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Monoanionic bis(carbene) pincer complexes featuring cobalt(I-III) oxidation states

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Supporting Information Table of Contents:

General Considerations. All manipulations of air- and moisture-sensitive compounds were carried out in the absence of water and dioxygen 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 for sensitive manipulations were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves purchased from f following a literature procedure prior to use.[1] Chloroform-*d*, and benzene-d_6 were purchased from Cambridge Isotope Labs and were degassed and stored over 4 Å molecular sieves prior to use. Lithium hexamethyldisilazane was purchased from Sigma-Aldrich and recrystallized from toluene under an inert atmosphere prior to use. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150˚C prior to use in a glovebox. DPEPhos (>99%) and $CoCl_2$ (99% anhydrous) were purchased from Strem and used as received. $PdCl_2$ was purchased from Pressure Chemicals. $[Co(N(SiMe_3)_2)_2]_2$•THF[2,3] and $Pd(PPh_3)_4$[4] were prepared by literature procedures. NMR Spectra were recorded at room temperature on a Varian spectrometer operating at 500 MHz (^1H NMR) and 126 MHz (^{13}C NMR) (U500, VXR500, UI500NB) and referenced to the residual $CHCl_3$ and C_6D_5H resonance (δ in parts per million, and *J* in Hz). Solid-state infrared spectra were recorded using a PerkinElmer Frontier FT-IR spectrophotometer equipped with a KRS5 thallium bromide/iodide universal attenuated total reflectance accessory. Elemental analyses were performed by the University of Illinois at Urbana−Champaign School of Chemical Sciences Microanalysis Laboratory in Urbana, IL. Electrospray ionization mass spectrometry (ESI) was recorded on a Water Q-TOF Ultima ESI instrument. Cyclic voltammetry studies were collected on CH Instruments 1410C potentiostat. EPR samples were prepared in an MBraun glovebox. The sample concentration is approximately 10mM in tetrahydrofuran/toluene (1:1) mixture. EPR spectra were recorded on a Varian E-line 12” Century series X-band CW spectrometer and the spectra were simulated using the program SIMPOW6.[5,6] EPR parameters for **2a** (2.5E+3 gain; 2.00G modulation amplitude; 20.00dB power; microwave frequency = 9.2903GHz) and **2b** (1.60E+3 gain; 4.00G modulation amplitude; 20.00dB power; microwave frequency = 9.2907GHz).

Modified Ligand Procedure

Preparation of N-(2-bromophenyl)-2,6-diisopropylaniline (L1a). A 20 mL scintillation vial charged with $Pd(PPh_3)_4$ (0.454 g, 0.39 mmol) and DPEPhos (0.317 g, 0.589 mmol) was stirred at 80°C for 20 minutes in toluene (20 mL). The DPEPhos/$Pd(PPh_3)_4$ solution was then filtered through a pad of celite into a 150 mL Schlenk bomb and 2-bromoiodobenzene (6.696 g, 23.7 mmol), 2,6-diisopropylanailine (2.784 g, 15.70 mmol) and sodium *tert*-butoxide (6.074 g, 63.20 mmol) were added and the mixture was diluted toluene to a final volume of approximately 80 mL. After stirring the mixture at 100^{o}C for 36 h, the suspension was allowed to cool to ambient temperature and then filtered through a plug of silica, eluting with 250 mL of Et_2O. The filtrate was concentrated to an oil under reduced pressure and loaded on a silica gel column. The product was separated using hexanes as the eluent; yielding a white solid after removal of the solvent under reduced pressure (4.80 g, 14.44 mmol, 92%). The ^{1}H and ^{13}C NMR spectra match those of the reported compound.[7]

Preparation of N^1,N$^{1'}$-(1,3-phenylene)bis(N^2-(2,6-diisopropylphenyl)bezene-1,2-diamine) (L2a). A 20 mL scintillation vail charged with Pd(PPh$_3$)$_4$ (1.692 mg, 1.464 mmol) and DPEPhos (1.176 g, 2.184 mmol) were stirred at 80°C for 20 minutes in toluene (20 mL). The DPEPhos/Pd(PPh$_3$)$_4$ solution was then filtered through a pad of celite into a 250 mL Schlenk bomb and **L1a** (3.044 g, 9.161 mmol), 1,3-diaminobenzene (0.393 g, 3.634 mmol) and sodium *tert*-butoxide (1.7563 g, 18.28 mmol) were added and the mixture was diluted with *ca.* 120 mL of toluene. After stirring the mixture at 100^{o}C for 24 h, the suspension was allowed to cool to ambient temperature and then filtered through a plug of silica, eluting with 500 mL of Et$_2$O. The solvent was removed under reduced pressure and the residue adsorbed on 30 g of dry silica and loaded onto a silica gel column. The product is separated with a stepwise gradient of 2-5% ethyl acetate/hexanes, yielding an off-white solid after the removal of solvent (1.931 g, 3.16 mmol, 87%). The ^{1}H and ^{13}C NMR spectra match those of the reported compound.[8]

Preparation of 1,1'-(1,3-phenylene)bis(3-(2,6-diisopropylphenyl)-1H-benzo[d]imidazole-3-ium) chloride [H$_3$(^{DIPP}CCC)]Cl$_2$. Compound **L2a** (2.00 g, 3.274 mmol) was suspended in 20 mL triethyl orthoformate and heated to reflux at 80^{o}C under an N$_2$ atmosphere. Concentrated hydrochloric acid (37% w/w, 808 mg of solution, 8.20 mmol) was added dropwise and the color of the suspension turned off-white. After stirring the mixture for 4 h, the volatiles were removed under reduced pressure and a beige solid was collected. The solid was triturated with Et$_2$O (approx. 5 x 10 mL) until washes were colorless and dried under vacuum at 70^{o}C overnight (2.142 g, 3.045 mmol, 93%). The ^{1}H and ^{13}C NMR spectra match those of the reported compound.[8]

Preparation of N-(2-bromophenyl)-2,4,6-trimethylaniline (L1b). A 20 mL scintillation vial charged with Pd(PPh$_3$)$_4$ (0.404 g, 0.35 mmol) and DPEPhos (0.566 g, 1.05 mmol) was stirred at 80°C for 20 minutes in toluene (20 mL). The DPEPhos/Pd(PPh$_3$)$_4$ solution was then filtered through a pad of celite into a 150 mL Schlenk bomb and 2-bromoiodobenzene (2.97 g, 10.5 mmol), 2,4,6-trimethylanailine (0.947 g, 7 mmol) and sodium *tert*-butoxide (2.69 g, 28 mmol) were added and the mixture was diluted with 80 mL of toluene. After stirring the mixture at 100^{o}C for 20 h, the suspension was allowed to cool to ambient temperature and then filtered through a plug of silica, eluting with 500 mL of Et$_2$O. The filtrate was concentrated to an oil under reduced pressure and filtered through a pad of silica, eluting with 800 mL of hexanes. The filtrate was concentrated to an oil under reduced pressure, taken up in *ca.* 10 mL hot ethanol, and upon cooling, the product was obtained as a white solid (2.00 g, 6.89 mmol, 98%). The ^{1}H and ^{13}C NMR spectra match those of the reported compound.[8]

Preparation of N^1,N$^{1'}$-(1,3-phenylene)bis(N^2-mesitylbezene-1,2-diamine) (L2b). A 20 mL scintillation vial charged with Pd(PPh$_3$)$_4$ (0.550 mg, 0.476 mmol) and DPEPhos (0.800 g, 1.48 mmol) was stirred at 80°C for 20 minutes in toluene (20 mL). The DPEPhos/Pd(PPh$_3$)$_4$ solution was then filtered through a pad of celite into a 250 mL Schlenk bomb and **L1b** (3.00 g, 10.34 mmol), 1,3-diaminobenzene (0.502 g, 4.64 mmol) and sodium *tert*-pentoxide (2.500 g, 22.7

mmol) were added and the mixture was diluted with *ca.* 120 mL of toluene. After stirring the mixture at 100^{o}C for 24 h, the suspension was allowed to cool to ambient temperature and then filtered through a plug of silica, eluting with 500 mL of Et_2O. The solvent was removed under reduced pressure and the residue adsorbed on 30 g of dry silica and loaded onto a silica gel column. The product is separated with a stepwise gradient of 2-5% ethyl acetate/hexanes, yielding a green powder. This powder is further recrystallized from hexanes to give the desired compound (2.23 g, 4.24 mmol, 91%). The ^{1}H and ^{13}C NMR spectra match those of the reported compound.[8]

Preparation of 1,1'-(1,3-phenylene)bis(3-mesityl-1H-benzo[d]imidazole-3-ium) chloride [H_3(^{Mes}CCC)]Cl_2. Compound **L2b** (2.245 g, 4.24 mmol) was suspended in 55 mL triethyl orthoformate and heated to reflux at 80^{o}C under an N_2 atmosphere. Concentrated hydrochloric acid (37% w/w, 0.8 mL, 9.7 mmol) was added dropwise and the color of the suspension turned off-white. After stirring the mixture for 19 h, the suspension was allowed to cool to ambient temperature and 55 mL of Et_2O, followed by 165 mL of hexanes were added. After stirring for 20 min, the solid was collected by filtration and washed with excess ether. The off-white solid was taken into the drybox, dissolved in *ca.* 100 mL of DCM and stored under 4 Å molecular sieves for 24 h. The solution was decanted and *ca.* 120 mL hexanes was added and a white solid was isolated by filtration (2.015 g, 3.25 mmol, 77%). The ^{1}H and ^{13}C NMR spectra match those of the reported compound.[8]

Synthesis of Metal Complexes

Synthesis of (^{DIPP}CCC)$CoCl_2$py (1a). A 20 mL scintillation vial charged with [H_3(^{DIPP}CCC)]Cl_2 (0.0585 g, 0.08321 mmol) in *ca.* 5 mL of THF, a solution of lithium hexamethyldisilazide (0.0135 g, 0.0801 mmol) were stirred at ambient temperature for 5 min. Dropwise addition of a THF (*ca.* 3 mL) a solution of $[Co(N(SiMe_3)_2)_2]_2$•THF (0.0376 g, 0.0832 mmol) and 5 drops of anhydrous pyridine were then added, followed by a THF (*ca.* 3 mL) solution of trityl chloride (0.0232 g, 0.832 mmol). After stirring the mixture for 18 h, the volatiles were removed under reduce pressure and the green solid was washed with hexanes (2 × 10 mL), dissolved in DCM (10 mL), filtered over a plug of Celite and the solvent was removed under reduced pressure to give a green solid (0.0558g, 0.0666 mmol, 80%). Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene. ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.82 (d, *J* = 4, 2H), 8.27 (d, *J* = 8.0, 2H), 7.87 (d, *J* = 8.0, 2H), 7.55 (t, *J* = 7.8, 1H), 7.41 (t, *J* = 7.5, 2H), 7.20 (t, *J* = 7.8, 2H), 7.16 (t, *J* = 7.8, 2H), 7.09 – 7.13 (m, 1H), 6.96 (d, *J* = 7.5, 4H), 6.75 (d, *J* = 8.0, 2H), 6.41 (s, 2H), 2.69 (sept, *J* = 6.5, 4H), 0.98 (d, *J* = 6.0, 12H), 0.68 (d, *J* = 6.5, 12H). ^{13}C NMR (CDCl3): δ 195.3, 156.4, 153.6, 148.7, 147.5, 138.6, 134.6, 133.0, 132.2, 130.2, 124.6, 124.1, 123.8, 122.2, 122.1, 112.8, 112.1, 110.3, 27.8, 26.2, 22.8. HRMS (ESI), calc. for $C_{44}H_{45}CoN_4$ $(M - Cl - C_5H_5N)^+$: 723.2665; found 723.2668.

Alternative Synthesis of 1a. A solution of trityl chloride (0.052 g, 0.187 mmol) in approximately 2 mL of THF was prepared and added to a solution of **2a** (0.150 g, 0.187 mmol) in ca. 4 mL of THF at room temperature. Additional solvent (2 mL) was used to rinse and complete the transfer and the reaction mixture was stirred for 1 h. The solvent was removed under reduced pressure to afford a solid bright green residue. Trituration with diethyl ether (2 X 2 mL) and subsequent evacuation of solvent under reduced pressure afforded a green solid (0.132 g, 0.157 mmol, 84%).

Synthesis of (^{Mes}CCC)CoCl$_2$py (1b) A 20 mL scintillation vial charged with [H$_3$(CCC^{Mes})]Cl$_2$ (0.050 g, 0.08 mmol) in *ca.* 5 mL of THF, a solution of lithium hexamethyldisilazide (0.013 g, 0.08 mmol) were stirred at ambient temperature for 5 min. Dropwise addition of a THF (*ca.* 3 mL) solution of [Co(N(SiMe$_3$)$_2$)$_2$]$_2$•THF (0.036 g, 0.08 mmol) and 4 drops of anhydrous pyridine were added, followed by solution of trityl chloride (0.023 g, 0.83 mmol) in *ca.* 2 mL THF was stirred at ambient temperature for 18 h. After stirring the mixture for 18 h, the volatiles were removed under reduce pressure and the green solid was washed with hexanes (2 × 10 mL), dissolved in DCM (10 mL), filtered over a plug of Celite and the solvent was removed under reduced pressure to give a green solid (0.057 g, 0.075 mmol, 93%). Crystal suitable for X-ray diffraction were grown from slow evaporation of a concentrated solution of complex **1b** in benzene and chloroform at room temperature. Anal. Calcd for **1b***C$_6$H$_6$/CH$_2$Cl$_2$ (C$_{50}$H$_{45}$Cl$_4$CoN$_5$): C, 65.51; H, 4.95; N, 7.64. Found: C, 65.54; H, 4.6; N, 7.64. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.79 (d, *J* = 6.0, 2H), 8.25 (d, *J* = 8.0, 2H), 7.83 (d, *J* = 8.0, 2H), 7.55 (t, *J* = 7.8, 1H), 7.43 (t, *J* = 7.5, 2H), 7.31 (t, *J* = 7.8, 1H), 7.20 (t, 7.5, 2H), 6.78 (d, *J* = 8.0, 2H), 6.56-6.50 (m, 6H), 2.19 (s, 6H), 1.83 (s, 12H). ^{13}C NMR (CDCl3): δ 196.7, 154.3, 152.3, 148.8, 138.6, 136.8, 136.7, 133.2, 132.6, 132.3, 129.0, 124.9, 123.7, 123.0, 122.7, 112.0, 110.4, 110.2, 21.0, 18.1.

Alternative Synthesis of 1b from 3b-PPh$_3$: A solution of trityl chloride (0.063 mg, 0.226 mmol) in *ca*. 5 mL of THF was added to a 20 mL scintillation vial charged with a pre-stirred suspension of **3b-PPh$_3$** (0.101 g, 0.113 mmol) and 5 drops of anhydrous pyridine in *ca.* 5 mL THF. After stirring the mixture for 3 h at ambient temperature, the volatiles were removed under reduced pressure to give a green solid mixture. The crude product was washed with Et$_2$O (2 × 5 mL), pumped to dryness *in vacuo*, taken up in *ca*. 10 mL DCM and filtered over a plug of Celite. Removal of the solvent under reduced pressured resulted in a green powder (0.070 g, 0.0882 mmol, 78%).

Alternative Synthesis of 1b from 2b: A solution of trityl chloride (0.004 mg, 0.014 mmol) in *ca*. 5 mL of THF was added to a 20 mL scintillation vial charged with a pre-stirred suspension of **2b** (0.010 g, 0.014 mmol) in *ca.* 5 mL THF. After stirring the mixture for 1 h at ambient temperature, the volatiles were removed under reduced pressure to give a green solid mixture. The crude product was triturated with Et$_2$O (2 × 5 mL), pumped to dryness *in vacuo*, taken up in *ca*. 10 mL DCM and filtered over a plug of Celite. Removal of the solvent under reduced pressured resulted in a green powder (0.009 g, 0.0119 mmol, 85%).

Synthesis of (^{DIPP}CCC)CoClpy (2a). A 20 mL scintillation vial was charged with Co(N(SiMe$_3$)$_2$)$_2$•THF (0.128 g, 0.283 mmol), LiN(SiMe$_3$)$_2$ (0.048 g, 0.287 mmol), and approximately 4 mL of C$_6$H$_6$. Subsequent addition of anhydrous pyridine (30 drops) to this dark green solution resulted in an immediate color change to dark blue and the mixture was stirred for approximately 5 min. Upon completion of the stirring period, the solution was added to a 15 mL high-pressure vessel containing the benzimidazolium salt, [H$_3$(^{DIPP}CCC)]Cl$_2$ (0.200 g, 0.284

mmol). The vessel was sealed, taken outside of the glovebox, and heated in an oil bath at 70 °C overnight. Following the conclusion of the heating period, the vessel was brought into a glove box and filtered over a frit layered with Celite. Benzene was added to the solid until the washes became colorless and the filtrate was subsequently evacuated of all solvent under reduced pressure to afford a bright orange solid. The solid was stirred in a 4:1 mixture of hexanes (8 mL) and diethyl ether (2 mL) for 15 min and filtered over a frit. Subsequent washes with ether (*ca.* 5 mL) and hexanes (10 mL) followed by drying under reduced pressure yielded the pure solid (0.171 g, 0.213 mmol, 75%). Crystals suitable for X-ray diffraction were grown by slow evaporation from a benzene solution containing a few drops of hexanes and a drop of THF. Analysis for $C_{49}H_{50}ClN_5$•LiCl: Calcd. C, 69.59; H, 5.96; N, 8.28. Found C, 70.01; H, 6.15; N, 8.28. ^1H NMR (500 MHz, C_6D_6) δ 18.62, 13.29, 11.67, 10.78, 8.47, 7.96, 7.72, 7.55, 7.32, 7.00, 6.86, 4.18, 1.14, -8.80. HRMS (ESI), calc. for $C_{44}H_{45}CoN_4$ (M - Cl - py)$^+$: 688.2980; found 688.2976.

Synthesis of (^{Mes}CCC)CoClpy (2b) A suspension of Mg($C_{14}H_{10}$)•3THF (0.142mg, 0.068 mmol) in ca. 2 mL of THF was added to a 20 mL scintillation vial charged with a pre-stirred solution of **1b** (0.100 g, 0.136 mmol) in approximately 3 mL of THF. The resulting reaction was stirred for 2 h at room temperature and then pipette-filtered over Celite. Removal of volatiles from the filtrate under reduced pressure yielded a solid residue, which was washed with THF (2 × 1 mL) to give an orange solid. Further washing with hexanes (2 × 1 mL), followed by the removal of solvents under reduced pressure afforded 6 mg of pure compound. A second cropping from the THF washes provided an additional 21 mg of the crystalline orange product (0.027 g, 0.038 mmol, 28 %). Crystals suitable for X-ray diffraction were grown from these THF washes, as well as recrystallization of the compound from THF. The product is ^1H NMR silent. HRMS (ESI), calc. for $C_{43}H_{38}ClCoN_5$ (M)$^+$: 718.2148; found 718.2137.

Alternative Synthesis of 2b from 3b-PPh$_3$: A solution of trityl chloride (0.004 mg, 0.015 mmol) in *ca*. 2 mL of THF was added to a 20 mL scintillation vial charged with a pre-stirred suspension of **3b-PPh$_3$** (0.015 g, 0.017 mmol) and 2 drops of anhydrous pyridine in *ca.* 5 mL THF. After stirring the mixture for 3 h at ambient temperature, the volatiles were removed under reduced pressure to give an orange residue. The crude product was washed with Et_2O (2 × 5 mL), pumped to dryness *in vacuo*, taken up in *ca*. 5 mL of THF and filtered over a plug of Celite. Removal of the solvent under reduced pressured resulted in an orange powder (0.009 g, 0.0128 mmol, 85%).

Synthesis of (^{DIPP}CCC)Co(N$_2$) (3a). A 20 mL scintillation vial was charged with **2a** (0.350 g, 0.436 mmol) and approximately 4 mL of benzene. The resulting solution was frozen at -35 °C and Mg($C_{14}H_{10}$)•3THF (0.182 g, 0.435 mmol) was added as a solid. The reaction mixture took on a dark brown color and was stirred to room temperature for 4 h. Following the completion of the stirring period, the mixture was filtered over a frit. Removal of solvent from the filtrate under reduced pressure afforded a solid brown residue that was stirred in hexanes (20 mL) for 15 min and subsequently filtered. The collected solid was washed with ca. 40 mL hexanes to remove anthracene and dried under reduced pressure (0.240 g, 0.335 mmol, 77%). Crystals suitable for X-ray diffraction were grown by slow evaporation from benzene. ^1H NMR (500 MHz, C_6D_6) δ 7.63 (d, *J* = 7.5, 2H), 7.32 (d, *J* = 7.0, 2H), 7.29 – 7.23 (m, 2H), 7.20 (t, *J* = 7.5, 3H), 7.11 (d, *J* =

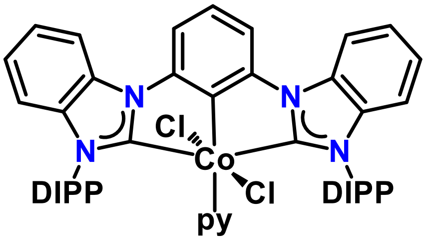
7.5, 4H), 7.04 (t, *J* = 7.5, 2H), 6.86 (t, *J* = 7.5, 2H), 6.55 (d, *J* = 8.0 Hz, 2H), 2.71 (sept, *J* = 6.8, 4H), 1.26 (d, *J* = 6.5, 12H), 0.87 (d, *J* = 6.5, 12H). ^{13}C NMR (500 MHz, C_6D_6) δ 149.9, 147.0, 139.1, 133.9, 131.4, 130.4, 124.5, 123.7, 123.5, 122.5, 110.5, 110.3, 107.2 28.8, 24.7, 24.1. The C-NHC and C-aryl resonances were not observed. HRMS (ESI), calc. for $C_{44}H_{45}CoN_4$ $(M - N_2)^+$: 688.2976; found 688.2973. IR: 2063 cm^{-1} (N_2).

Synthesis of (^{DIPP}CCC)CoN$_2$(PPh$_3$) (3a-PPh$_3$). A 20 mL scintillation vial was charged with **3a** (0.040 g, 0.056 mmol), PPh$_3$ (0.015g, 0.056 mmol) and benzene (*ca.* 2 mL). Immediately upon addition, the solution turned dark red and the benzene was removed after 5 min of stirring under reduced pressure to furnish a red solid (0.049 g, 0.050 mmol, 89%). NMR data (in benzene-*d*$_6$, 25 °C): ^{1}H *δ* = 7.76 (d, *J* = 8.0, 2H), 7.39 (d, *J* = 7.5, 2H), 7.23 (t, *J* = 7.5, 2H), 7.03 (t, *J* = 7.5, 2H), 6.98-6.73 (m, 10H), 6.53 (d, *J* = 8, 2H), 3.05-2.41 (broad, 4H), 1.04-0.60 (broad, 24H). ^{13}C *δ* = 210.8, 164.0, 144.0, 141.1. 137.3, 135.9, 133.5, 132.1, 129.8, 128.6, 124.4, 121.8, 121.0, 119.6, 110.8, 109.9, 105.8, 28.8, 25.2, 23.5. IR: 2117 cm^{-1} (N_2). HRMS (ESI), calc. for $C_{44}H_{45}CoN_4$ (M – $P(C_6H_5)_3$ N_2): 689.3054; found 689.3037.

Synthesis of (^{Mes}CCC)CoN$_2$(PPh$_3$) (3b-PPh$_3$). A 20 mL scintillation vial was charged with **1b** (0.108 g, 0.141 mmol) and THF (10 mL). After stirring for 10 min, the green suspension was transferred to a THF suspension (5 mL) of freshly prepared sodium amalgam (Na: 0.012 g, 0.53 mmol; Hg 3.80 g). After stirring the mixture at ambient temperature for 18 h, the dark suspension was filtered over Celite and to the filtrate, triphenylphosphine (0.037 g, 0.141 mmol) was added, resulting in the color change of the mixture to dark red. After stirring the solution for 2 h, the THF was removed under reduced pressure. The product was then extracted into benzene (3 x 5 mL), filtered over Celite and concentrated to a red solid. The solid was triturated with hexane (10 mL) and concentrated under vacuum to give a fine red powder (0.094 g, 0.105 mmol, 73%). Crystals suitable for X-ray diffraction were grown from slow evaporation of a concentrated solution of complex **3b-PPh$_3$** in benzene layered with hexanes at room temperature. NMR data (in benzene-*d*$_6$, 25 °C): ^{1}H *δ* = 7.76 (d, *J* = 8.0, 2H), 7.41 (d, *J* = 7.5, 2H), 7.25 (t, *J* = 7.5, 2H), 7.12 (t, *J* = 7.8, 2H), 6.95-6.89 (m, 8H), 6.85 (t, *J* = 7, 3H), 6.79-6.74 (m, 8H), 6.71 (s, 1H), 6.55 (d, *J* = 8, 2H), 2.01 (s, 6H), 2.00 (s, 6H), 1.66 (s, 6H); ^{13}C *δ* = 208.9, 165.1, 143.8, 138.5, 138.4, 137.1, 136.9, 136.7, 134.4, 133.0, 132.9, 132.4, 129.9, 121.9, 121.7, 119.4, 109.7, 108.5, 105.8, 21.1, 18.2, 17.8. HRMS (ESI), calc. for $C_{56}H_{49}CoN_4P$ $(M)^+$: 867.3027; found 867.2997. IR: 2112 cm^{-1} (N_2).

Alternative Synthesis of 3b-PPh$_3$ from 2b: A 20 mL scintillation vial was charged with **2b** (0.027 g, 0.0375 mmol) and *ca.* 5 mL of THF. After stirring for 10 min, the orange solution was transferred to a *ca*. 5 mL THF suspension of freshly prepared sodium amalgam (Na: 0.010 g, 0.43 mmol; Hg 1.61 g). After stirring the mixture at ambient temperature for 17 h, the dark suspension was filtered over Celite and to the filtrate, triphenylphosphine (0.010 g, 0.038 mmol) was added, resulting in the change of the mixture to dark red. After stirring the solution for 1 h, the THF was removed under reduced pressure. The product was then extracted into benzene (3 x 5 mL), filtered over Celite and concentrated to a red solid. The solid was triturated with hexane (10 mL) and concentrated under vacuum to give a fine red powder (0.025 g, 0.028 mmol, 75%).

^{1}H NMR Spectrum, 500 MHz, $CDCl_3$ (1a)



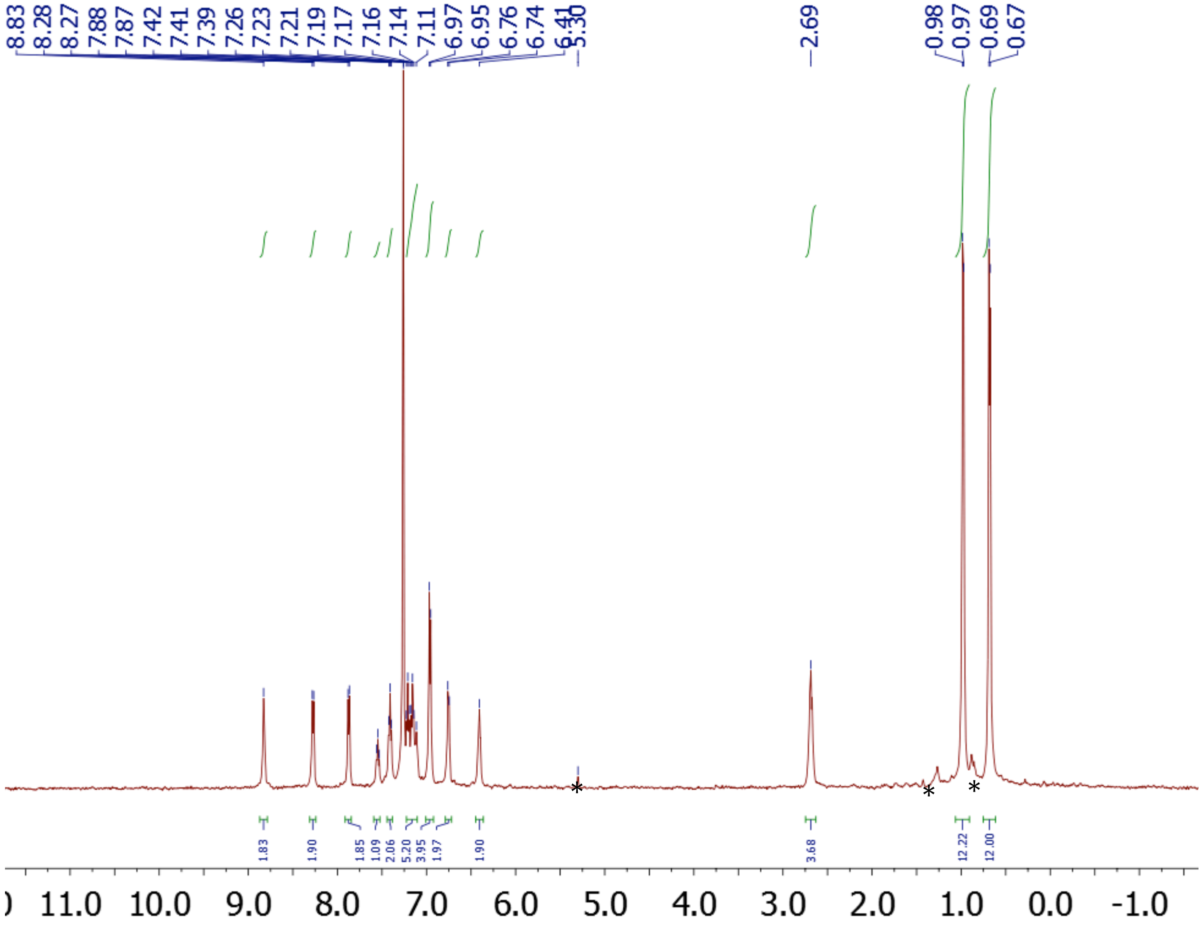
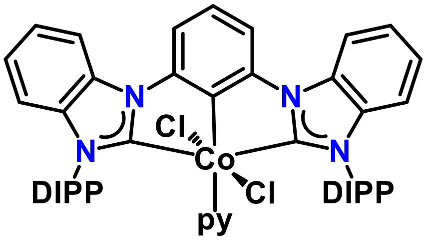


Figure S1. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (^{DIPP}CCC)$CoCl_2$py (**1a**). (* denotes residual solvent and H grease)

^{13}C NMR Spectrum, 126 MHz, CDCl$_3$ (1a)



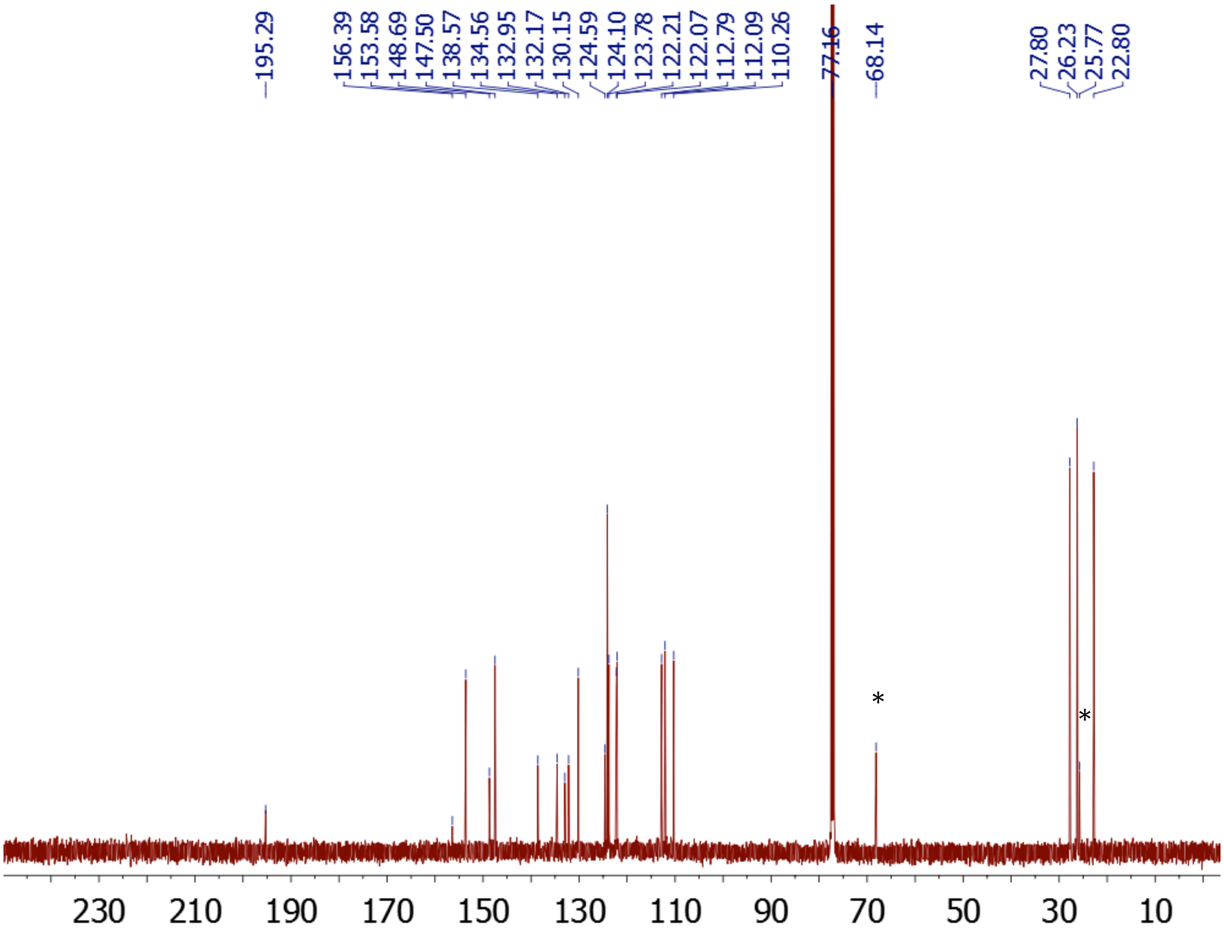
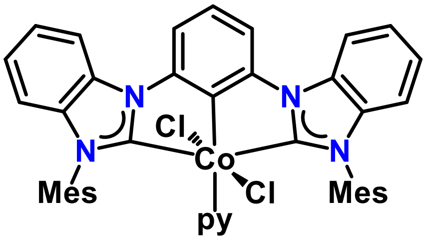


Figure S2. ^{13}C NMR (CDCl$_3$, 126 MHz) spectrum of (^{DIPP}CCC)CoCl$_2$py (**1a**). (* denotes THF)

^{1}H NMR Spectrum, 500 MHz, CDCl$_3$ (1b)



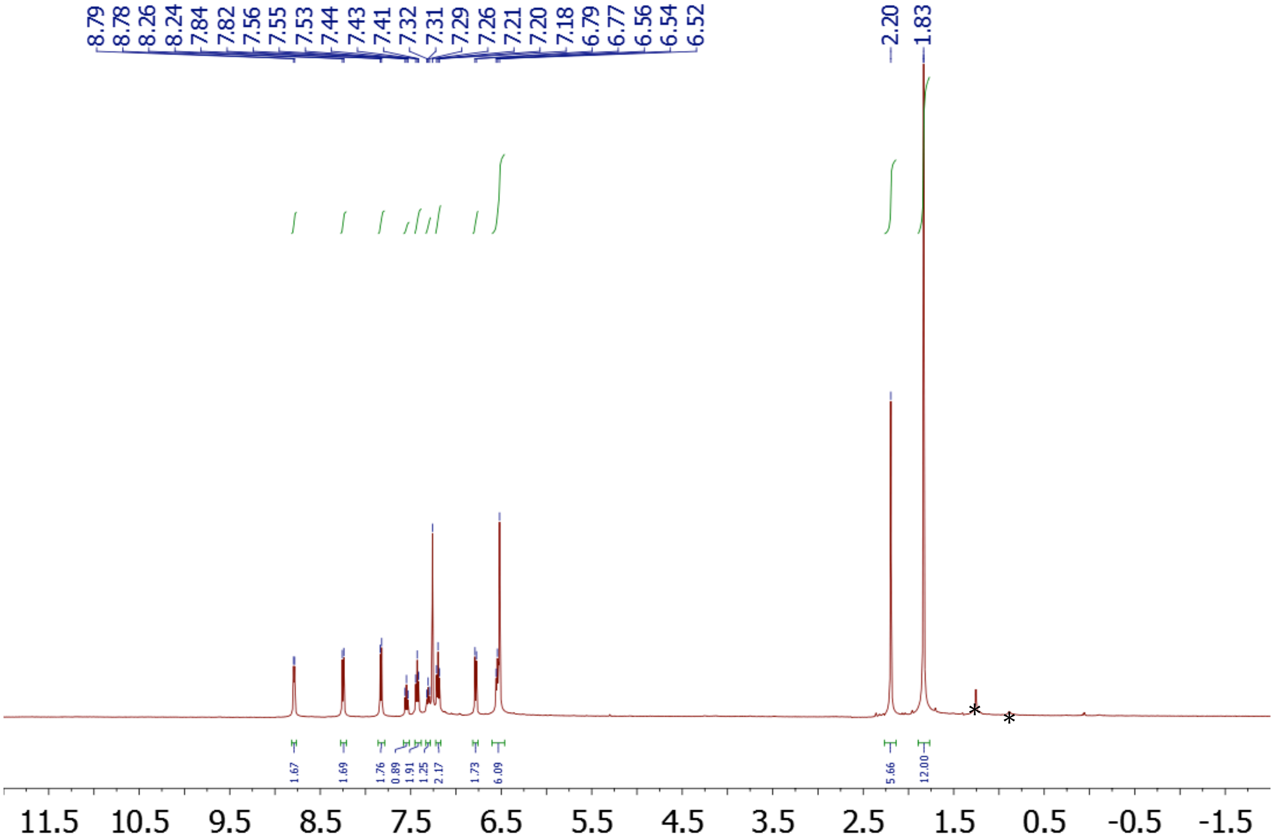
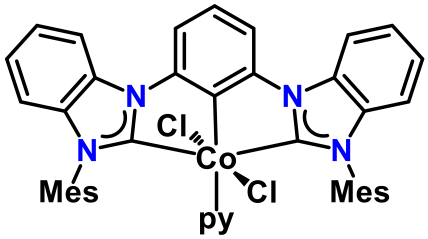


Figure S3. ^{1}H NMR (CDCl$_3$, 500 MHz) spectrum of (^{Mes}CCC)CoCl$_2$py (**1b**). (* denotes H grease)

^{13}C NMR Spectrum, 126 MHz, CDCl$_3$ (1b)



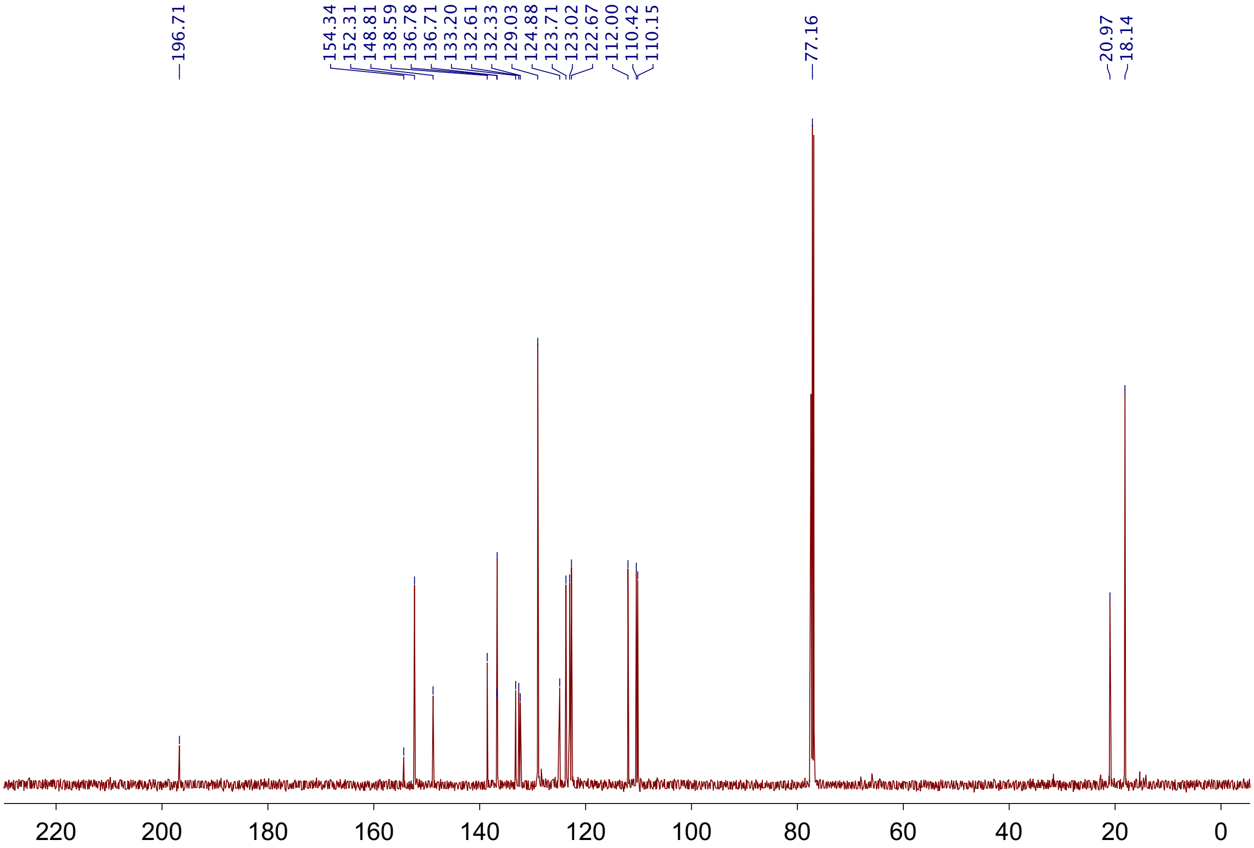
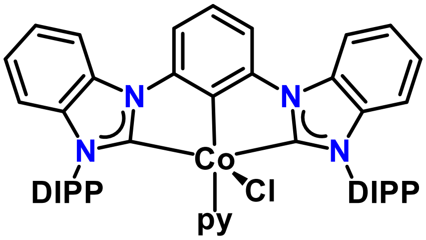


Figure S4. ^{13}C NMR (CDCl$_3$, 126 MHz) spectrum of (^{Mes}CCC)CoCl$_2$py (**1b**).

^{1}H NMR Spectrum, 500 MHz, C_6D_6 (2a)



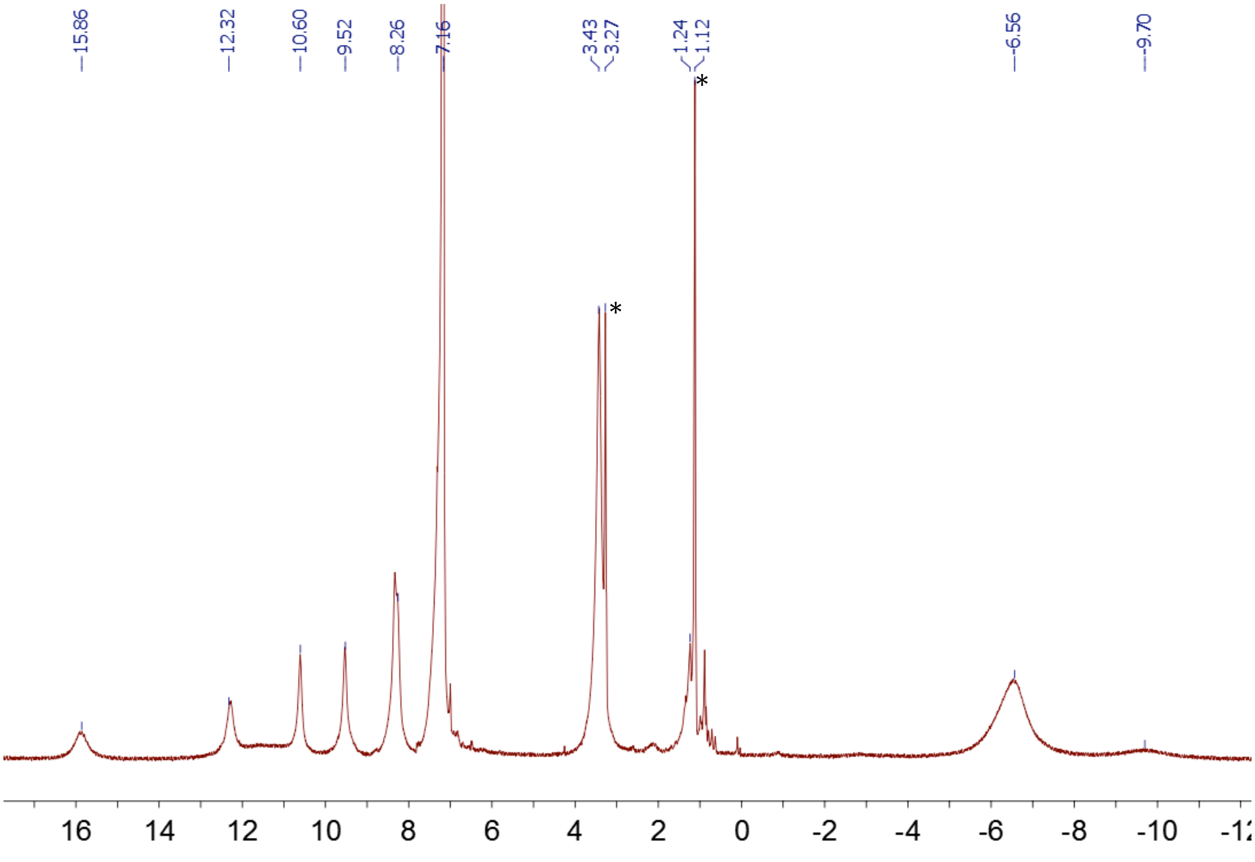
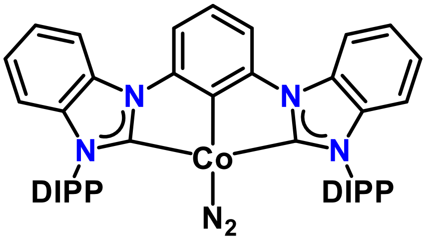


Figure S5. ^{1}H NMR (C_6D_6, 500 MHz) spectrum of (^{DIPP}CCC)CoClpy (**2a**). (* denotes Et_2O)

^{1}H NMR Spectrum, 500 MHz, C_6D_6 (3a)



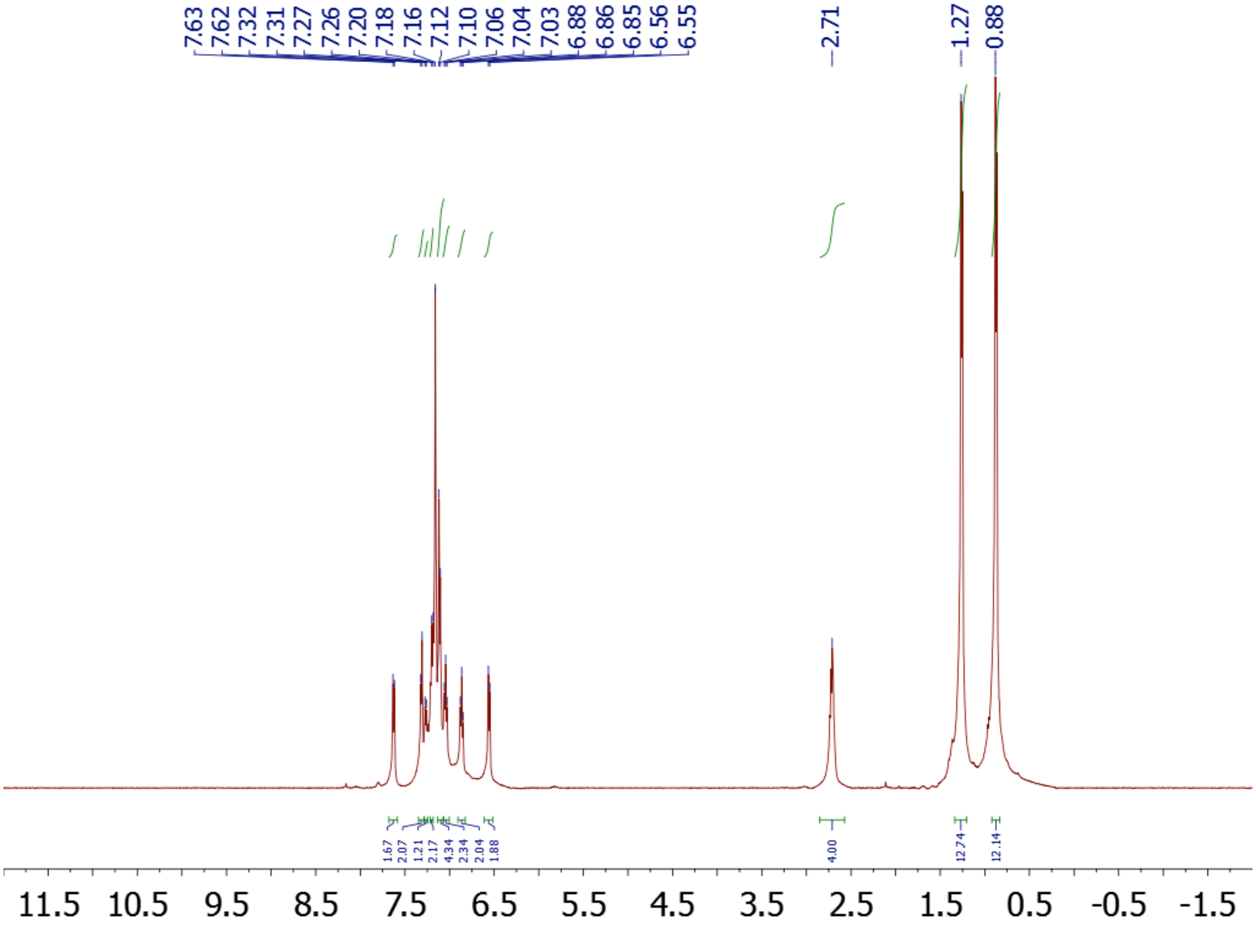
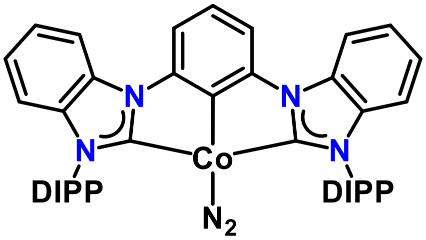


Figure S6. ^{1}H NMR (C_6D_6, 500 MHz) spectrum of (^{DIPP}CCC)Co(N_2) (**3a**).

^{13}C NMR Spectrum, 126 MHz, C_6D_6 (3a)



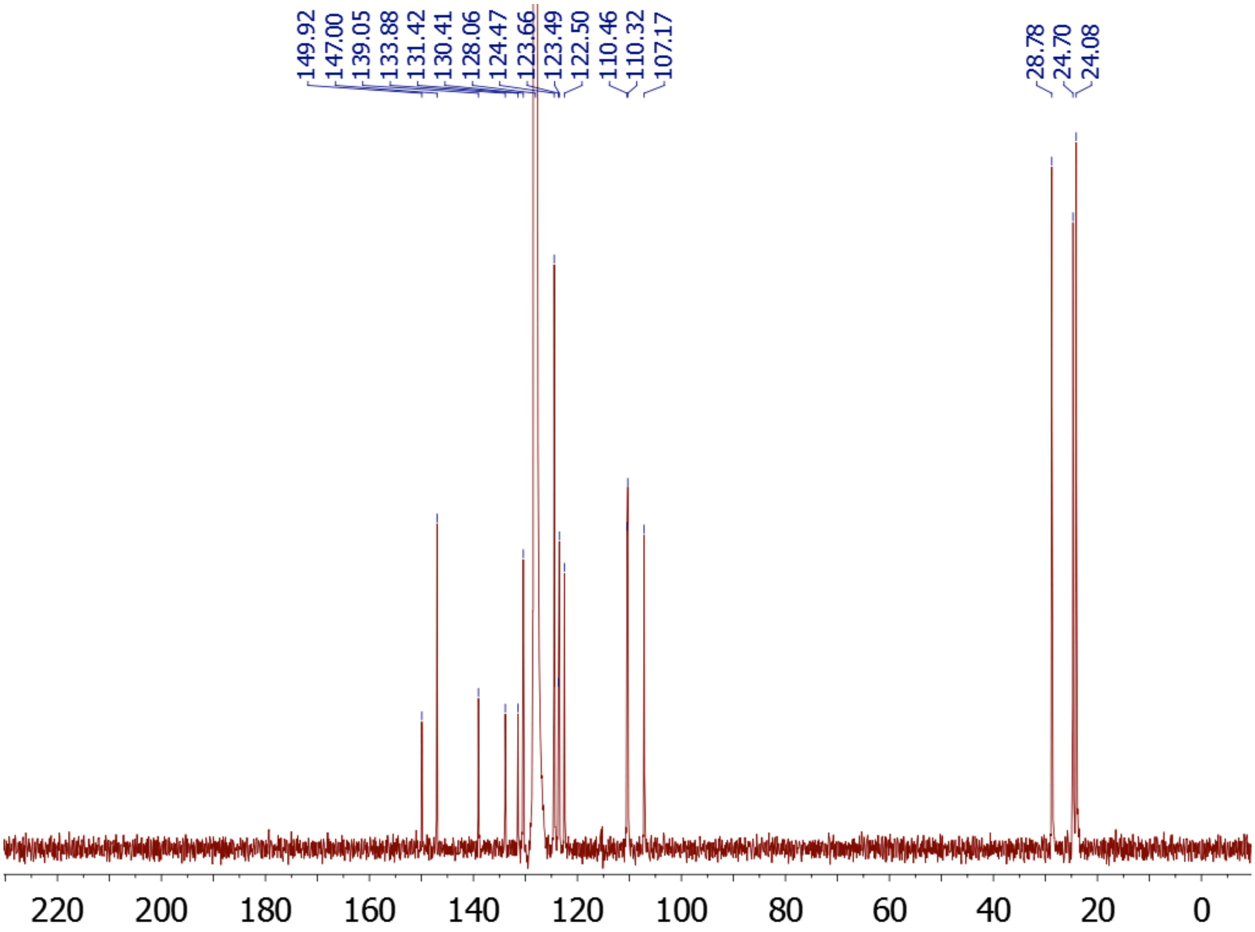
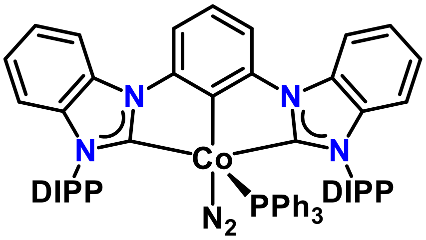


Figure S7. ^{13}C NMR (C_6D_6, 126 MHz) spectrum of (^{DIPP}CCC)Co(N_2) (**3a**).

^{1}H NMR Spectrum, 500 MHz, C_6D_6 (3a-PPh$_3$)



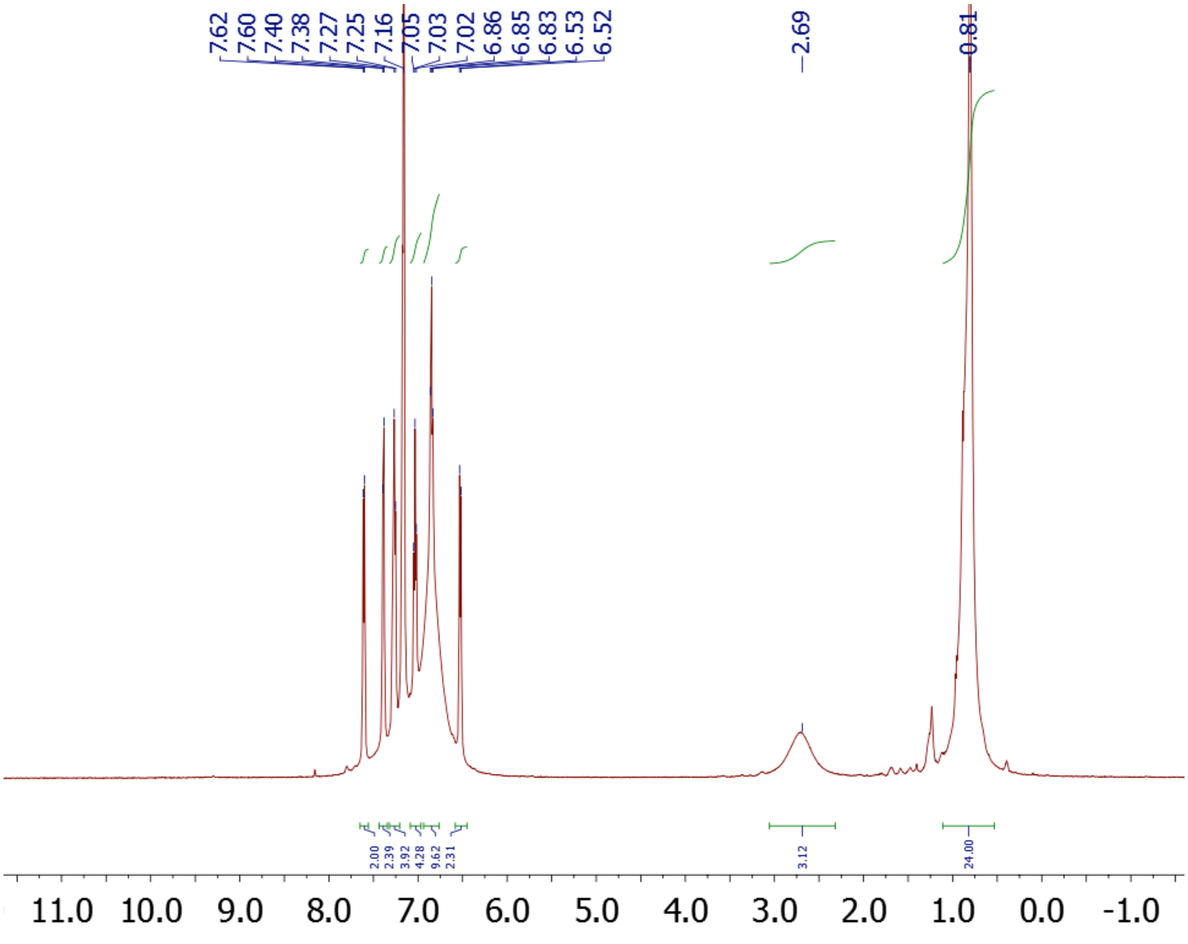


Figure S8. ^{1}H NMR (C_6D_6, 500 MHz) spectrum of (^{DIPP}CCC)Co(N_2)(PPh$_3$) (**3a-PPh$_3$**).

^{13}C NMR Spectrum, 126 MHz, C_6D_6 (3a-PPh$_3$)

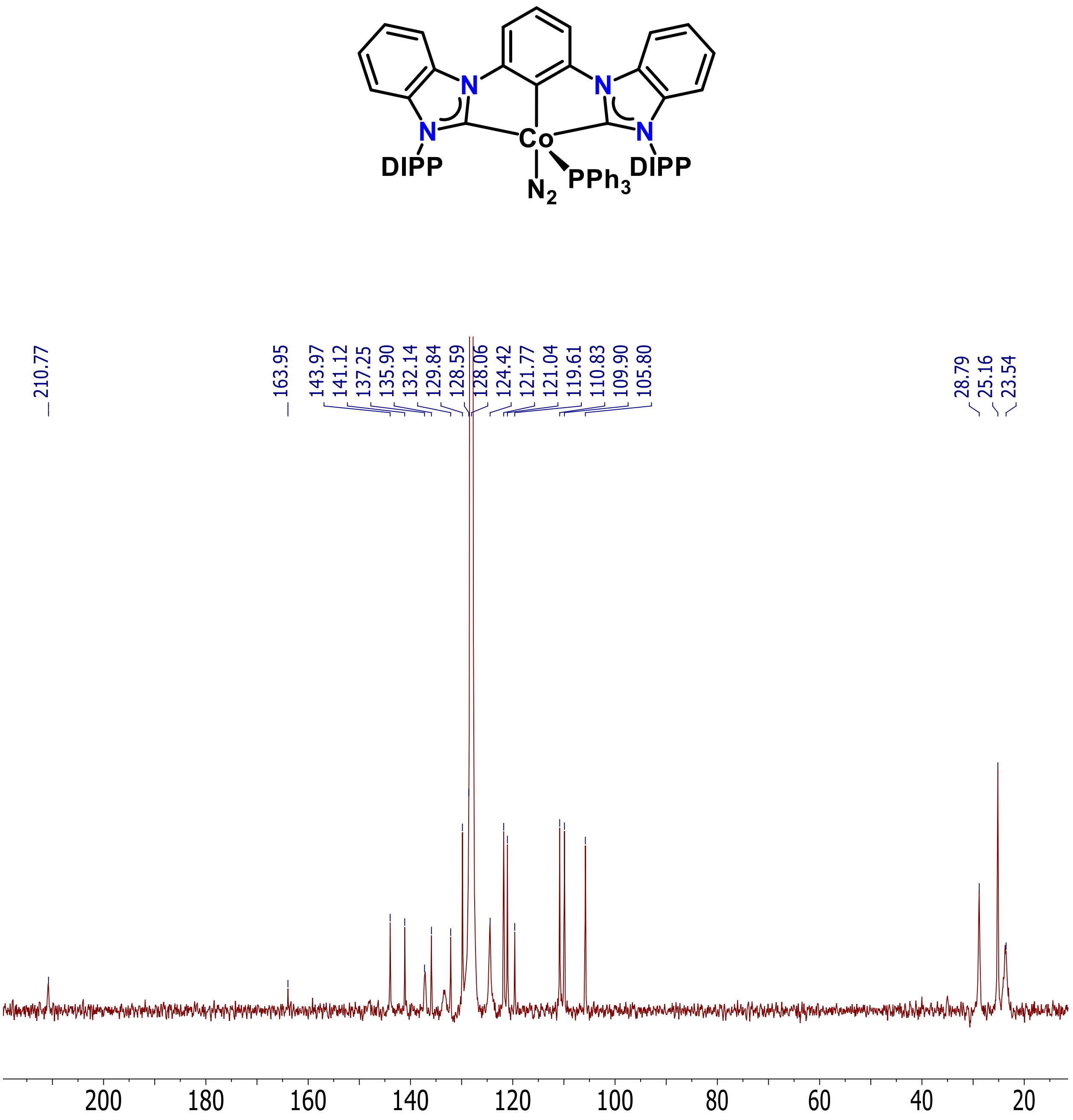
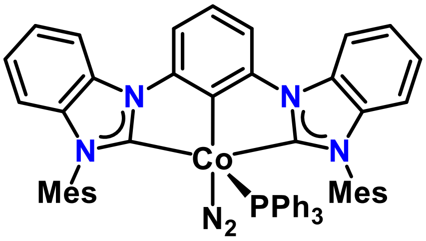


Figure S9. ^{13}C NMR (C_6D_6, 126 MHz) spectrum of (^{DIPP}CCC)Co(N_2)(PPh_3) (**3a-PPh$_3$**).

^{1}H NMR Spectrum, 500 MHz, C_6D_6 (3b-PPh$_3$)



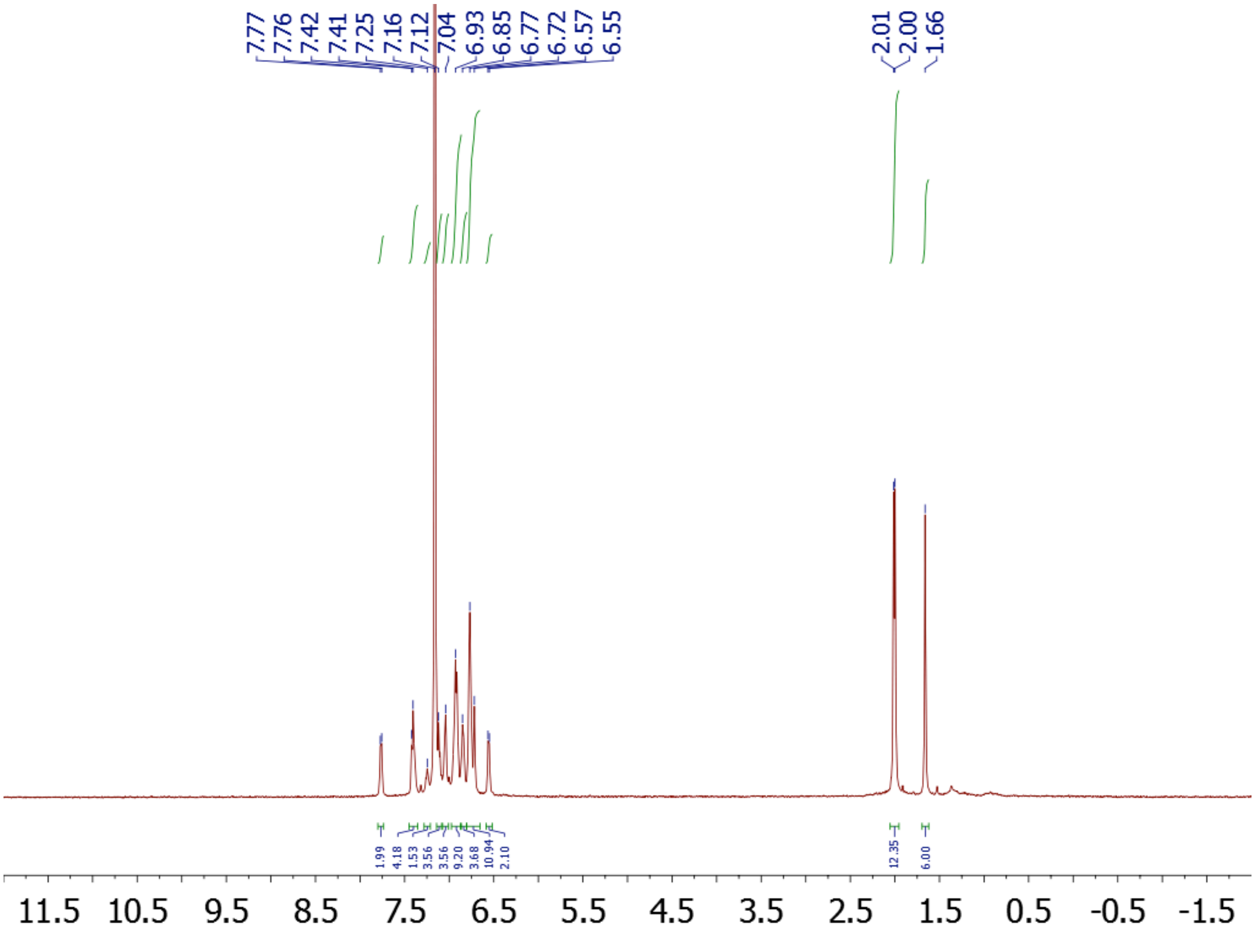
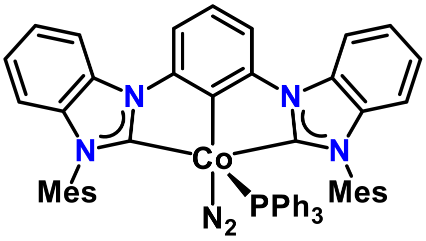


Figure S10. ^{1}H NMR (C_6D_6, 500 MHz) spectrum of (^{Mes}CCC)Co(N_2)(PPh_3) (**3b-PPh$_3$**).

^{13}C NMR Spectrum, 126 MHz, C_6D_6 (3b-PPh$_3$)



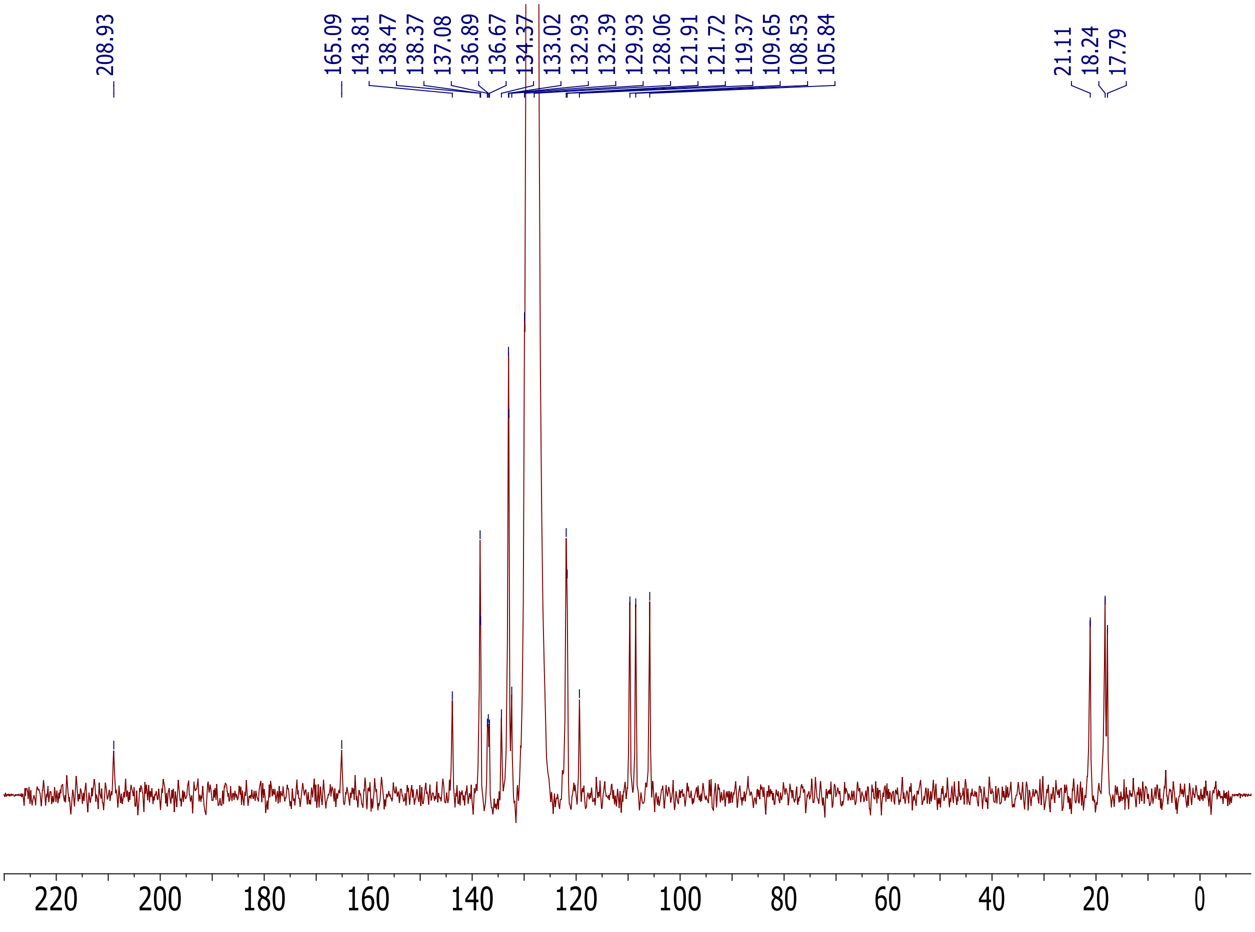


Figure S11. ^{13}C NMR (C_6D_6, 126 MHz) spectrum of (^{Mes}CCC)Co(N_2)(PPh_3) (**3b-PPh$_3$**).

Table S1. Crystallographic Parameters for complexes **1a**, **2a**, and **3a**.

	(^{DIPP}CCC)CoCl$_2$py (**1a**) cd99da	(^{DIPP}CCC)CoClpy (**2a**) cm49f	(^{DIPP}CCC)CoN$_2$ (**3a**) cd06h
Empirical Formula	C55 H56 Cl2 Co N5	C49 H50 Cl Co N5	C47 H48 Co N6
Formula Weight	916.88	803.32	755.84
Temperature	105(2) K	173(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 2_1/c	C 2_1/c	P-1
Unit Cell Dimensions	a = 14.7605(5) Å b = 17.6571(6) Å c = 17.9623(3) Å α= 90° β= 91.1198(13)° γ = 90°	a = 36.876(3) Å b = 15.1289(11) Å c = 22.0454(17) Å α = 90° β = 121.969(8)° γ = 90°	a = 10.9123(19) Å b = 13.358(2) Å c = 15.720(3) Å α = 65.272(7)° β = 78.937(8)° γ = 69.194(8)°
Volume	4654.5(3) Å^3	10433.6(14) Å^3	1943.0(6) Å^3
Z	4	8	2
Reflections collected	122537	30721	7133
Independent reflections	10300	9540	7133
Goodness-of-fit on F2	1.023	0.979	1.087
Final R indices [I>sigma(I)]	R1 = 0.0500 wR2 = 0.1416	R1 = 0.0577 wR2 = 0.1612	R1 = 0.0481 wR2 = 0.1106

Table S2. Crystallographic Parameters for complexes **1b**, **2b**, and **3b-PPh$_3$**.

	$(^{Mes}CCC)CoCl_2Py$ (**1b**) bm27vsa1	$(^{Mes}CCC)CoClPy$ (**2b**) cm69jsaq1	$(^{Mes}CCC)CoN_2(PPh_3)$ (**3b-PPh$_3$**) cd62hsa
Empirical Formula	C47 H42 Cl5 Co N5	C51 H54 Cl Co N5 O2	C56 H48 Co N6 P
Formula Weight	913.04	863.07	894.90
Temperature	183(2) K	296(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 21/n	P 21/c	P-1
Unit Cell Dimensions	a = 9.069(2) Å b = 22.886(6) Å c = 20.280(5) Å α= 90° β= 92.301(4)° γ = 90°	a = 14.4441(18) Å b = 20.502(3) Å c = 16.521(2) Å α = 90° β = 98.680(8)° γ = 90°	a = 12.3483(6) Å b = 13.3152(7) Å c = 16.1489(9) Å α = 107.661(3)° β = 90.213(2)° γ = 115.791(2)°
Volume	4206.0(18) Å^3	4836.5(11) Å^3	2249.4(2) Å^3
Z	4	4	2
Reflections collected	46522	8946	115626
Independent reflections	7747	8946	13805
Goodness-of-fit on F2	1.005	0.901	1.030
Final R indices [I>sigma(I)]	R1 = 0.0532 wR2 = 0.0953	R1 = 0.0596 wR2 = 0.1394	R1 = 0.0371 wR2 = 0.0862

Table S3: Selected bond lengths and angles for **1a**, **2a**, and **3a**.

	(^{DIPP}CCC)CoCl$_2$Py (1a)	**(^{DIPP}CCC)CoClPy (2a)**	**(^{DIPP}CCC)Co(N$_2$) (3a)**
Bond Distances (Å)			
Co – C1	1.981(2)	1.963(4)	1.911(3)
Co – C13	1.880(2)	1.871(3)	1.872(2)
Co – C20	2.000(2)	1.948(4)	1.899(3)
Co – Cl1	2.2787(6)	2.4465(9)	N/A
Co – Cl2	2.3175(6)	N/A	N/A
Co – N	2.098(2)	2.025(3)	1.802(2)
N – N	N/A	N/A	1.111(3)
Bond Angles (°)			
C13-Co-N5	179.26(9)	175.65(14)	178.73(12)
C1-Co-C13	79.90(10)	80.04(15)	79.76(11)
C13-Co-C20	79.82(10)	80.73(15)	79.95(12)
C1-Co-C20	159.69(10)	159.88(14)	159.54(11)
C1-Co-Cl	176.93(2)	N/A	N/A

Table S4: Selected bond lengths and angles for **1b**, **2b**, and **3b-PPh$_3$**.

	(^{Mes}CCC)CoCl$_2$Py (1b)	**(^{Mes}CCC)CoClPy (2b)**	**(^{Mes}CCC)Co(N$_2$)(PPh$_3$) (3b-PPh$_3$)**
Bond Distances (Å)			
Co – C1	1.961(4)	1.948(3)	1.9147(13)
Co – C13	1.871(4)	1.872(3)	1.8750(13)
Co – C20	1.958(4)	1.930(3)	1.9001(13)
Co – Cl1	2.2751(13)	2.4561(10)	N/A
Co – Cl2	2.2651(12)	N/A	N/A
Co – N	2.090(3)	2.011(3)	1.8270(12)
Co – P	N/A	N/A	2.2483(4)
N – N	N/A	N/A	1.1005(16)
Bond Angles (°)			
C13-Co-N5	179.13(16)	166.81(13)	157.89(5)
C1-Co-C13	80.29(18)	96.60(10)	79.14(5)
C13-Co-C20	80.44(18)	79.53(13)	79.21(5)
C1-Co-C20	160.73(17)	159.07(13)	152.73(4)
C1-Co-Cl	173.28(5)	N/A	N/A
N5-Co-P	N/A	N/A	106.68(4)

ATR-IR Spectrum of **3a**.

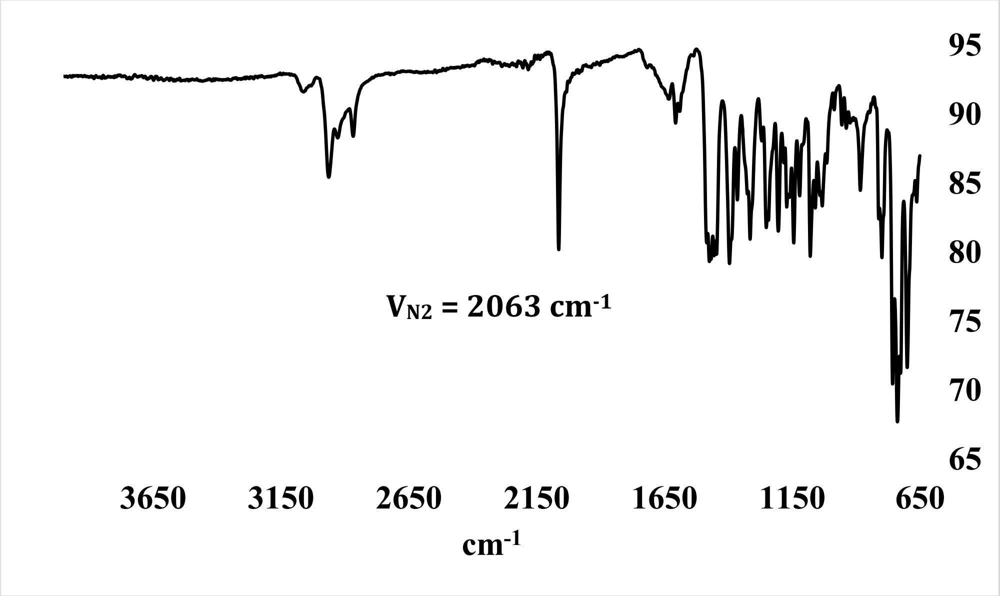


Figure S12. ATR IR Spectrum of (^{DIPP}CCC)Co(N$_2$) (**3a**).

ATR-IR Spectrum of **3a-PPh$_3$**.

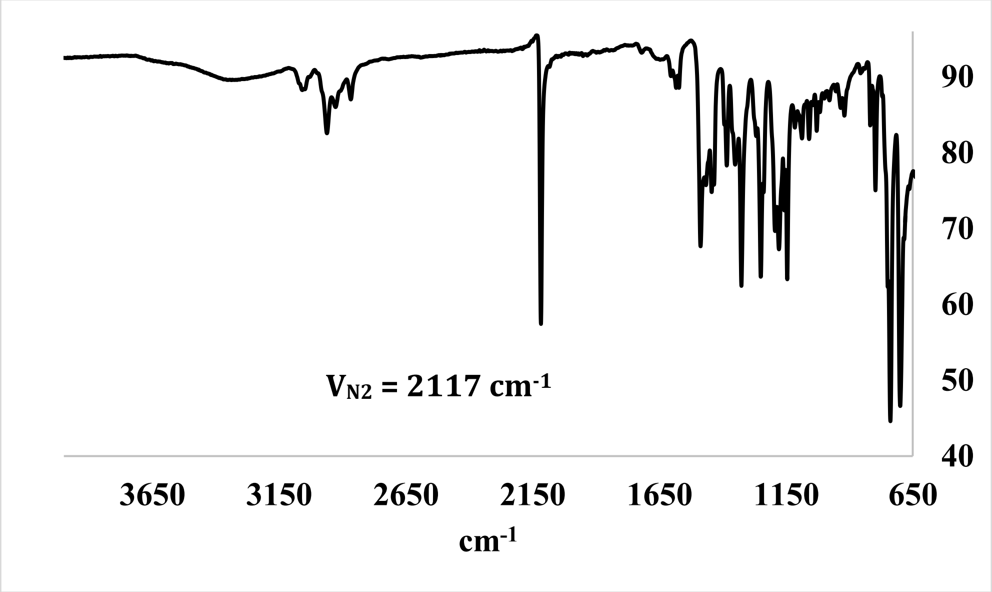


Figure S13. ATR IR Spectrum of (^{DIPP}CCC)Co(N$_2$)(PPh$_3$) (**3b-PPh$_3$**).

ATR-IR Spectrum of **3b-PPh₃**.

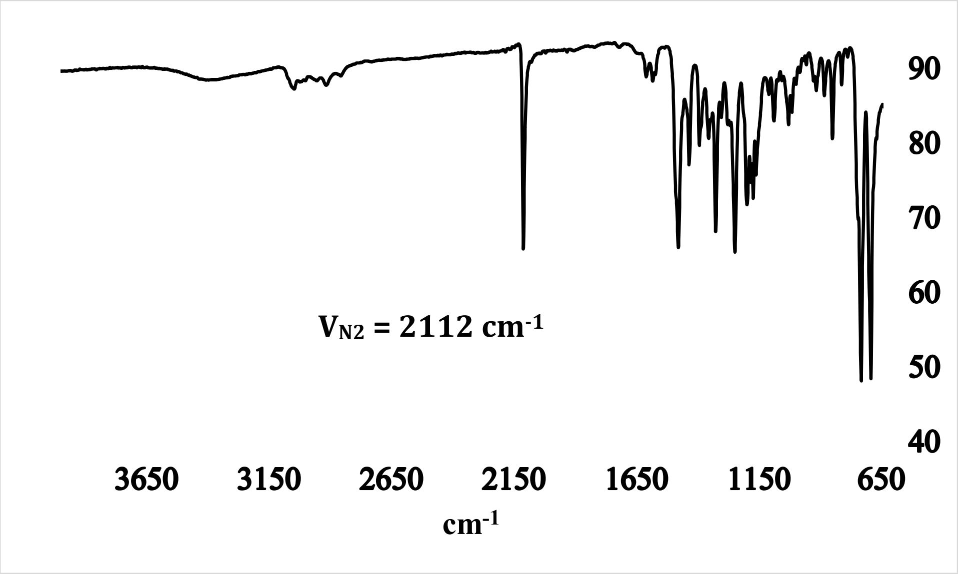
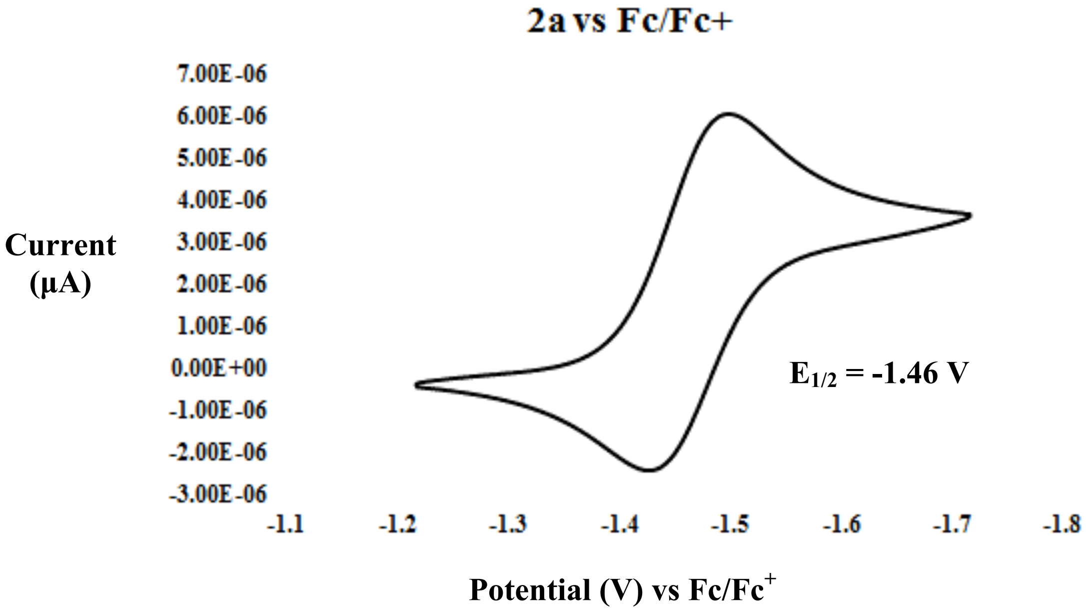
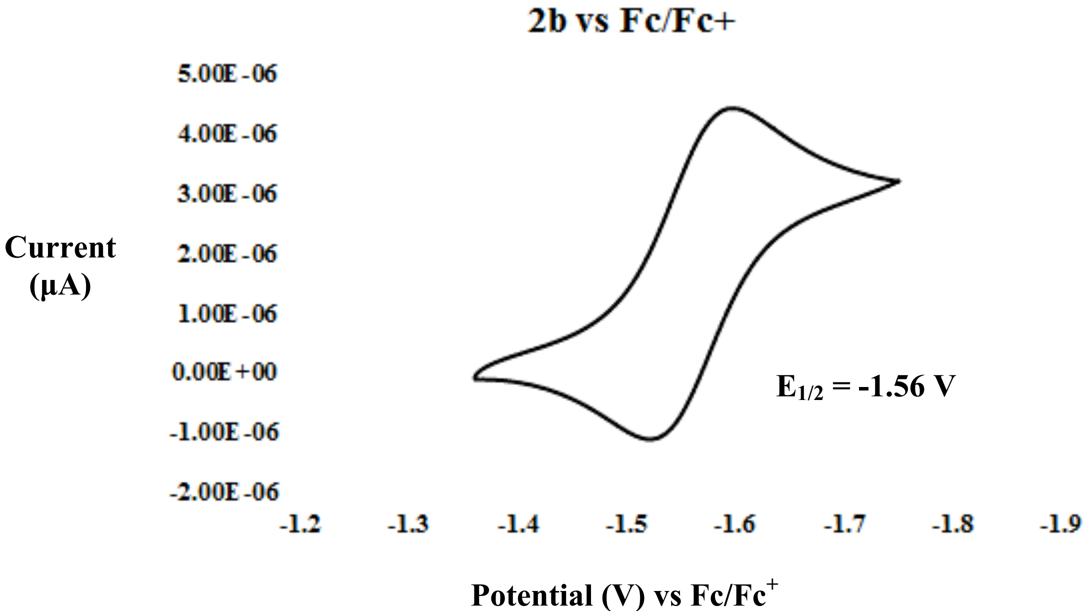


Figure S14. ATR IR Spectrum of (^{Mes}CCC)Co(N_2)(PPh_3) (**3b-PPh$_3$**).

Figure S15: Cyclic voltammogram of (^{R}CCC)CoClpy (R = DIPP (**2a**), Mes (**2b**)) (1 mM CH_3CN) were analyzed in CH_3CN with 0.1 M $[NEt_4][PF_6]$ as electrolyte, 100 mV/s scan rate and Pt as the working electrode.





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