

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

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The synthesis and characterization of a series of cobalt complexes featuring a pincer bis(carbene) ligand of the *meta*-phenylene-bridged bis-*N*-heterocyclic carbene (^{Ar}CCC, Ar = 2,6-diisopropylphenyl or mesityl) are reported. Cleavage of the aryl C–H bond of the ligand was achieved in a one-pot metalation procedure using Co(N(SiMe₃)₂)₂(py)₂, an equivalent of exogenous base, and trityl chloride to form the (^{DIPP}CCC)CoCl₂py complex. This species could be reduced to the Co(II) and Co(I)–N₂ molecules with the appropriate equivalents of reductant. Subsequent generation of (^{Mes}CCC)Co^{I–III} derivatives with the mesityl ligand proceeded in good yields. A suite of characterization techniques and the interconversion between all three oxidation states of the cobalt complexes is described.

Introduction

Electron-rich pincer complexes featuring late first-row metal centers have emerged as a prominent class of compounds for the mediation of interesting chemical transformations. Recent reports on first-row transition metal centers have demonstrated the functionalization of unactivated C–H bonds,¹ the oxidative addition of dihydrogen,^{1,2} and the functionalization of traditionally unreactive substrates.³ In the case of PNP (bis-(phosphino)pyridine) complexes with low-valent cobalt metal centers, such processes are thought to proceed through two-electron oxidative addition/reductive elimination pathways, in contrast to the one-electron pathways traditionally characteristic of first-row transition metal reactivity.^{1,3,4} Chirik and coworkers, for example, have reported the isolation of Co^{III} oxidative addition products in the course of their work with the catalytically active (^{IPr}PNP)CoCH₃ (^{IPr}PNP = 2,6-bis-(diisopropylphosphino-methyl)-pyridine) species.^{1,3} Similarly, recent reports by Caulton, Arnold, and others provide compelling evidence for the oxidative addition of various substrates such as dihydrogen,⁵ phenylsilane,⁶ and acetonitrile⁷ with low-valent cobalt metal centres.

In this regard, we sought to develop a modular approach for the synthesis of complexes bearing electron-rich ligands and build upon the two-electron paradigm for first-row transition metals. We recently reported the catalytic amination of aryl halides featuring a tris(triphenylphosphine) cobalt(I) chloride pre-catalyst.⁸ Hammett studies established a close-shelled mechanism consistent with a proposed Co^I/Co^{III} redox couple over the course of catalysis. Reasoning that such reactivity was the result of a highly donating, electron-rich ligand environment, we reasoned that a pincer ligand featuring a strongly-donating bis(carbene) ligand would confer a

similar electronic environment. The substitution of strongly-donating *N*-heterocyclic carbenes (NHCs) for phosphines in second- and third-row transition metal systems utilized in cross-coupling,⁹ alcohol oxidation,¹⁰ and olefin metathesis¹¹ has been met with a great degree of success. Such systems maintain the advantages imparted on the metal center by the phosphine ligands while retaining a greater resiliency towards deleterious ligand oxidation. Furthermore, CCC bis(carbene) ligand have been placed on second and third row transition metal ions.^{12,13}

Pursuant to this goal, we explored the ^{DIPP}CCC (^{DIPP}CCC = bis(2,6-diisopropylphenyl-benzimidazol-2-ylidene)phenyl) pincer ligand, first reported by Chianese,¹³ with first-row metal centers. Our initial investigations featured a family of nickel complexes on this ligand platform.¹⁴ Metalation of the ^{DIPP}CCC ligand with nickel was achieved via two different synthetic pathways: 1) the oxidative addition of the aryl C–H bond across a Ni⁰ starting material; and 2) via the *in situ* deprotonation of the benzimidazolium salt of the ligand with NiCl₂py₄.¹³ Given the limited availability of Co⁰ starting materials, we explored the use of alternative Co^{II} sources for metalation of the ligand platform. Herein, we report the synthesis of a series of cobalt complexes ranging in oxidation states, including a strategy for the room temperature cleavage of the backbone aryl C–H bond of the ligand platform over the course of metalation.

Results and Discussion

Synthesis of (^{Ar}CCC)Co^{III}Cl₂py. Interested in extending our studies of late first-row transition metal centers supported by strong-field ligand scaffolds, we set out to metalate the previously reported bis(carbene) ligands, ^{DIPP}CCC and ^{Mes}CCC (^{Mes}CCC = bis(2,4,6-trimethylphenyl-benzimidazol-2-ylidene)phenyl) with cobalt. Traditional metalation pathways for monoanionic pincer platforms on cobalt have been reported, citing the importance of lithiation of the aryl ring for the installation of the anionic Co–C_{aryl} bond as in the case of [(POCOP)CoI] (POCOP = κ³-C₆H₃-1,3-[OP(^tBu)₂]₂).¹⁵ Addition of an equivalent of ⁿBuLi to the previously reported free carbene, H(^{Mes}CCC),¹³ resulted in the undesired activation of the

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sterically unencumbered C–H bond *ortho* to the NHC moiety, suggesting that lithiation would not be a plausible route for accessing the desired cobalt complexes.

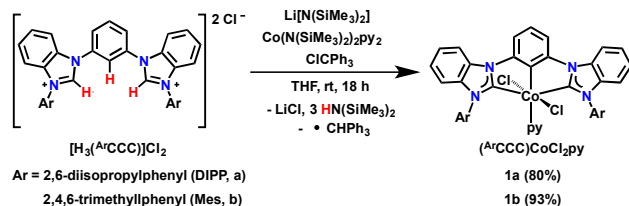
Initial attempts at metalation of the CCC ligand platform with cobalt focused on the preparation and subsequent reaction of the *in situ* generated bis(carbene) ligand¹⁴ with CoCl_2 , pyridine, and an equivalent of oxidant to generate $(^{\text{Ar}}\text{CCC})\text{Co}^{\text{III}}\text{Cl}_2\text{py}$ derivatives. While such attempts proved to be successful, low yields (< 50%) of the target complexes following workup deemed this route not synthetically useful.

We next explored the synthesis of a cobalt derivative using a metal reagent featuring multiple equivalents of internal base. In the same vein as the aminolysis methodology employed by Danopoulos for the preparation of analogous CNC (CNC = 2,6-bis(aryl)imidazol-2-ylidene), aryl = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$) cobalt bis(carbene) pincer complexes,¹⁶ we selected $\text{Co}(\text{N}(\text{SiMe}_3)_2)_2(\text{py})_2$ as our metal reagent. The sequential addition of $\text{LiN}(\text{SiMe}_3)_2$, $\text{Co}(\text{N}(\text{SiMe}_3)_2)_2(\text{py})_2$,¹⁷ and an equivalent of ClCPh_3 as an oxidant to the benzimidazolium salts of the CCC platform, $[\text{H}_3(^{\text{Ar}}\text{CCC})]\text{Cl}_2$, in THF, followed by stirring of the mixture at room temperature overnight, resulted in the formation of a green solution (Scheme 1). Following workup, the products, $(^{\text{Ar}}\text{CCC})\text{CoCl}_2\text{py}$ (Ar = 2,6-diisopropylphenyl (**1a**), 2,4,6-trimethylphenyl (**1b**)) were isolated as bright green powders in good yields (**1a** = 80%, **1b** = 93%). Characterization of **1a** by ^1H NMR spectroscopy revealed a diamagnetic spectrum with 14 resonances, consistent with the formation of a low-spin, Co^{III} product, assigned as the desired $(^{\text{DIPP}}\text{CCC})\text{CoCl}_2\text{py}$ (Figure S1). Two doublets

integrating to 12H each were located at 0.68 and 0.98 ppm, corresponding to the ^iPr methyl moieties of the flanking aryl substituents. The presence of one septet integrating to 4H corresponds to the methine protons of the ^iPr moieties, signifying a symmetric coordination of the ligand platform. Additional resonances integrating to 22H between 6.41 and 8.83 ppm were assigned to the aryl backbone of the pincer ligand and the bound pyridine. The corresponding signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 195.29 and 156.39 ppm were assigned to the C_{NHC} and C_{Ar} carbons (Figure S2), respectively, and were significantly shifted from those of the free carbene, $\text{H}(^{\text{DIPP}}\text{CCC})$ (231.27 ppm (C_{NHC}), 147.30 ppm (C_{Ar})). These values compare favourably with the previously reported $(^{\text{DIPP}}\text{CCC})\text{NiCl}$ complex (185.89 ppm (C_{NHC}); 150.88 ppm (C_{Ar})).

Similarly, the ^1H NMR spectrum of $(^{\text{Mes}}\text{CCC})\text{CoCl}_2\text{py}$ (**1b**) was consistent with the formation of a C_2 -symmetric Co^{III} compound with 12 resonances assigned to the target compound (Figure S3). Two singlets integrating to 12H and 6H, respectively, were located at 1.83 and 2.19 ppm, corresponding to the mesityl methyl moieties of the flanking aryl substituents. Additional resonances integrating to 20H between 6.52 and 8.79 ppm were assigned to the aryl backbone of the CCC ligand and bound pyridine. Signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 195.74 and 151.33 ppm (C_{NHC} and C_{Ar} carbons, respectively) are shifted from those of **1a**, but are consistent with the previously reported nickel complex (*vide supra*) (Figure S4).

Further characterization of **1a** and **1b** by single-crystal X-ray diffraction studies established the identity of the compounds. Green crystals of both complexes suitable for analysis were obtained via slow evaporation of a concentrated benzene solution (**1a**) and a 1:1 mixture of benzene and chloroform (**1b**) at room temperature, confirming the formation of the desired octahedral Co^{III} products (Figure 1, Tables S3 & S4). The two $\text{Co}-\text{C}_{\text{NHC}}$ bond lengths of 1.981(2) and 2.000(2) Å of **1a**, as well as those of **1b** (1.961(4) and 1.958(4) Å), are comparable to those of $(\text{CNC})\text{CoBr}_3$ (CNC = 2,6-bis(aryl)imidazol-2-ylidene), aryl = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$), 1.962(7) and 1.962(7) Å, reported by Danopoulos and coworkers¹⁶ and



Scheme 1. Synthesis of **1a** and **1b**

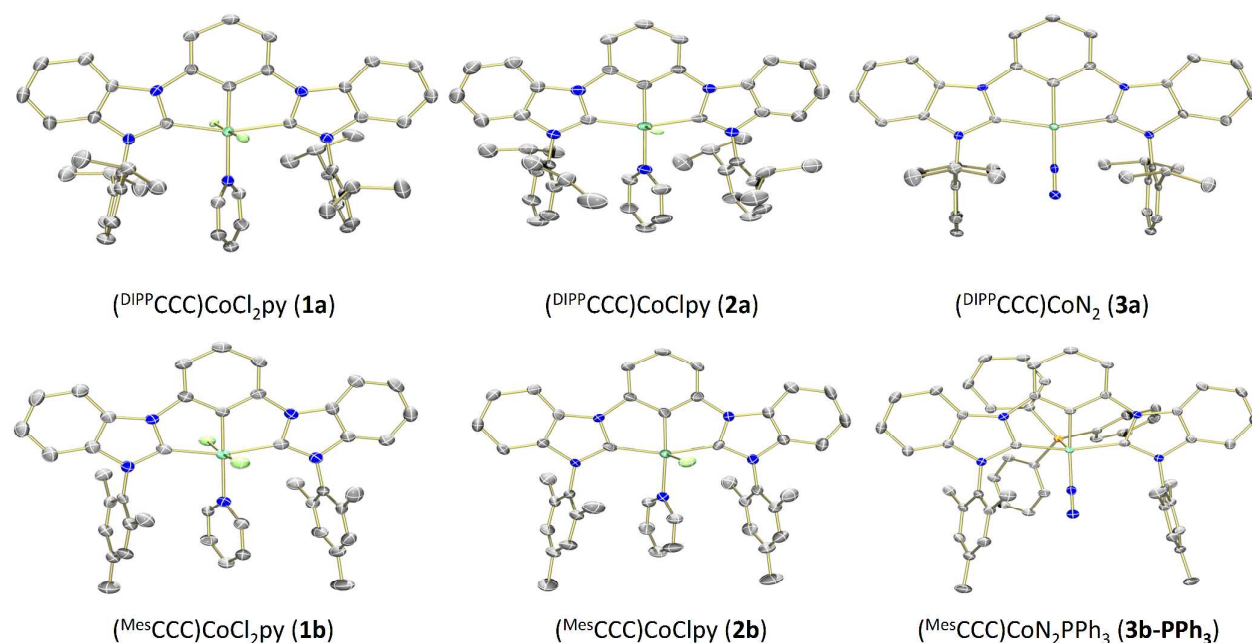
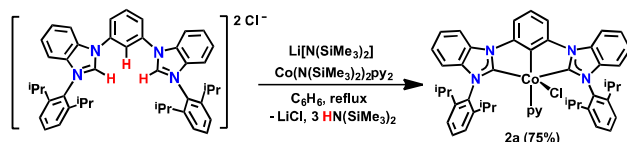


Figure 1. Molecular structures of **1-3a** (top) and **1-3b-PPh₃** (bottom) with 50% probability ellipsoids. Solvent molecules and hydrogen atoms have been omitted for clarity.

within the range reported for $\text{Co}^{\text{III}}\text{-C}_{\text{NHC}}$ bonds, 1.815 Å – 2.012 Å.^{18–20} Likewise, the $\text{Co}\text{-C}_{\text{Ar}}$ bond lengths of 1.880(2) Å and 1.871(4) Å for **1a** and **1b**, respectively, are within the range of $\text{Co}^{\text{III}}\text{-C}_{\text{Ar}}$ bonds, which range from 1.845 – 2.057 Å,^{20,21} but are shorter than the bond length for the analogous Co^{III} species, $(\text{PCP}^{\text{Me-}i\text{Pr}})\text{CoCl}_2$ ($\text{PCP} = N,N'$ -bis(diisopropylphosphino)- N,N' -dimethyl-1,2-diaminobenzene), reported by Kirchner and coworkers (1.937(1) Å).²² This is likely due to the increased rigidity of the CCC ligand backbone compared to the PCP system. The $\text{Co}\text{-Cl}$ bond lengths, 2.2787(6) and 2.3175(6) Å for **1a** and 2.2751(13) and 2.2651(12) Å for **1b**, also fall within the regime of recently reported Co^{III} complexes featuring an anionic $\text{Co}\text{-C}_{\text{Ar}}$ linkage, 2.229 – 2.429 Å.^{20,23,24} Finally, the $\text{C}_{\text{Ar}}\text{-Co}\text{-N}_{\text{py}}$ and $\text{C}_{\text{Ar}}\text{-Co}\text{-Cl}$ bond angles, 179.26(9) and 89.23(7)° respectively for **1a** and 179.13(16) and 90.11(12)° for **1b**, signify a nearly idealized octahedral geometry at cobalt.

Strongly-donating monoanionic pincer ligands featuring a $\text{Co}\text{-C}_{\text{aryl}}$ linkage are uncommon in the literature. Van Koten's report of a $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2]\text{CoClpy}$ species signifies one of the first cobalt pincer complexes containing an ECE ligand (E = donor groups).²⁵ More recently, Nishiyama and coworkers reported the synthesis of $\text{NCN}\text{-Co}$ complexes containing bis(oxazolinyl)phenyl (phebox) as auxiliary ligands.²¹ Similarly, the work of Sun,²⁶ Heinekey,¹⁵ Wass,²⁷ and Kirchner²² has been instrumental in establishing facile synthetic protocols to cobalt complexes featuring monoanionic PCP pincer ligands. Nevertheless, due to the difficulty in metalating these ligands with first-row transition metals such compounds remain largely underexplored.

Synthesis of $(^{\text{Ar}}\text{CCC})\text{Co}^{\text{II}}\text{Clpy}$. Interested in accessing a family of cobalt complexes with a variety of oxidation states, we next turned our attention to the preparation of a Co^{II} derivative. Reasoning that withholding an equivalent of oxidant should provide the target complex, we employed a similar synthetic protocol to the preparation of **1a** and **1b** but without the use of an additional oxidant. Refluxing a mixture of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$, $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2\text{py}_2$ ¹⁶ with the benzimidazolium salt of the $[\text{H}_3(^{\text{DIPP}}\text{CCC})]\text{Cl}_2$ platform in benzene resulted in the formation of an orange solution (Scheme 2). Following workup, the product, $(^{\text{DIPP}}\text{CCC})\text{CoClpy}$ (**2a**) was isolated as an orange powder in 75% yield. Characterization of **2a** by ^1H NMR spectroscopy was consistent with the formation of a new paramagnetic species with resonances ranging from -10 to 16 ppm (Figure S5).



Scheme 2. Synthesis of **2a**.

Interestingly, extension of this protocol to the mesityl variant of the ligand platform was unsuccessful and another route to the Co^{II} species was explored. The addition of half an equivalent of 9,10-dihydro-9,10-anthracenediyl-tris(THF)magnesium to a solution of **1b** in THF resulted in the formation of $(^{\text{Mes}}\text{CCC})\text{CoClpy}$ (**2b**), albeit in low yield of crystalline product (28%) following workup. In contrast to the broad resonances observed in the paramagnetic ^1H NMR spectrum for **2a**, the **2b** analogue is NMR silent.

EPR Spectroscopy. The X-band EPR spectrum of crystalline **2b** obtained from a 1:1 toluene:THF glass at 77 K is depicted in Figure

2. The EPR parameters for **2b** ($g_x = 2.380$, $g_y = 2.259$, and $g_z = 1.985$) are consistent with a low-spin $d^7 S = 1/2$ molecule.²⁸ Additionally, the hyperfine interaction to the ^{59}Co nucleus ($S = 7/2$) is not the sole contributor to the hyperfine coupling observed ($A_{\text{Co}}(x,y,z) = 224$ MHz, 132 MHz, 355 MHz). Superhyperfine coupling to the ^{35}Cl and ^{37}Cl ($S = 3/2$) nuclei was also observed ($A_{\text{Cl}}(x,y,z) = 10$ MHz, 10 MHz, 41 MHz).

Intriguingly, a comparison of EPR parameters to **2a** ($g_x = 2.259$, $g_y = 2.215$, and $g_z = 1.995$; $A_{\text{Co}}(x,y,z) = 9$ MHz, 7 MHz, 266 MHz) revealed notable differences between the ligand variants. While superhyperfine interactions to the ^{14}N nuclei ($A_{\text{N}}(x,y,z) = 24$ MHz, 27 MHz, 31 MHz) were observed in **2a**, such interactions were weakly resolved. Moreover, no resolved superhyperfine coupling to the ^{35}Cl and ^{37}Cl nuclei was discernable. Such differences between the ligand variants may be linked to the spatial orientation of the chloride ligand. In the case of **2b**, it is likely that the chloride ligand binds trans to the $\text{Co}\text{-C}_{\text{Ar}}$ in the solution state, in contrast to its apical position in the solid state, while **2a** maintains the structure observed in the solid state.

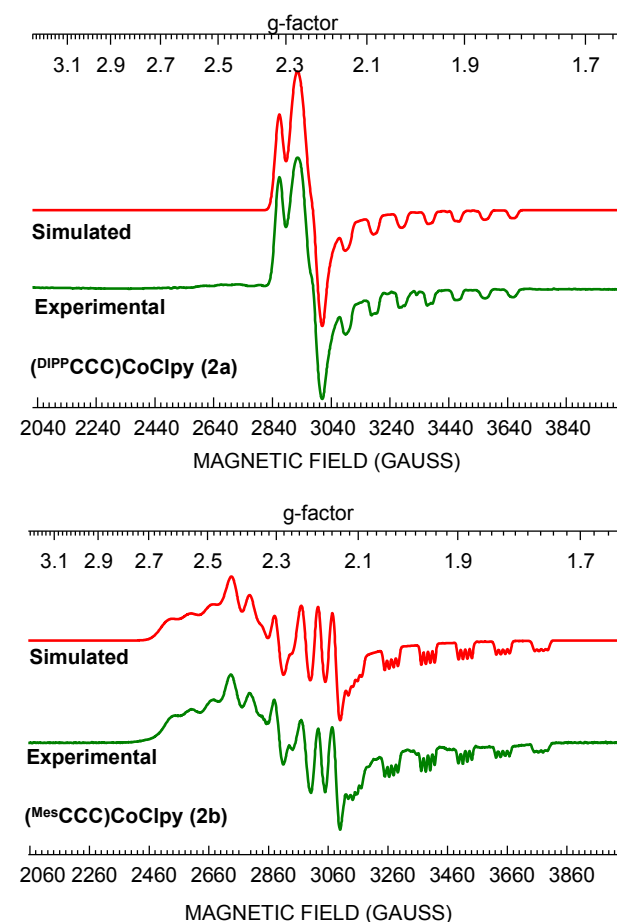


Fig. 2 EPR spectra of **2a** (left) and **2b** (right) recorded in toluene:THF (1:1) glass at 77 K. EPR parameters for **2a** (2.5E+3 gain; 2.00 G modulation amplitude; 20.00 dB power; microwave frequency = 9.2903 GHz) and **2b** (1.60E+3 gain; 4.00 G modulation amplitude; 20.00 dB power; microwave frequency = 9.2907 GHz).

To unambiguously identify the structures of complex **2a** and **2b**, orange crystals suitable for X-Ray diffraction were grown by slow evaporation from a concentrated solution of benzene and THF at

room temperature, respectively. Crystallographic characterization of **2a** and **2b** confirmed the formation of the target complexes, revealing a square pyramidal geometry ($\tau = 0.26$ (**1a**), $\tau = 0.13$ (**1b**))²⁸ about a Co^{II} center with a chloride occupying the apical position (Figure 1, Table S3 & S4). The two Co–C_{NHC} bond lengths of 1.963(4) and 1.948(4) Å for (^{DIPP}CCC)CoClpy (**2a**) and 1.948(3) and 1.930(3) Å for (^{Mes}CCC)CoClpy (**2b**) are very similar to those reported for [*trans*-(CNC)Co(κ^1 -CF₃-SO₃)₂(py)], 1.942(6) and 1.941(6) Å,¹⁶ and typical for Co^{II}–C_{NHC} bonds (1.845 – 2.127 Å).²⁰ In contrast, the Co–C_{Ar} bond lengths of 1.871(3) Å and 1.872(3) Å for **2a** and **2b**, respectively, are noticeably shorter than typical Co^{II}–C_{Ar} bonds reported in the literature (1.9020 – 2.0570 Å)^{20,30,31} and shorter than those observed in the [Co^{II}(PCP^{Me}-iPr)] complexes recently reported by Kirchner and coworkers (1.919 to 1.953 Å)²² or the ^RPOCOP^RCoI complex reported by Heinekey (1.924(4) Å).¹⁵ The Co–Cl bond lengths of 2.4465(9) Å for **2a** and 2.4561(10) Å for **2b** also differ considerably the bond lengths in the [Co^{II}(PCP^{Me}-iPr)]²² and [Co(PCP-ⁱBu)Cl]³² complexes (2.234(1) – 2.3103(4) Å) and 2.260(1) Å, respectively. Furthermore, the pyridine ligands of **2a** and **2b** lie in the basal position with a Co–N_{py} bond length of 2.025(3) Å and 2.011(3) Å, in contrast to the apical position of the pyridine ligand observed in the analogous PCP system (Co–N: 2.1417(8) Å).²² Finally, the C_{Ar}–Co–N_{py} and Cl–Co–N_{py} angles in **2a** (175.65(14)° and 93.66(9)°, respectively) and **2b** (166.81(13)° and 96.58(9)°, respectively), are distorted from an idealized square pyramidal geometry but similar to those reported for (PCP^{Me}-iPr)Co(py)Cl (166.89(3)° and 96.28(3)°).²²

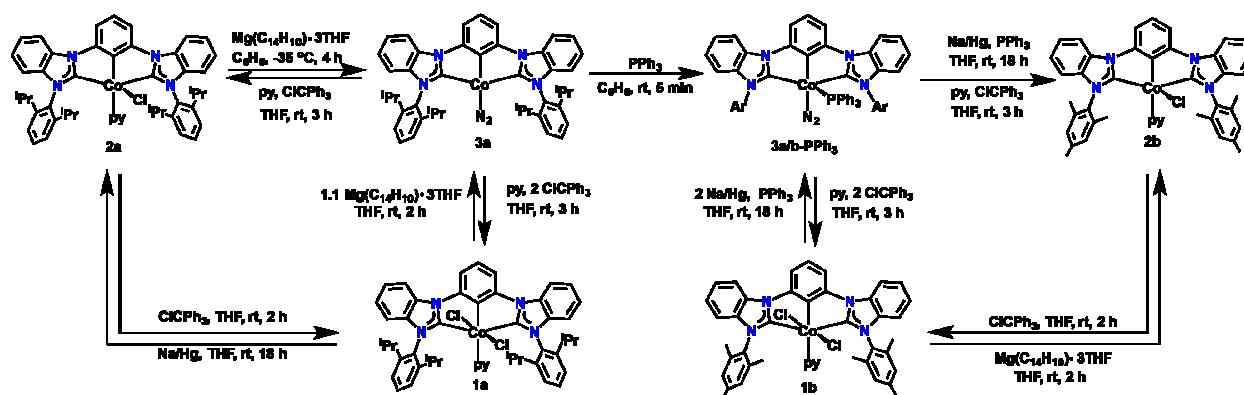
Cyclic Voltammetry. Seeking to investigate the accessibility of a Co^I derivative of the ^RCCC ligand platform, we studied the electrochemical properties of **2a** and **2b** using cyclic voltammetry (Figure S15). The study was carried out in a 1 mM solution of **2** in acetonitrile with 0.1 M [NBu₄][PF₆] as electrolyte. At a scan rate of 100 mV/s, a single reversible redox event assigned to the Co^{II}/Co^I redox couple was observed in the window between -1 and -2 V with an E_{1/2} at -1.46 V (**2a**) and -1.56 V (**2b**) vs Fc/Fc⁺, respectively. Taken together, the cyclic voltammograms of **2a** and **2b** suggest that the Co^{II} species may be amenable to chemical reduction.

Synthesis of (^{Ar}CCC)Co^IN₂. Encouraged by these results, and interested in the synthesis of low-valent complexes featuring the ^{Ar}CCC ligand platform, we investigated the chemical reduction of **2a** and **2b**. This goal was readily accomplished by the addition of an equivalent of 9,10-dihydro-9,10-anthracendiyI-tris(THF)magnesium

as a solid to a frozen solution of **2a** in benzene (Scheme 3). Workup of the dark brown reaction mixture afforded a brown powder in good yields (77%). Characterization of the product by ¹H and ¹³C NMR spectroscopies confirmed the formation of a new diamagnetic species, consistent with the predicted low-spin Co^I product, (^{DIPP}CCC)CoN₂ (**3a**). The presence of 11 resonances in the ¹H NMR spectrum, shifted from those of **1a**, indicated the loss of the pyridine ligand and is consistent with a C₂ symmetric ligand environment (Figure S6). Resonances located at 0.88 and 1.27 ppm and integrating to 12H each were assigned to the methyls of the ⁱPr moiety, while a septet at 2.71 ppm integrating to 4H was assigned to the methine protons of the ⁱPr groups. The presence of 15 resonances in ¹³C NMR spectrum are also consistent with the proposed formulation (Figure S7). The complex was additionally characterized by IR spectroscopy, revealing an intense feature at 2063 cm⁻¹, assigned to the vibrational mode of a bound dinitrogen molecule, shifted from that of free N₂ (2331 cm⁻¹).³³ The presence of this N₂ ligand suggests formation of a monomeric species due to the steric bulk of the flanking aryl substituents.

Due to the limited amount of structural data on four-coordinate Co^I compounds featuring a terminal dinitrogen ligand, complex **3a** was further characterized by X-ray crystallography. Red-brown crystals were grown by slow evaporation from benzene at room temperature. Crystallographic characterization of the complex provided definitive evidence of a square planar geometry about the metal, with an N₂ molecule bound *trans* to the Co–C_{aryl} bond (Figure 1, Table S3). The Co–C_{NHC} bond lengths of 1.911(3) and 1.899(3) Å and the Co–C_{aryl} bond length of 1.872(3) Å are comparable to those reported for the (CNC)CoBr (Co–C_{NHC}: 1.917(5) and 1.909(5) Å) and (CNC)Co(CH₃) (Co–C_{NHC}: 1.914(4) and 1.898(4) Å)¹⁶ and shorter than those reported for complex **1a**, perhaps due to greater electron density in the Co–C bonds and coordinative unsaturation about the cobalt metal center. An N₂ bond length of 1.111(3) Å indicates a largely unactivated dinitrogen ligand (d_{N₂}: 1.09 Å). Indeed, a comparison to structurally analogous cobalt dinitrogen complexes reveals that the bond distance of the dinitrogen ligand typically falls within a narrow regime of 1.011 – 1.122 Å,^{6,34–37} signifying that a lack of activation of the dinitrogen ligand is not uncommon with low-valent cobalt compounds.

In analogy to the preparation of **3a**, reduction of (^{Mes}CCC)CoClpy, **2b**, was also readily accomplished with the use of 9,10-dihydro-9,10-anthracendiyI-tris(THF)magnesium reductant. The use of sodium amalgam and subsequent addition of



Scheme 3. The interconversion between complexes **1-3** (a = 2,6-diisopropylphenyl, b = mesityl).

triphenylphosphine also proved to be a facile method for the synthesis of a Co^I derivative of the mesityl ligand variant and was selected as the principal synthetic route to the reduced compound, furnishing (^{Mes}CCC)CoN₂(PPh₃) (**3b-PPh₃**) in excellent yields (Scheme 3). Characterization of the deep red product by ¹H NMR spectroscopy confirmed the formation of a diamagnetic species, consistent with the predicted low-spin Co^I product, **3b-PPh₃**. The presence of 12 resonances in the ¹H NMR spectrum, shifted from those of **1b**, indicated a C_s symmetric ligand environment and the presence of a triphenylphosphine ligand (Figure S10). Intense resonances in the aryl region, shifted from those of free triphenylphosphine, further corroborate this assignment. Resonances located at 1.66, 2.00 and 2.01 ppm and integrating to 6H each, were assigned to the methyls of the mesityl moiety. Characterization by ³¹P NMR spectroscopy revealed no resonances, precluding a more detailed analysis of the compound with this method and prompting our synthesis of a (^{DIPP}CCC)CoN₂, **3a**, resulted in an immediate color change to deep red, affording (^{DIPP}CCC)CoN₂(PPh₃) (**3a-PPh₃**) in excellent yields (89%). In parallel to **3b-PPh₃**, this compound possessed no resonances in the ³¹P NMR spectrum likely attributed to coupling of the phosphorous ligand to the ⁵⁹Co nucleus (*I* = 7/2, 100% abundance). However, the additional aryl resonances in the ¹H NMR spectrum compared to **3a** are in agreement with the binding of a triphenylphosphine ligand.

Additional characterization of **3b** by infrared spectroscopy revealed an intense stretch at 2112 cm⁻¹, consistent with the presence of a bound, unactivated dinitrogen molecule to attain a formally 18-electron complex. We hypothesized that the presence of this dinitrogen ligand, coupled with the steric demands of the appended triphenylphosphine, would ensure a monomeric complex. Characterization by X-ray crystallography was consistent with this hypothesis, revealing a square pyramidal species with an N₂ molecule bound *trans* to the Co–C_{aryl} bond (Figure 1, Table S4). The two Co–C_{NHC} bond lengths of 1.9147(13) and 1.9001(13) Å and the Co–C_{aryl} bond length of 1.8750(13) Å are comparable to those of complex **3a**. Similarly, an N₂ bond length of 1.1005(16) Å indicated a largely unactivated dinitrogen ligand in agreement with the IR stretch observed for the compound.

As depicted in Scheme 3, the interconversion of all of these molecules is readily achieved. Conversions of the Co^I derivatives **3a** and **3b-PPh₃** to their Co^{II} (**2a**, **2b**) analogues were accomplished by the addition of one equivalent of ClCPh₃ as the oxidant and subsequent formation of Gomberg's dimer. An additional equivalent of ClCPh₃ to **2a** or **2b** furnished the Co^{III} (**1a**, **1b**) analogues, although some reactions, particularly those of the ^{DIPP}CCC variant, were accompanied by the formation of small amounts of impurities that could readily be overcome through the previously described synthetic pathways.

Conclusions

In conclusion, a series of cobalt pincer complexes featuring the electron-rich, monoanionic bis(carbene) (^{DIPP}CCC) and (^{Mes}CCC) ligands have been synthesized. The Co^{III} derivatives of these compounds have been prepared in good yields, including the room temperature synthesis of a Co^{III} derivative from the benzimidazolium salt precursor of the (^{Ar}CCC) ligand framework. In contrast to traditional routes that make use of lithiation and subsequent addition of cobalt halide compounds, this room temperature synthesis utilizes Co^{II} sources featuring equivalents of internal base for the room temperature aryl C–H bond cleavage to generate the metal derivative. A suite of characterization

techniques was used to identify and study these complexes, including NMR spectroscopy and X-ray crystallography. Such complexes provide an interesting platform from which to study two-electron processes on base metals, particularly given the extensively characterized nature of the different oxidation states of cobalt with the ligand platform.

Acknowledgements

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