Meridional vs. Facial Coordination Geometries of a Dipodal Ligand Framework Featuring a Secondary Coordination Sphere

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General Considerations. All manipulations were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere except where specified otherwise. All glassware was oven dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. Solvents were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves purchased from Strem following literature procedure prior to use. Chloroform-*d*, Tetrahydrofuran-d_8 and Acetontrile-d_3 were purchased from Cambridge Isotope Labs and were degassed and stored over 4 Å molecular sieves prior to use. 2,2'-bipyridine was purchased from Sigma-Aldrich and recrystallized from diethylether under an inert atmosphere prior to use. Ferrous chloride, cuprous chloride, and potassium carbonate were purchased from Strem and used as received. Cyclohexylamine was purchased from Acros and used as received. Dimethylformamide and sodium hydroxide were purchased from Fisher and used as received. $POCl_3$ and hydrochloride etherate (2.0 M) were purchased from Sigma Aldrich and used as received. Ferrous triflate and cuprous triflate were prepared according to literature procedures. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 ℃ prior to use in a drybox. NMR Spectra were recorded at room temperature on a Varian spectrometer operating at 400, 500 MHz (^{1}H NMR) and 126 MHz (^{13}C NMR) and referenced to the residual solvent resonance (δ in parts per million, and *J* in Hz).

Physical Measurements: Cyclic voltammetry was performed under nitrogen at room temperature using a CH Instruments CHI600D electrochemical analyzer with a glassy carbon working electrode, Pt wire counter electrode, and the pseudoreference electrode Ag wire. Zero-field, ^{57}Fe Mössbauer spectra were measured on a constant acceleration spectrometer (SEE Co, Minneapolis, MN) with a Janis SVT-100 cryostat. Isomer shifts are quoted relative to α-Fe foil (< 25 μm thick) at room temperature. Samples were prepared using approximately 30 mg of sample suspended in paratone-N oil. Temperatures were controlled using a LakeShore 321 autotuning temperature controller. Temperature variations were no greater than ±10 K, and were generally within ±2 K. Data were analyzed using an in-house package in Igor Pro (Wavemetrics). Elemental analysis was performed by Complete Analysis Laboratories, Inc. in Parsippany, NJ and the University of Illinois at Urbana-Champaign School of Chemical Sciences Microanalysis Laboratory in Urbana, IL.

Preparation of H_2dpma. This preparation is a slight modification of the literature procedure[1]. In a 500 mL round bottom flask methylamine hydrochloride (6.81 g, 0.101 mol) and aqueous formaldehyde (37%, 16.35 g, 0.202 mol) were combined in 100 mL of absolute ethanol. The colorless solution was heated to 55 ºC. Once the methylamine hydrochloride was dissolved, pyrrole (13.49 g, 0.201 mol) was added drop-wise to the reaction. The resulting mixture was stirred at 55 ºC for 4 h; during this time the solution developed a red-brown color. After cooling the reaction to room temperature, volatiles were removed under reduced pressure to yield the crude product as a thick brown oil. This oil was then diluted with water (~100 mL), and basified by slow addition of anhydrous K_2CO_3. The product was extracted with chloroform (3x, 50 mL). Volatiles were again removed under reduced pressure, yielding the neutralized product as a thick

brown oil. This oil was triturated with a Et_2O/DCM mixture (10:1, 50 mL), resulting in an off-white powder (14.62 g, 0.077 mol, 77%). ^{1}H NMR was consistent with the formation of the desired product, despite minor differences from the published data. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ = 2.44 (3H, s, $CH_2NC\mathit{H_3}$), 4.16 (4H, s, $C\mathit{H_2}NCH_3$), 6.13 (2H, m, 3-C_4H_3N), 6.24 (2H, m, 4-C_4H_3N), 6.92 (2H, m, 5-C_4H_3N), 10.39 (2H, s, N(*H*)-pyrrole)

Preparation of $H_2[^{Me}N(pi^{Cy})_2]\bullet H_2O$. In a 500 mL three-neck round bottom flask di(pyrrolyl-α-methyl)methylamine (H_2dpma) (3.8767 g, 0.021 mol) and DMF (9.50 mL, 0.12 mol) were combined in 10 mL of 1,2-dichloroethane. The dark brown solution was cooled to -10 °C. The flask was fitted with an addition funnel containing a solution of $POCl_3$ (9.50 mL, 0.10 mol) in 1,2-dichloroethane (20 mL), then purged with nitrogen for 5-10 minutes. The $POCl_3$ solution was added drop-wise over an hour with vigorous stirring. The mixture was removed from the ice bath and heated to 50 °C for one hour. The reaction mixture was allowed to cool to room temperature, before adding a saturated solution of aqueous sodium acetate (42 g, 0.51 mol). The contents were heated to 50 °C for two hours. After cooling the reaction to room temperature, the mixture was neutralized by slow addition of anhydrous Na_2CO_3, resulting in copious evolution of CO_2. The product was extracted with dichloromethane (3x, 150 mL). Volatiles were removed under reduced pressure to yield the preligand, H_2dpma^{CO}, as a dark brown oil. The oil was dissolved in approximately 250 mL dry acetonitrile. Cyclohexyamine (H_2NCy) (6.1061 g, 0.062 mol) was added dropwise and the mixture was stirred for 16 hours. The product, $H_2[^{Me}N(pi^{Cy})_2]\bullet H_2O$, precipitates from solution as a tan powder, which is isolated by filtration (6.8003 g, 0.016 mol, 78 %). Analysis for $C_{25}H_{37}N_5\bullet H_2O$: Calcd. C, 70.55; H, 9.24; N, 16.45. Found C, 70.19; H, 9.12; N, 15.99. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.16 – 1.83 (m, 20 H, Cy-C$\mathit{H_2}$), 2.24 (s, 3H, NC$\mathit{H_3}$), 3.07 (tt, *J* = 10.9, 3.5 Hz, 2H, Cy-C*H*), 3.56 (s, 4H, NC$\mathit{H_2}$), 5.99 (d, *J* = 3.4 Hz, 2H, Ar-C*H*), 6.37 (d, *J* = 3.5 Hz, 2H, Ar-C*H*), 7.96 (s, 2H, imine-C*H*). ^{13}C NMR (101 MHz, C_6D_6, 25 °C): δ = 25.31 (Cy-C3,C5), 26.00 (Cy-C4), 35.20 (Cy-C2,C6), 42.05 (methyl-C), 54.71 (methylene-C), 69.09 (Cy-C1), 107.92 (pyr-C), 116.47 (pyr-C), 129.77 (pyr-C), 136.42 (pyr-C), 150.52 (imine-C).

Preparation of $H_2[^{Me}N(pi^{Cy})_2]$ (1). The water adduct of the ligand, $H_2[^{Me}N(pi^{Cy})_2]\bullet H_2O$, was dried in the glovebox under a dry, inert atmosphere. Ligand (4.1971 g, 9.86 mmol) was dissolved in a minimal amount of dry DCM (~20 mL), molecular sieves were added, then the solution was diluted with dry Et_2O (~80 mL). The solution was dried at room temperature over 48 hr, then filtered to separate the sieves and a small amount of precipitate. Volatiles were removed in vacuo to yield the dried ligand $H_2[^{Me}N(pi^{Cy})_2]$ (3.5824 g, 8.79 mmol, 89%) Analysis for $C_{27}H_{35}N_5$: Calcd. C, 73.67; H, 9.15; N, 17.18. Found C, 73.54; H, 9.33; N, 16.95. ^{1}H NMR (500 MHz, CD_3CN, 25 ºC): δ = 1.24-1.29 (m, 2H, Cy-C$\mathit{H_2}$), 1.33-1.48 (m, 8H, Cy-C$\mathit{H_2}$), 1.63-1.70 (m, 6H, Cy-C$\mathit{H_2}$), 1.77-1.80 (m, 4H, Cy-C$\mathit{H_2}$), 2.04 (s, 3H, NC$\mathit{H_3}$), 3.09 (tt, *J* = 9.8, 4.1 Hz, 1H, Cy-C*H*), 3.49 (s, 4H, NC$\mathit{H_2}$), 6.00 (d, *J* = 3.2 Hz, 2H, Ar-C*H*), 6.31 (d, *J* = 3.2 Hz, 2H, Ar-C*H*), 8.03 (s, 2H, imine-C*H*), 9.50 (broad, 2H, pyrrole N*H*). ^{13}C NMR (126 MHz, C_6D_6, 25 °C): δ = 25.17 (Cy-C3,C5), 26.10 (Cy-C4), 35.31 (Cy-C2,C6), 41.55 (methyl-C), 53.95 (methylene-C), 69.43 (Cy-C1), 109.17 (pyr-C), 113.62 (pyr-C), 131.02 (pyr-C), 132.97

(pyr-C), 148.93 (imine-C).

Preparation of [^{Me}N(afa^{Cy})$_2$]MCl$_2$ [M = Fe (2); Cu (5)]. A 20 mL scintillation vial was charged with MCl_2 (M = Fe, 0.013 g, 0.103 mmol; Cu, 0.014 g, 0.104 mmol) and approximately 3 mL of THF. In a separate vial, $H_2[^{Me}N(pi^{Cy})_2]$ (0.044 g, 0.108 mmol) was dissolved in 3 mL of THF and added drop wise with vigorous stirring to the previously prepared MCl_2 slurry.

[^{Me}N(afa^{Cy})$_2$]FeCl$_2$ (2). Upon addition of the ligand, formation of an orange suspension was observed, with simultaneous dissolution of $FeCl_2$. After one hour, solvents were removed under reduced pressure and the remaining orange residue was washed with diethyl ether and dried *in vacuo*. The product, $[^{Me}N(afa^{Cy})_2]FeCl_2$, was isolated as an orange powder in high yields (> 90 %). For analytically pure samples, **2** was crystallized by vapor diffusion of a THF/MeCN solution (3:1) with Et_2O (0.037 g, 0.070 mmol, 68%). Crystals suitable for X-ray analysis were grown from a solution of acetonitrile layered with diethyl ether. Analysis for $FeC_{25}H_{37}N_5Cl_2$: Calcd. C, 56.19; H, 6.98; N, 13.11. Found C, 56.00; H, 6.99; N, 12.86. ^{1}H NMR, (500 MHz, CD_3CN, 25 ºC) δ = -5.80, -3.73, -1.50, -1.34, -0.42, -0.79, 11.72, 42.49, 55.29, 138.54, 154.16.

[^{Me}N(afa^{Cy})$_2$]CuCl$_2$ (5). Upon addition of the ligand, a gradual color change to green was observed. The mixture was stirred overnight, after which time residual solvents were removed under reduced pressure. The green residue was washed with THF and dried *in vacuo*. The product was isolated as a green powder in quantitative yields. Due to the insolubility of **5**, bulk recrystallization of the compound was not possible. Crystals suitable for X-ray analysis were grown from a solution of DMA/MeCN (1:1) layered with diethyl ether. Analysis for $CuC_{25}H_{37}N_5Cl_2$: Calcd. C, 55.40; H, 6.88; N, 12.92. Found C, 55.18; H, 6.77; N, 12.43.

Preparation of [^{Me}N(afa^{Cy})$_2$]M(OTf)$_2$ [M = Fe (3); Cu (6)]. A 20 mL scintillation vial was charged with $M(OTf)_2(MeCN)_2$ (M = Fe, 0.043 g, 0.098 mmol; Cu, 0.044 g, 0.099 mmol) and approximately 3 mL of THF. In a separate vial, $H_2[^{Me}N(pi^{Cy})_2]$ (0.041 g, 0.101 mmol) was dissolved in 3 mL of THF and added drop wise with vigorous stirring to the previously prepared $M(OTf)_2$ slurry.

[^{Me}N(afa^{Cy})$_2$]Fe(OTf)$_2$(THF)$_2$ (3). Upon addition of the ligand, an immediate color change to yellow was noted. The reaction mixture was stirred for an hour to ensure conversion. Solvents were removed *in vacuo*. The resulting yellow residue was washed with diethyl ether. The product was isolated as a yellow powder in high yields (>90%) and was used for subsequent experiments. For analytically pure samples, **3** was crystallized by vapor diffusion of a THF/MeCN solution (3:1) with Et_2O (0.052 g, 0.057 mmol, 58%). Crystals suitable for X-ray analysis were grown using the same conditions. Analysis for $FeC_{35}H_{53}N_5O_8F_6S_2$: Calcd. C, 46.41; H, 5.90; N, 7.73. Found C, 46.27; H, 5.84; N, 7.81.

[^{Me}N(afa^{Cy})$_2$]Cu(OTf)$_2$ (6). After addition of the ligand, an immediate color change to green was observed. The reaction mixture was stirred for an additional hour to ensure

complete conversion, after which time solvents were removed under reduced pressure. The resulting green residue was washed with diethyl ether (2 x 5 mL) and dried *in vacuo*, leaving the product as a green powder in high yields (>90%) and was used for subsequent experiments. Analytically pure product was obtained by recrystallization from a concentrated solution of acetonitrile layered with diethyl ether (1:2) (0.063 g, 0.082 mmol, 84 %). Crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a concentrated acetonitrile/benzene solution (1:1) of the product. Analysis for $CuC_{27}H_{37}N_5O_6F_6S_2$: Calcd. C, 42.15; H, 4.85; N, 9.10. Found C, 42.34; H, 4.76; N, 8.89.

Preparation of [^{Me}N(afa^{Cy})$_2$]M(bipy)(OTf)$_2$ [M = Fe (4); Cu (7)]. A 20 mL scintillation vial was charged with [^{Me}N(afa^{Cy})$_2$]M(OTf)$_2$ (M = Fe, 0.090 g, 0.100 mmol; 0.076 g, 0.099 mmol) and approximately 3 mL of THF. An equivalent of 2,2'-bipyridine (0.016 g 0.102 mmol) was weighed by difference and added as a solid to the metal solution.

[^{Me}N(afa^{Cy})$_2$]Fe(bipy)(OTf)$_2$ (4). Following addition of 2,2'-bipyridine, an immediate and striking color change to a dark red was noted. The mixture was stirred for 45 minutes to ensure complete conversion, after which time solvents were removed under reduced pressure. The product was isolated as a dark pink powder in high yields (>90%). Crystals of complex **4** suitable for X-ray analysis were grown from a concentrated MeCN/Et_2O solution (3:1) at -35 °C. Due to the instability of complex **4**, elemental analysis could not be obtained.

[^{Me}N(afa^{Cy})$_2$]Cu(bipy)(OTf)$_2$(THF) (7). Following addition of 2,2'-bipyrdine, an immediate color change to brown was observed. The mixture was stirred for two hours, after which time an off white precipitate had formed. The solid was collect by filtration, washing multiple times with diethyl ether to insure purity. The product was isolated as an off-white powder in good yields (0.086 g, 0.082 mmol, 83 %). Analytically pure species was isolated via recrystallization from a concentrated solution of acetonitrile layered with diethyl ether (1:3). Crystals suitable for X-ray diffraction were grown from slow diffusion of diethyl ether and acetonitrile (2:1). Analysis for $CuC_{41}H_{53}N_7O_7F_6S_2$: Calcd. C, 49.36; H, 5.35; N, 9.83. Found C, 49.41; H, 5.21; N, 10.18.

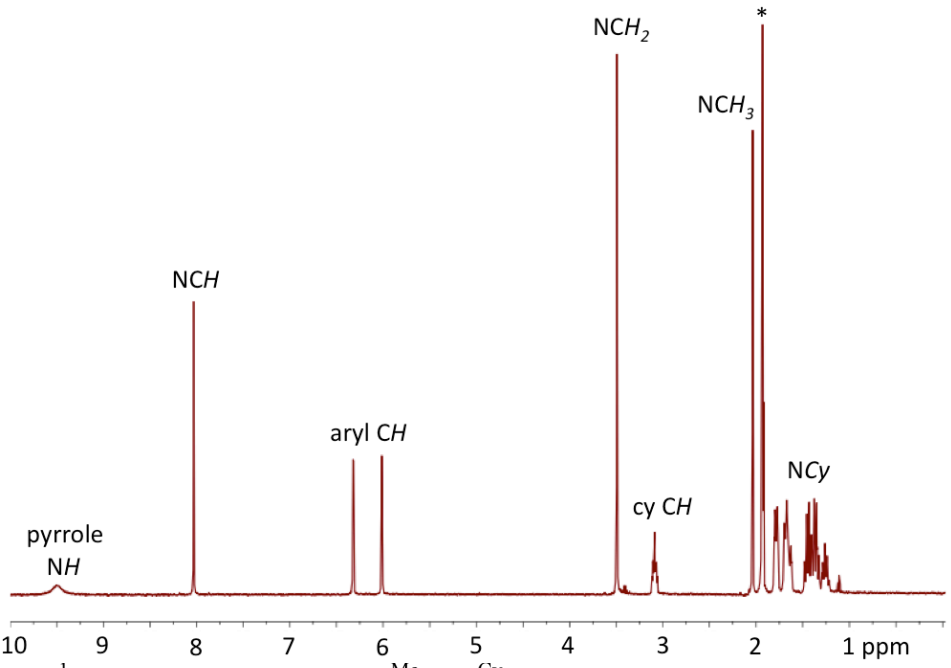

Figure S1. ^{1}H NMR Spectrum of $H_2[^{Me}N(pi^{Cy})_2]$ (**1**) (500 MHz, CD_3CN, 25 °C)

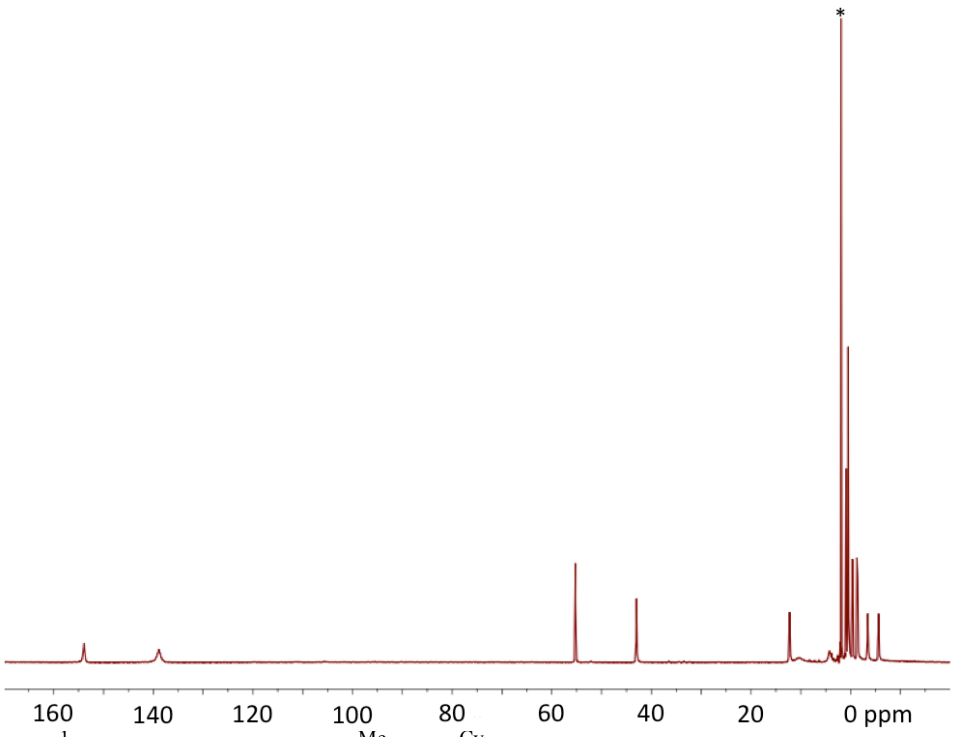

Figure S2. ^{1}H NMR Spectrum of $[^{Me}N(afa^{Cy})_2]FeCl_2$ (**2**) (500 MHz, CD_3CN, 25 °C)

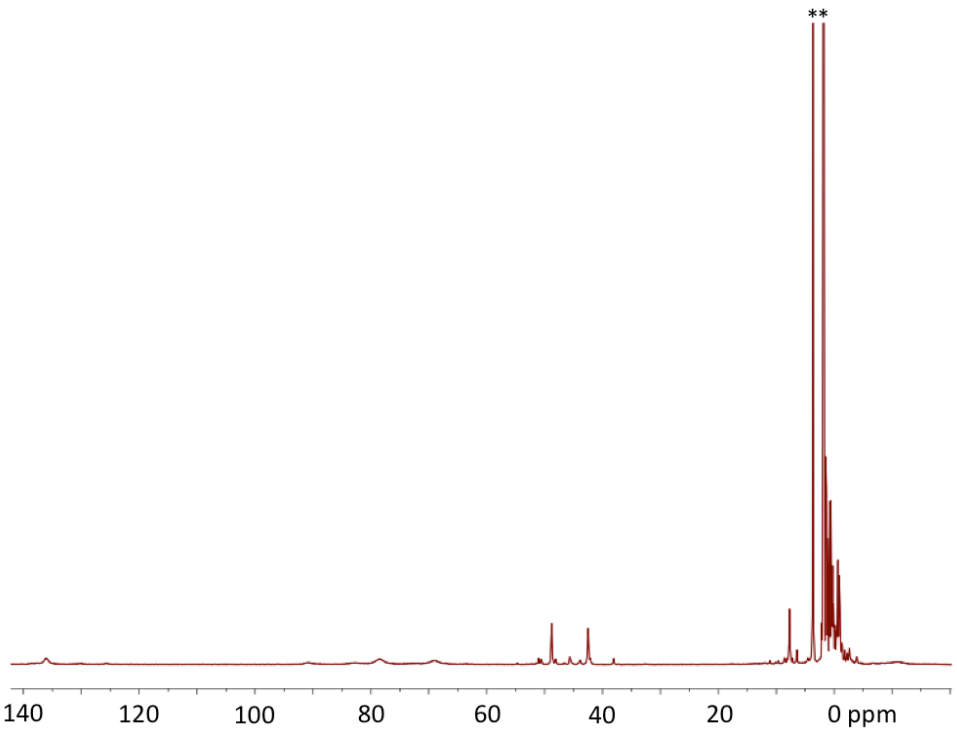

Figure S3. ^{1}H NMR Spectrum of [^{Me}N(afa^{Cy})$_2$]Fe(OTf)$_2$ (**3**) (500 MHz, CD_3CN, 25 °C)

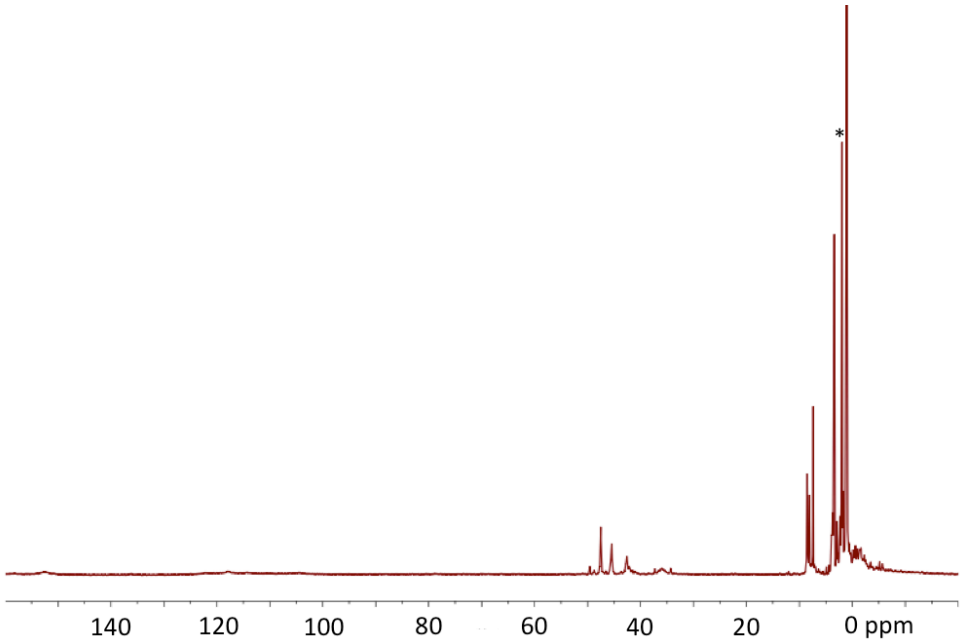

Figure S4. ^{1}H NMR Spectrum of [^{Me}N(afa^{Cy})$_2$]Fe(bipy)(OTf)$_2$ (**4**) (500 MHz, CD_3CN, 25 °C)

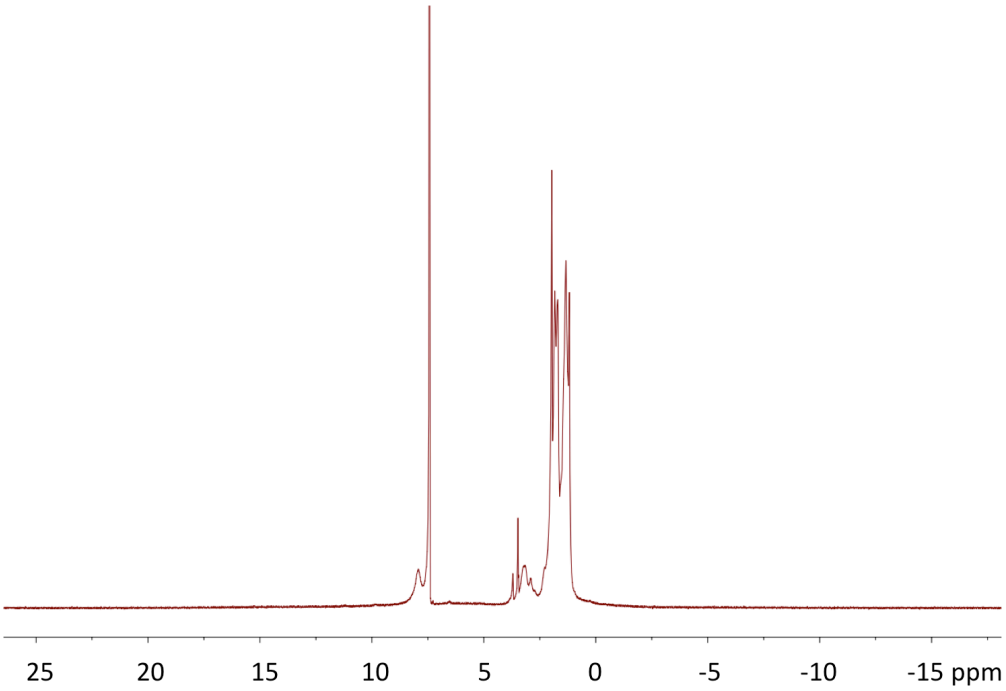

Figure S5. ^{1}H NMR Spectrum of [^{Me}N(afa^{Cy})$_2$]Cu(OTf)$_2$ (**6**) (500 MHz, CD_3CN, 25 °C)

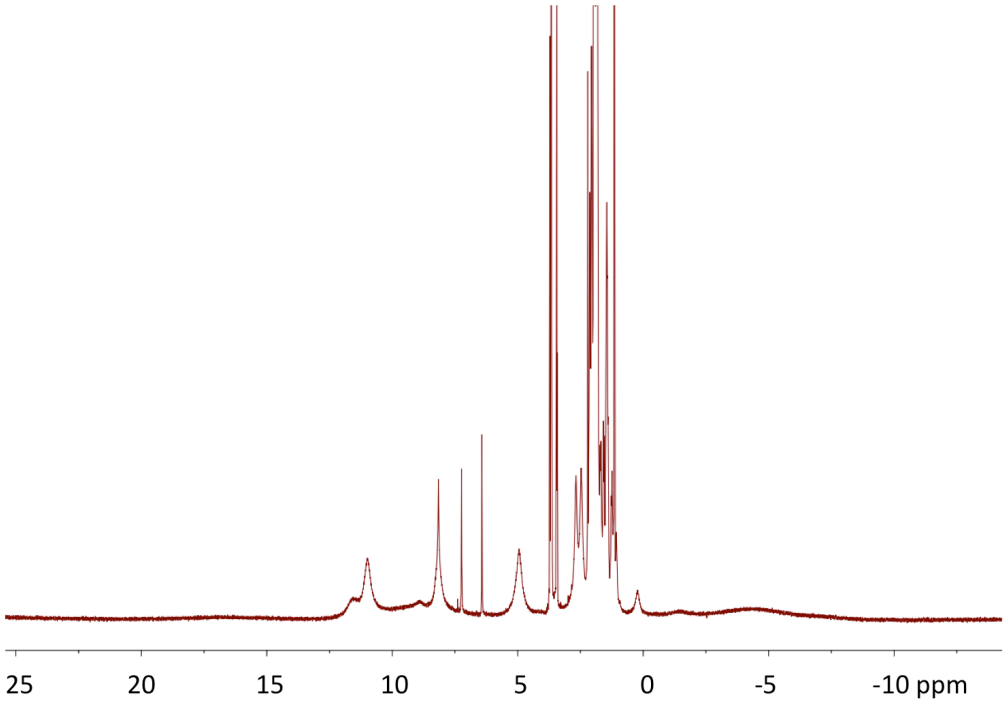

Figure S6. ^{1}H NMR Spectrum of [^{Me}N(afa^{Cy})$_2$]Cu(bipy)(OTf)$_2$ (**7**) (500 MHz, CD_3CN, 25 °C)

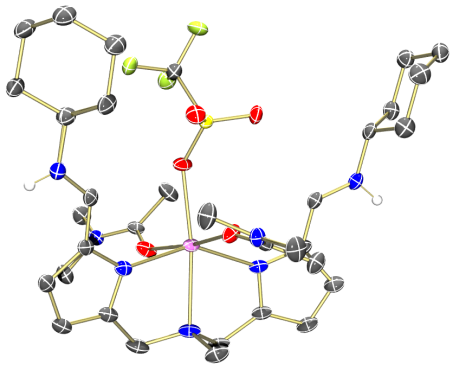

Figure S7. Molecular structure of [^{Me}N(afa^{Cy})$_2$]Fe(DMA)$_2$(OTf)$_2$ (**3-DMA**) shown with 30% probability ellipsoids. Solvent molecules, selected hydrogen atoms and outer-sphere counter ions have been removed for clarity.

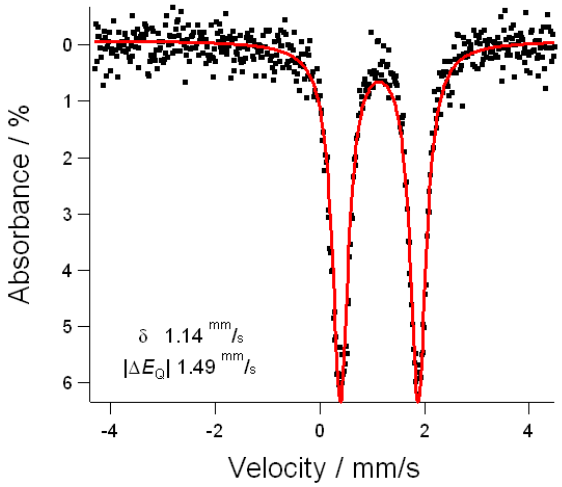

Figure S8. Mössbauer spectrum of **3-DMA.**

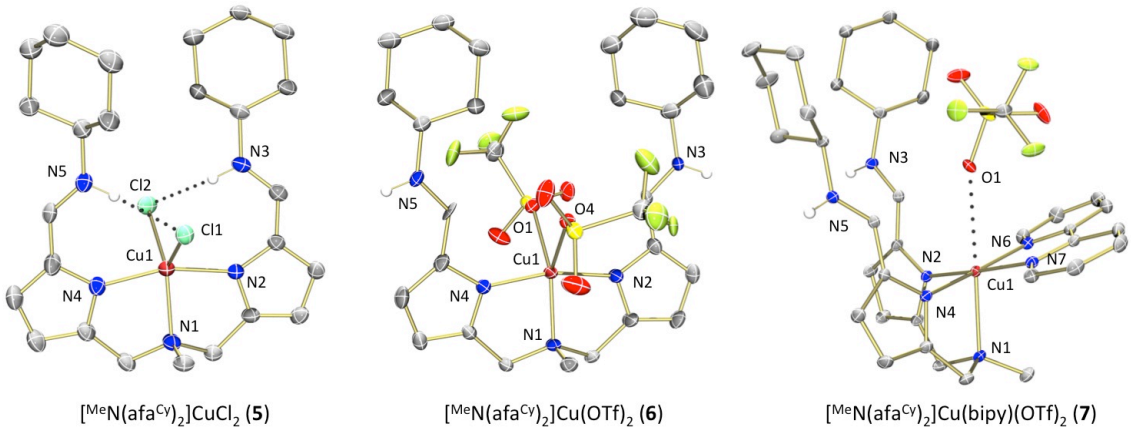

Figure S9. Molecular structures of complexes **5-7** shown with 50% probability ellipsoids. Solvent molecules, selected hydrogen atoms and outer-sphere counter ions have been removed for clarity.

Table S1. Structural parameters of complexes **5-7**.

Bond	**5 (Å)**	**6 (Å)**	**7 (Å)**
Cu1-N1	2.059(2)	2.025(2)	2.333(4)
Cu1-N2	1.972(4)	1.939(3)	1.988(4)
Cu1-N4	1.977(2)	1.937(3)	1.973(4)
Cu1-N6	--	--	2.019(4)
Cu1-N7	--	--	2.007(4)
Cu1-Cl1	2.3406(9)	--	--
Cu1-Cl2	2.4682(9)	--	--
Cu1-O1	--	2.189(3)	2.833(8)
Cu1-O4	--	2.182(5)	--

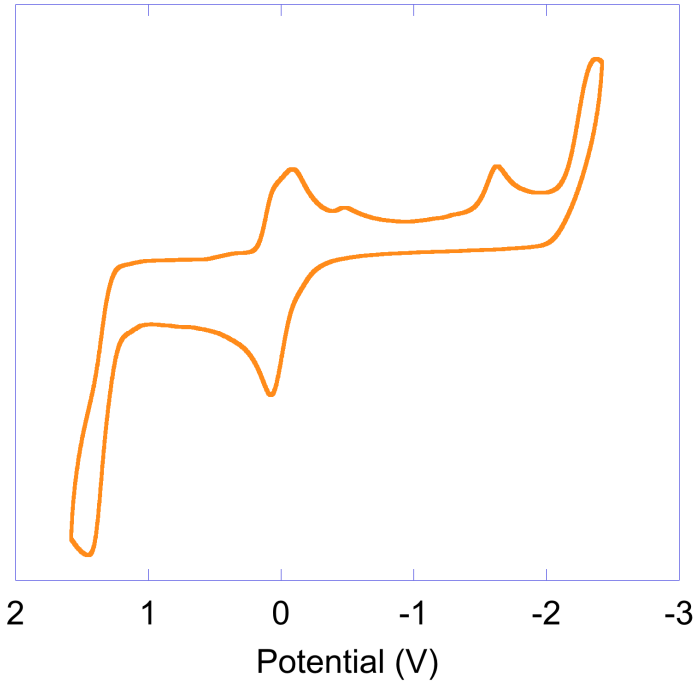

Figure S10. Cyclic voltammogram of **2** recorded in a 0.20 mM acetonitrile solution of $(n\text{-Bu})_4NPF_6$ at a scan rate of 0.1 V/s referenced to the Cp_2Fe/Cp_2Fe^+ couple.

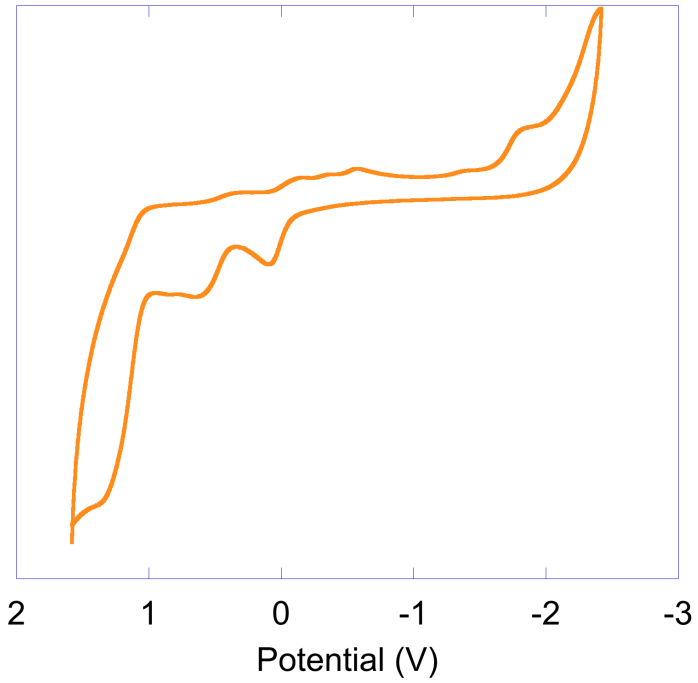

Figure S11. Cyclic voltammogram of **3** recorded in a 0.20 mM acetonitrile solution of $(n\text{-Bu})_4NPF_6$ at a scan rate of 0.1 V/s referenced to the Cp_2Fe/Cp_2Fe^+ couple.

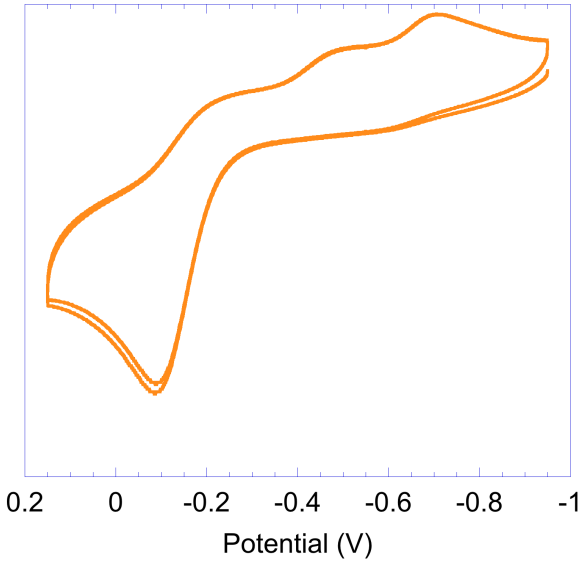

Figure S12. Cyclic voltammogram of **3** recorded in a 0.20 mM acetonitrile solution of $(n\text{-Bu})_4NPF_6$ at a scan rate of 0.1 V/s within potential range of 0.2 to -1 V referenced to the Cp_2Fe/Cp_2Fe^+ couple.

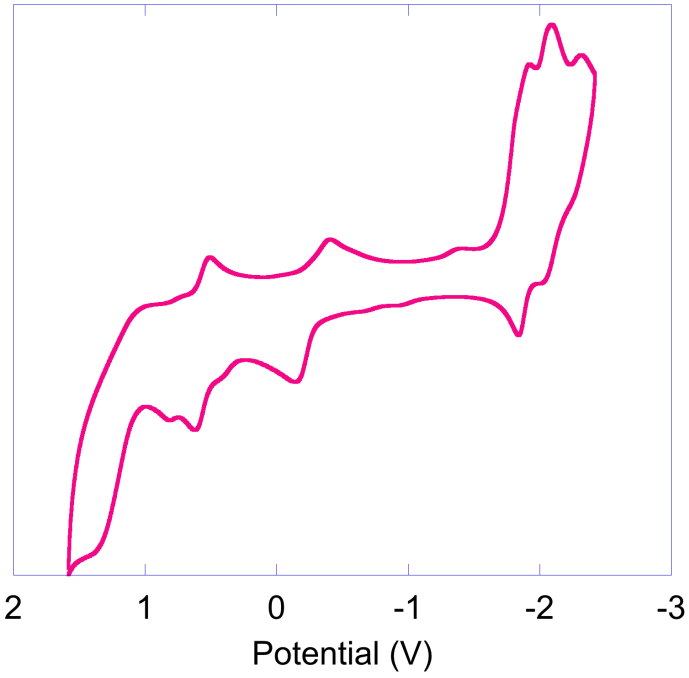

Figure S13. Cyclic voltammogram of **4** recorded in a 0.20 mM acetonitrile solution of $(n\text{-Bu})_4NPF_6$ at a scan rate of 0.1 V/s referenced to the Cp_2Fe/Cp_2Fe^+ couple.

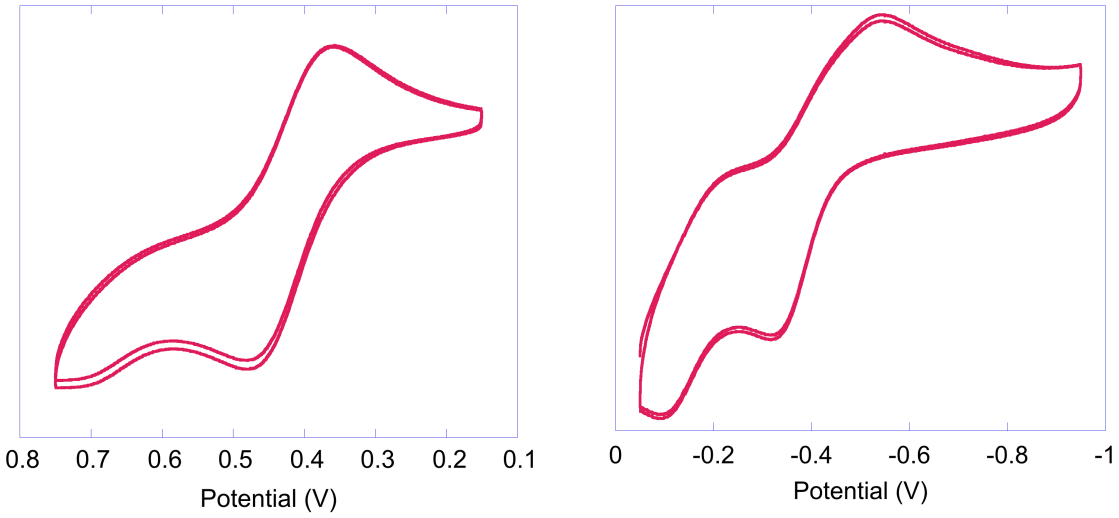

Figure S14. Cyclic voltammogram of **4** recorded in a 0.20 mM acetonitrile solution of $(n\text{-Bu})_4NPF_6$ at a scan rate of 0.1 V/s. Left is region of potentials ranging from 0.8 to 0.1, right shows window of 0 to -1V. Both voltammograms are referenced to the Cp_2Fe/Cp_2Fe^+ couple.

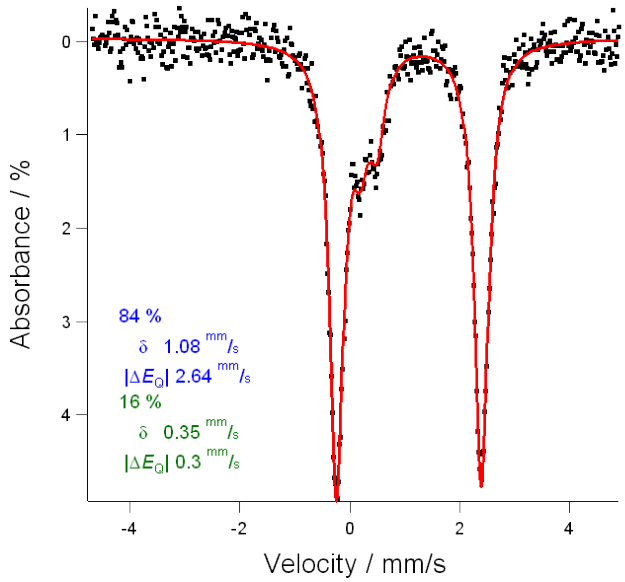

Figure S15. Mössbauer spectrum of **4**.

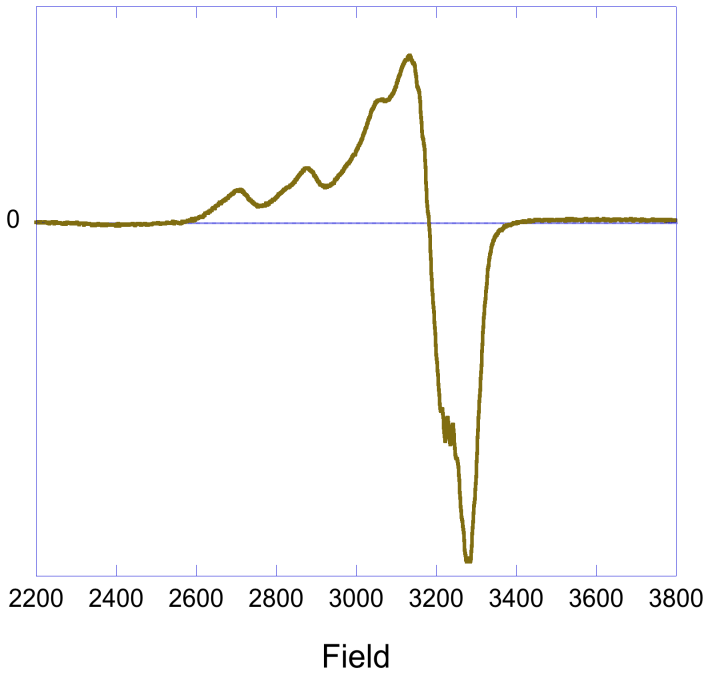

Figure S16. EPR spectrum of **7**

Table S2. EPR Parameters for complexes **6** and **6-DMA** determined by simulation.

Compound	**6**	**6-DMA**
g_x	2.0152	2.0074
g_y	2.0999	2.0909
g_z	2.2218	2.2354
$^{Cu}A_x$ /(MHz)	14	29
$^{Cu}A_y$ /(MHz)	5	3
$^{Cu}A_z$/(MHz)	413	438
$^{N}A_x$ /(MHz)		41
$^{N}A_y$ /(MHz)		37
$^{N}A_z$/(MHz)		37

1. Yahong Li, Angie Turnas, A. James T Ciszewski, and A. L. Odom, *Inorg Chem*, 2002, **41**, 6298–6306.