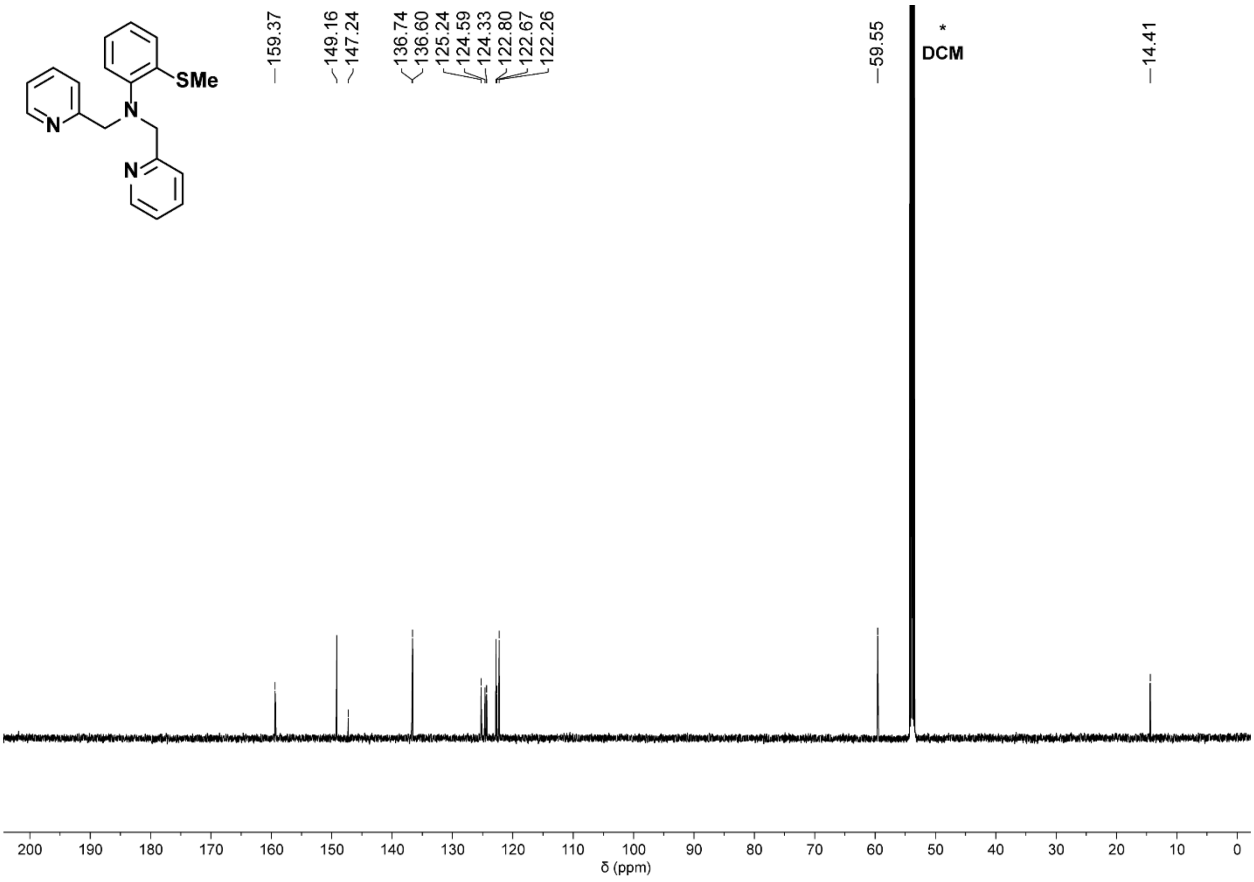


Figure S9. ^{13}C-NMR spectrum of dpa^{SMe} in CD_2Cl_2 measured at 600 MHz.

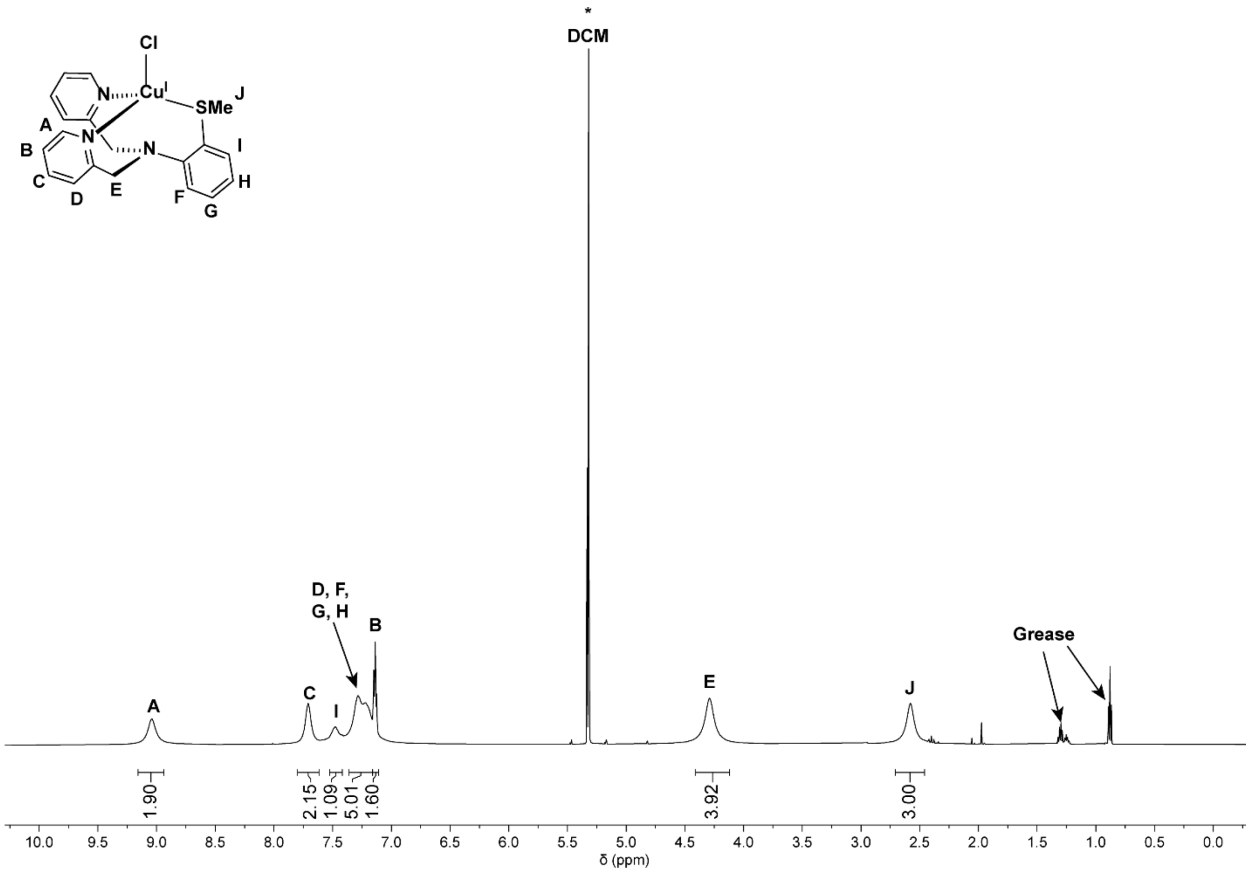


Figure S10. ^{1}H-NMR spectrum of CuCl(dpa^{SMe}) in CD_2Cl_2 at 600 MHz.

Table S6. DFT-Optimized Coordinates of Trigonal Bipyramidal Cu^{II}

Coordinates from ORCA-job A_TrigonalBipyramid

H	5.71307167381593	15.42803709033522	12.54893936201652
H	3.57282846394482	16.52155420483008	13.17923496933752
Cu	5.16728403166943	13.08966847613621	18.49792079407237
Cl	4.54253577263685	13.30843399606997	20.63119785815386
S	3.14977911315309	14.04986230519953	17.39570716003247
N	6.78486400128891	14.42977167759170	18.49843751577104
N	5.79981407192296	12.90397761218191	16.42602020649553
N	5.26060216941026	11.01848036715463	18.36751308624780
C	7.03784840610777	15.39847628604667	19.38343201013360
H	6.35631234510563	15.46219271002492	20.22241556871987
C	8.11683623698283	16.25907326744480	19.23585468883432
H	8.29818929849211	17.02864131929587	19.97328440010829
C	7.59383116622707	14.26350605590404	17.44133459648016
C	7.27037181783653	13.06747064729897	16.58406664137884
H	7.63558349521079	12.17113370158168	17.09284114964145
H	7.78435046267153	13.12026935719304	15.62383201932450
C	5.44154439041542	11.52194313754999	15.99662499976562
H	4.42733223490238	11.56234430213362	15.59388030851301
H	6.09148845238372	11.19024385189623	15.18101693310806
C	5.46487760020407	10.52826512977099	17.13616093193665
C	5.61320525037900	9.16595885736278	16.91371812362350
H	5.78106980507071	8.79112669594066	15.91215277783301
C	5.53647264541985	8.29727356779946	17.99571605278068
H	5.64801283087316	7.23090224521089	17.84627458109293
C	5.31978480880285	8.81384018531889	19.26659303192864
H	5.25310537119605	8.17088217968112	20.13301665018772

C	5.18966733004452	10.18544109035025	19.41353579714076
H	5.01742072274336	10.65367838497779	20.37409901197889
C	5.19753829553463	13.90862806250166	15.54251810092916
C	5.79615765639018	14.23645072751473	14.32677912055574
H	6.71773276018767	13.75865866930934	14.02317207171799
C	5.22631800841158	15.17976806881943	13.48297603006379
C	4.02995795203279	15.79263110488056	13.83532670335653
C	3.40940432785086	15.45105948251414	15.02701579071365
H	2.46377432596629	15.90675664791095	15.28805053815407
C	3.98491089327004	14.51900496296428	15.89206738584543
C	2.83991640259060	15.64654826168290	18.21834854653800
H	3.74755812781032	16.24375264210280	18.24365990997795
H	2.03655718788466	16.17855359787981	17.71506257503546
H	2.53591121145513	15.38947673026944	19.23181976583679
C	8.94461586447348	16.10905320777737	18.13184930440258
H	9.78729073787937	16.77121651686474	17.98062520405335
C	8.67927884130601	15.09639854820421	17.21576115968961
H	9.31031343804450	14.95168406652096	16.34889656649139

Table S7. DFT-Optimized Coordinates of Square Pyramidal Cu^{II}

Coordinates from ORCA-job A_SquarePyramidal

Cl	15.44065252281358	16.05253981756838	10.26685394889865
C	12.83075231567409	16.11592014213865	8.19570106823886
H	13.32687437350123	15.39253831613503	8.82922274852351
C	11.87626582804126	15.75618215008374	7.25729449612345
H	11.60346403050531	14.71670212393609	7.13704290236684
H	13.45402634957670	17.57629749870401	13.55910208707328
Cu	14.46284404599870	18.02136678640489	9.83778724236516
S	12.52969050859586	18.43555903785753	11.56272864782432
N	13.20670319399357	17.39133253218593	8.36840698134472
N	13.79800389590317	20.00661477702466	9.11707996566478
N	15.87630808089171	19.17350720768153	10.74764451179371
C	11.27828747646036	16.75116959526370	6.49559633778799
H	10.51736721147263	16.50401686696960	5.76670193092974
C	11.66994140070464	18.07081277675324	6.68003645040880
H	11.22667123221139	18.86913433056461	6.09954569902159
C	12.65191847311893	18.35704605066997	7.61847059630088
C	13.22089354324402	19.74847029869540	7.76405010240817
H	14.02031802343280	19.85881143892004	7.02726075256919
H	12.46148530935719	20.48961740572458	7.51428739951747
C	15.11758860927547	20.69967771781045	9.04909478093031
H	15.01573747314782	21.77184565786589	8.87171672395371
H	15.66032805802898	20.28003065034948	8.19834953382538
C	15.93700572397284	20.43309007596378	10.28588467517421
C	16.77347981294870	21.37495681485239	10.86415695490709
H	16.80484438965296	22.38512068522842	10.47780372294281
C	12.25271576520161	20.13790764157111	11.10984710324876

C	12.85147987571350	20.72448872862395	9.98625833067631
C	12.52550267357480	22.04334232744070	9.65543967620797
H	12.96535918303564	22.50009164987695	8.77725831712444
C	11.64747986014602	22.78745786147900	10.42550548894815
H	11.40720124292322	23.80321708024330	10.13932686983746
C	11.06294409716581	22.20979418328779	11.54819113130206
H	10.36781715974085	22.77346853878154	12.15650390835832
C	11.35770075805901	20.89813466192779	11.87418586309239
H	10.87316772805474	20.43994191419085	12.72598442005305
C	13.14145236894190	18.57987317467782	13.27290819597634
H	12.34580845746053	18.91141283095066	13.93609761833432
H	13.98854271242762	19.25994700536830	13.32872057770187
H	16.56965344546282	17.76181664237147	12.06884696970766
C	17.57371258133725	20.99555213091224	11.93655407717731
H	18.23352844762428	21.71494615118008	12.40416261949379
C	17.51740644292002	19.68626458456410	12.39307166832485
H	18.13174717745572	19.34856744749315	13.21620448381974
C	16.65110814023022	18.79891468970643	11.77141241972016

References

1 C. Reichardt, *Chem. Rev.*, 1994, 94, 2319–2358.