# Synthesis and Structure of 2,5-Bis[N-(2,6mesityl)iminomethyl]pyrrolylcobalt(II): Evidence for One-Electron-Oxidized, Redox Noninnocent Ligand Behavior

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# **Supporting Information**

**ABSTRACT:** The title complex  $Co(Mes_2pyr)Cl_2$  is prepared from  $CoCl_2$  and  $(Mes_2pyr)H$ . Instead of the expected  $(Mes_2pyr)CoCl$  complex, a complex with formula  $(Mes_2pyr)CoCl_2$  is isolated wherein the angle strain of the  $Mes_2pyr$  ligand results in metal ligation by only two of the three ligand donor atoms. Careful examination of structural, spectroscopic, and magnetic features indicates this compound is best described as a complex of high-spin Co(II) with a neutral radical ligand.



# INTRODUCTION

Redox noninnocent ligands are of substantial interest to the chemical community due to the ability of these ligands to serve as electron reservoirs, a role traditionally played by transition metals. The use of redox noninnocent ligands in coordination complexes can impart redox reactivity not normally observed using redox innocent ligands and even promote redox reactions at complexes of redox-inactive metals. Their utility from biological<sup>1–3</sup> to synthetic<sup>4–6</sup> systems makes them of broad interest in the field of inorganic chemistry. One ligand system of interest is the pyridine diimine ligand (PDI), which illustrates well these characteristics.<sup>7–12</sup> In particular, work on small molecule activation at complexes of cobalt by the group of Chirik is worthy of note.<sup>13–15</sup> PDI can exist in a wide range of four oxidation states from 0 to -3.<sup>16,17</sup> To date, the oxidation of PDI to positive ligand states has not been observed. Exploration of oxidation to Fe(I) rather than ligand-centered oxidation to a formal PDI<sup>+</sup> state.<sup>18</sup>

We have been exploring the chemistry of pyrrolato analogues of pyridine-based ligand systems. The 2,5-bis[N-(2,6-mesityl)iminomethyl]pyrrolato ligand (Mes<sub>2</sub>pyr) was prepared by modification to literature procedures<sup>19,20</sup> and is  $\pi$ -isoelectronic to the PDI ligand but exhibits greater donor capability by the central nitrogen atom while maintaining an extended  $\pi$ -electron structure that could facilitate backbonding. The resulting HOMO is higher in energy due to increased electron density distributed over a smaller bonding network, making these ligands easier to oxidize than the analogous PDI ligands, as evidenced by the accessibility of oxidized radicals of extended pyrrole-based ligands.<sup>21–26</sup> A further difference is that as a result of the angle strain in the five-membered pyrrole ring, the imine donor arms are more splayed than those in PDI (Figure 1), leading to complexes which are typically bidentate.<sup>27–34</sup>



**Figure 1.** Comparative 2-D structures of pyridine diimine and pyrrole diimine ligand systems.

Most commonly, bond length measurements by single-crystal X-ray diffraction have been invoked as evidence for redox noninnocent behavior. For instance, in the case of diimino-pyrrolate, the lengths of the C–N and C–C bonds provide clues about the bond order and therefore oxidation state of the ligand (Figure 2).



Figure 2. Illustration of expected bond length perturbations from redox noninnocent behavior in pyrrole diimine.



Electronic descriptions of specific transition metal complexes of redox-noninnocent ligands have been a topic of discussion since the effect could be described as either ligand reduction/ oxidation or  $\pi$ -backbonding/ $\pi$ -donation with metal d orbitals<sup>9,10,35–38</sup> In particular, the groups of Neidig and Milstein have cautioned that reliance on bond lengths as the primary determinant of redox noninnocent behavior is risky and that more careful spectroscopic and magnetic experiments are important to properly assign electronic structure.<sup>39,40</sup>

In our attempt to prepare the Mes<sub>2</sub>pyr analogue of  $Co^{II}(PDI)-X$  complexes, we instead isolated (Mes<sub>2</sub>pyr)CoCl<sub>2</sub> in two polymorphs. The unexpected metal-ligand combination within this product makes assignment of its electronic structure not immediately obvious. Careful spectroscopic and magnetic investigations reveal a structure best assigned as a Co(II) ion coordinated by a redox noninnocent, oxidized, neutral (Mes<sub>2</sub>pyr)<sup>•</sup> ligand.

#### RESULTS AND DISCUSSION

**Synthesis and Structure.** Reflux of  $(Mes_2pyr)H$  with anhydrous CoCl<sub>2</sub> resulted in a green suspension, which when filtered, dried, and recrystallized from dichloromethane/ pentane gave dark green crystalline product in reasonable yield (68%). Recrystallization under these conditions has resulted in isolation of crystals in two polymorphs: A solventfree morphology (Figure 3, middle) and a CH<sub>2</sub>Cl<sub>2</sub> solvate (Figure 3, bottom). The structure is that of a planar diiminopyrrolate ligand with the imine donor arms in a cis conformation but with the CoCl<sub>2</sub> moiety disordered between the bidentate binding sites. The major component of the disorder (80%) is shown in Figure 3. This disorder could be viewed as a reflection or rotational disorder. A similar disorder



Figure 3. Thermal ellipsoid plots of  $(Mes_2pyr)H$  (top),  $(Mes_2pyr)-CoCl_2$  (middle), and  $Mes_2pyr)CoCl_2\cdot CH_2Cl_2$  (bottom). The major component of the Co atom disorder is shown. Ellipsoids set at the 50% probability level. C–H hydrogen atoms omitted for clarity.

was observed in the zinc complex  $(Cy_2pyr)_2Zn$  (Cy = cyclohexyl),<sup>31</sup> and the anionic version of this compound  $[NEt_4]^+[((Pr_2C_6H_3)_2pyr)Co^{II}Cl_2]^-$  was previously reported, but its crystal structure was too poor for accurate bond measurements due to crystal desolvation.<sup>20</sup> When (Mes<sub>2</sub>pyr)H is first deprotonated with BuLi, the same product is obtained based upon UV-vis spectroscopy (Figure S2) and single-crystal X-ray diffraction. It is worthwhile to note that upon metalation of the ligand a statistically significant lengthening of the C(1)= N(1) imine and the C(2)-C(3) ( $\alpha$ - $\beta$  pyrrole) bonds is observed, along with a simultaneous shortening of the C(1)-C(2) (methine-to- $\alpha$ -pyrrole) and the C(3)–C(4) ( $\beta$ – $\beta$ pyrrole) bonds. Finally, the pyrrole C-N distances are relatively unperturbed, remaining in the neighborhood of 1.36-1.37 Å for all measurements. These bond lengths are reasonably consistent with the expected structures calculated from geometry optimization using density functional theory

The crystal structures of  $(Mes_2pyr)CoCl_2$  are intriguing for several reasons. First, although a Co(II) monochloride complex was expected, the structure obtained illustrates a cobalt atom with three (formally) negatively charged ligands: two Cl<sup>-</sup> and one Mes<sub>2</sub>pyr<sup>-</sup>. On the basis of charge counting considerations this would imply a formal Co(III) oxidation state to achieve an overall neutral complex. Second, the coordination geometry about the metal is pseudotetrahedral, which, to our knowledge, has never been observed in any Co(III)–halide complex.

**Electronic Structure of (Mes<sub>2</sub>pyr)CoCl<sub>2</sub>.** We considered several possibilities for the formula and electronic description of this structure to achieve a neutral overall charge, which are illustrated in Figure 4. The first was that of a Co(II)complex of Mes<sub>2</sub>pyr protonated at the unbound imine nitrogen (Figure 4, left). Such protonation of the ligand would make the ligand zwitterionic, and the appropriate charge balance would be that of a high-spin Co(II). The second possibility considered is that of a fully deprotonated ligand coordinated to Co(III) in a tetrahedral environment (Figure 4, right). The third possibility considered is that of a complex between a Co(II) ion and a one-electron-oxidized, neutral ligand radical (Figure 4, bottom). This description would represent the first instance of a PDI-type ligand exhibiting an oxidized noninnocent oxidation state.



Figure 4. Electronic structures considered for Co(Mes<sub>2</sub>pyr)Cl<sub>2</sub>.

We first consider the case of the protonated structure of  $(Mes_2pyr-H)CoCl_2 \cdot CH_2Cl_2$ , shown in Figure 4 (left). The refinement of a proton on the imine position proceeds successfully, with similar but slightly better statistics ( $R_{1(obs)}$  = 2.64%,  $R_{1(a|l)} = 2.95\%$ , w $R_2 = 6.70\%$ ) from the unprotonated model  $(R_{1(obs)} = 2.78\%, R_{1(all)} = 3.08\%, wR_2 = 7.15\%)$ , and a canting of the Cl(2) ligand toward the putative proton position could be a result of hydrogen bonding but could also be due to crystal packing effects. In the structure of the pure (Mes<sub>2</sub>pyr)-CoCl<sub>2</sub> polymorph, refinement of a proton is not successful, though refinement of the structure with a fixed hydrogen atom on the imine position also proceeds with statistics  $(R_{1(obs)} =$ 6.02%,  $R_{1(all)} = 7.89\%$ ,  $wR_2 = 12.55\%$ ) indistinguishable from the unprotonated model ( $R_{1(obs)} = 6.09\%$ ,  $R_{1(all)} = 7.95\%$ , w $R_2 =$ 12.90%). Thus, since hydrogen atoms are not easily located by X-ray crystallography, X-ray crystallographic refinement consistent with either a protonated or an unprotonated structure is inconclusive to determine the protonation state of the ligand. A more definitive test for the presence of protonated imine substituents is analysis of the compound using infrared spectroscopy. This analysis shows a complete absence of the expected N-H stretch by FTIR in the region of 3200-3300  $cm^{-1}$  (Figure S1). Further, synthesis of Co(Mes<sub>2</sub>pyr)Cl<sub>2</sub> from deprotonated Li(Mes<sub>2</sub>pyr) gave the same material based upon UV-vis absorption spectroscopy and single-crystal X-ray diffraction. Thus, no compelling evidence for a protonated Co(II) complex has been found from XRD and IR spectroscopy or by variation of the synthetic procedure. Yet, further experimental methods in magnetometry and EPR are invoked (vide infra) to strengthen the assignment.

The proposed protonated  $(Mes_2pyr-H)CoCl_2$  would be expected to behave as a high-spin S = 3/2 spin system and should have an EPR spectrum consistent with this assignment. However, only a small contaminant signal for Co(II) is observed in the EPR experiment (Figure S4). Spin-counting experiments using double integration of the EPR signature in samples of known concentration indicate that this contaminant represents only about ~10 mol % of the material. Whatever the identity of the contaminant, it affects the apparent purity of the material from CHN analysis negligibly and is undetectable in powder XRD experiments, which show only peaks for the title compound.

Alternative spin states proposed in Figure 4 (middle and right) are invisible by normal perpendicular mode EPR due to the spin-forbidden nature of these transitions but may be observed in parallel mode. Indeed, a strong signature is observed for (Mes<sub>2</sub>pyr)CoCl<sub>2</sub> in parallel mode, which we assigned to belong to (Mes<sub>2</sub>pyr)CoCl<sub>2</sub> (Figure 5). Further, bulk magnetic susceptibility measurements using a Guoy balance and the Evans method on multiple samples reproducibly indicate (Mes<sub>2</sub>pyr)CoCl<sub>2</sub> is an S = 2 system, as evidenced from the measured  $\mu_{\text{eff}}$  of 5.27 and 4.98 for the Guoy



**Figure 5.** EPR spectrum of (Mes<sub>2</sub>pyr)CoCl<sub>2</sub> in parallel mode. MW freq 9.385 GHz, power 20 mW, mod. amplitude 6.0 G, mod. freq 100 kHz.

balance and Evans method, respectively (4.90 spin-only value of  $\mu_{\rm eff}$  expected). These values are significantly higher than the expected spin-only value of  $\sim 3.87$  for a S = 3/2 Co(II) system, and while spin-orbit coupling contributes additional angular momentum in S = 3/2 cobalt(II) systems, giving values of  $\mu_{\text{eff}}$ in the range of 4.4-4.8 Bohr magnetons at room temperature,<sup>41</sup> N-heterocyclic- and imine-based ligands tend to show much lower  $\mu_{\rm eff}$  values<sup>42–44</sup> than we observe. Further, in the case where spin-orbit coupling contributes substantial angular momentum at room temperature, the temperature-dependent magnetic profiles of the systems are nonlinear, with  $\mu_{eff}$ dropping toward the spin-only value with decreasing temperature.45 <sup>48</sup> In contrast, solid-state magnetometry on (Mes<sub>2</sub>pyr)- $CoCl_2$  shows the value of  $\mu_{eff}$  is temperature independent (Figure S6), suggesting that our values of  $\mu_{\text{eff}}$  comprise predominantly the spin-only contribution and are therefore most consistent with an S = 2 spin quantum number.

The combination of EPR and IR spectroscopic measurements and magnetic susceptibility point toward a one-electron oxidized complex. This alternative formulation of neutral, aprotic ( $Mes_2pyr$ )CoCl<sub>2</sub> would result from a one-electron oxidation (presumably by air to generate water) during synthesis under open reflux conditions.

There remain two proposed electronic structure descriptions of  $(Mes_2pyr)CoCl_2$ , both of which are nonstandard for cobalt complexes: A tetrahedral, high-spin complex of the deprotonated  $[Mes_2pyr]^-$  ligand with Co(III) and two chlorides or a complex of Co(II) with an oxidized, neutral radical Mes<sub>2</sub>pyr ligand, Mes<sub>2</sub>pyr. Both electronic structure descriptions are consistent with the IR spectrum and the spin state as determined by EPR and magnetometry. Some examples of high-spin, tetrahedral Co(III) do exist, featuring either chelating ligands,<sup>49</sup> terminal imido ligands,<sup>50–55</sup> or sterically bulky ligands.<sup>56,57</sup> To our knowledge, multichlorocobalt(III) complexes with pseudotetrahedral geometry have not been reported, while pseudotetrahedral geometries are extremely common for Co(II).

An examination of the bond metrics from the X-ray crystallographic structure can offer clues to the electronic structure of the complex. Selected metrics are given in Table 1. The Co $-N_{Pvr}$  distance greater than 2.0 Å is inconsistent with a Co<sup>III</sup>-pyrrole anion contact based upon analogous pyrroleand pyridine-monoimine chemistry. An analysis of reported crystal structures shows that these contacts are closer to 1.9 Å<sup>58-64</sup> for Co(II) complexes and usually less than 1.9 Å for  $Co(III)^{65-69}$  complexes with iminopyrrolate. The long 2.02 Å contact in the title complex is more consistent with a neutral nitrogen donor to Co(II). For analogous pyridine-monoimine chemistry, this value falls in between the observed length for  $Co(III)-N_{Py}$  distances  $(\sim 1.97 \text{ Å})^{70}$  and those for  $Co(II)-N_{Py}$  complexes (2.08-2.21 Å).<sup>71-80</sup> Finally, the pseudotetrahedral environment about the metal atom is inconsistent with Co(III), which prefers octahedral ligation. A recent report from Lippard et al.<sup>49</sup> provides useful benchmarks for tetrahedral Co(III) in an amide/imine ligation environment. In this report, Co-N bonds were far shorter (~1.85 Å) than ours (2.02 and 2.07 Å).

Arguments for ligand redox noninnocence typically come from an examination of the bond lengths within the ligand framework itself. Density functional calculations (B3LYP/6-31G<sup>\*</sup>) on the (Mes<sub>2</sub>pyr)H ligand indicate the HOMO (Figure 6, top) is a bonding orbital with respect to the pyrrole C(2)– C(3) and the imine C(1)=N(1) bonds, antibonding with respect to the pyrrole C(3)–C(4) and the imine C(1)–C(2)

Table 1. Selected Bond Metrics <sup><i>a</i></sup> (Angst	troms) for (Mes,pyr)H and	(Mes <sub>2</sub> pyr)CoCl <sub>2</sub> from Cr	systallography and DFT <sup>b</sup>
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	(Mes <sub>2</sub> pyr)H	(Mes <sub>2</sub> pyr)CoCl <sub>2</sub> (X-ray)	(Mes <sub>2</sub> pyr)CoCl <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub> (X-ray)	(Mes <sub>2</sub> pyr)CoCl <sub>2</sub> (Opt)
Co(1)-N(1/2)		2.0743(2)/2.02126(19)	2.076(3)/ 2.020(3)	2.08264/1.96367
Co(1)-Cl(1/2)		2.2350(8)/2.2452(6)	2.250(3)/2.222(3)	2.17043/2.17472
N(1/3)-C(1/6)	1.276(2)/1.282(2)	1.2918(19)/1.3041(19)	1.280(5)/1.306(4)	1.30708/1.27800
C(1/6) - C(2/5)	1.4513(2)/1.44143(18)	1.4453(19)/1.4100(19)	1.428(5)/1.417(4)	1.41643/1.44871
C(2/5)-C(3/4)	1.38421(17)/1.38148(18)	1.408(2)/1.416(2)	1.405(5)/1.417(4)	1.40746/1.41175
C(3) - C(4)	1.39631(18)	1.388(2)	1.368(6)	1.39647
N(2)-C(2/5)	1.36514(18)/1.3655(2)	1.3609(18)/ 1.3723(18)	1.370(4)/ 1.365(4)	1.35770/1.35719
$Co(1) \cdots N(3)$		3.5219(15)	3.483(3)	3.24551

<sup>a</sup>Divided entries refer to separate, related atoms and their associated metrics in the order given, e.g., N(1/3)-C(1/6) denotes two distances, N(1)-C(1) and N(3)-C(6). <sup>b</sup>Geometry optimization using the B3LYP functional and a 6-311G(d,p)/TZVP(Co) combined basis set.



Figure 6. Orbitals calculated using density functional theory (B3LYP). (Top) HOMO of geometry-optimized ( $Mes_2pyr$ )H (6-31G\*). (Bottom) SOMO of ( $Mes_2pyr$ )CoCl<sub>2</sub> from single-point calculation of the crystal-structure geometry using 6-311G(d,p)/TZVP(Co).

bonds, and nonbonding with respect to the pyrrole C(2)-N(2)bonds. Thus, oxidation of this ligand by removal of an electron from the HOMO is expected to lengthen the C(2)-C(3) and the imine C(1)=N(1) bonds, contract the C(3)-C(4) and the imine C(1)-C(2) bonds, and leave the C(2)-N(2) bonds unperturbed. Examination of the key bond metrics in the parent ligand and the cobalt complex indicate these bonding perturbations occur in (Mes<sub>2</sub>pyr)CoCl<sub>2</sub>, with alternating lengthening-shortening along the ligand backbone typically by a significant 0.03-0.04 Å but with the pyrrole C-N distances remaining relatively unperturbed. This is exactly the behavior expected by oxidation of the HOMO diagrammed in Figure 6 (top). A few examples of pyrrole diimine complexes have shown analogous bond length trends but to a lesser degree.<sup>29,32</sup> The combination of long Co-N bonds and the alternate lengthening and shortening of the bonds in the ligand backbone are most consistent with the description of  $(Mes_2pyr)CoCl_2$  as a high-spin d<sup>7</sup> Co(II) complex with a neutral radical Mes<sub>2</sub>pyr· ligand, with the unpaired electron on the ligand spin aligned with the metal d electrons, to give maximum multiplicity and a spin state of S = 2 (Figure 7). Finally, the presence of an intense and well-defined charge transfer band at 410 nm in the UV-vis spectrum is consistent with a metal-to-ligand charge transfer band where a d-based electron in the *e* orbital is excited into the vacancy in the low-



Figure 7. Frontier molecular orbital description of (Mes<sub>2</sub>pyr)CoCl<sub>2</sub>.

lying  $\pi$  orbital (Figure 7). Thus, the assignment as a high-spin d<sup>7</sup> Co(II) complex of a noninnocent ligand is consistent with X-ray crystallographic metrics, measured values of magnetic susceptibility, EPR, IR, and UV–vis absorption spectra and corroborated by a wealth of existing literature on the geometric behavior of Co(II) vs Co(III) coordination complexes.<sup>42–80</sup>

DFT calculations were carried out on this cobalt complex using several basis set combinations. The usage of the 6-31G\* and 6-311G(d,p)/TZVP(Co)<sup>81</sup> basis sets predicted the observed bidentate ligation as well as the alternating bond lengthening-shortening behavior in the pyrrole diimine ligand, though it underpredicted the degree of bond perturbation by redox noninnocent behavior in comparison to the crystal structure based upon the pyrrole bond metrics and the Co-N(2) distances (Table 1). Therefore, single-point calculations on the X-ray crystal structure of (Mes<sub>2</sub>pyr)CoCl<sub>2</sub> were used to visualize the frontier orbitals and examine the electronic structure of (Mes<sub>2</sub>pyr)CoCl<sub>2</sub>. For calculations on the geometry from X-ray structure determination, hydrogen atoms were removed and readded at 1.07 Å from their associated carbon atoms; this is due to the fact that bonds to hydrogen atoms are modeled shorter than reality (~0.95 Å) in X-ray crystallography due to the delocalization of the hydrogen electrons within the  $\sigma$ bond, which fits well to diffraction data but raises the energy of the molecular system in quantum calculations. Results are consistent with the description of the complex as a Co(II) ligated to an oxidized Mes<sub>2</sub>pyr<sup>•</sup> ligand (Figure 4, bottom). Mulliken spin density summations put 2.76 electrons on the metal center and 0.79 on the Mes<sub>2</sub>pyr ligand, consistent with the description of the system as a cobalt(II) ion with a single spin-aligned ligand electron, as shown in Figure 7 (0.26 and 0.19 electrons reside on the two chloride ligands). Of the four SOMOs, three are heavily metal based (Figure S3) and one is primarily ligand based and resembles the ligand HOMO (Figure 6), although its symmetry is broken due to the asymmetric cobalt coordination mode. The similarity between the ligand HOMO and the metal complex SOMO is consistent

with redox noninnocent behavior where the ligand has undergone an oxidation by one electron. Nevertheless, this SOMO does have some d-orbital character, consistent with some degree of character of a Co(III) with  $\pi$ -donor pyrrolate ligand, as is frequently the case in coordination complexes, since oxidation states are a formalism and electronic structure and covalent bonding are continuum phenomena. Nevertheless, the combination of X-ray structural metrics, spectroscopies (IR, EPR), magnetometry, theoretical calculations, and a wealth of literature precedent for Co(II) vs Co(III) favor the description of this system as a Co(II) complex of a neutral radical ligand, the first such example of a redox noninnocent oxidized PDItype ligand.

# CONCLUSION

In summary, the reaction of  $Co(II)Cl_2$  with  $(Mes_2pyr)H$  resulted in an unexpected complex  $(Mes_2pyr)CoCl_2$ . No firm evidence for protonation of the ligand is found from crystallography or IR spectroscopy, and synthesis from the deprotonated ligand yields the same compound. The observed intraligand and metal–ligand bond metrics, spin state from EPR and magnetometry, and frontier orbital description from DFT are difficult to rationalize without the invocation of redox noninnocent behavior of the ligand. The complex is best described as a neutral, oxidized  $Mes_2pyr^{\bullet}$  radical ligand bound to a high-spin Co(II) ion with all unpaired electrons spin aligned to minimize energy contributions from electron–electron repulsion and electron exchange.

#### EXPERIMENTAL SECTION

General. Where noted, operations were carried out under rigorous dry, anaerobic conditions using glovebox and Schlenk line techniques. All reagents and solvents were purchased and used as obtained from commercial providers (Aldrich, Fisher, Strem) unless otherwise specified. Deuterated NMR solvents were purchased from Sigma-Aldrich or Cambridge Isotope Laboratories. <sup>1</sup>H NMR spectra were recorded on a Bruker Biospin 400 MHz spectrometer. Chemical shifts were referenced to the residual protiosolvent signal. Visible absorption spectra were acquired on a Shimadzu 2540 spectrometer. X-ray crystal structure determinations were performed using a Bruker Kappa APEX II DUO diffractometer equipped with an Oxford Cryostream. Infrared spectra were obtained using a Nicolet iS5 spectrometer with a iD5 ATR accessory. CHN analyses were performed by the CENTC elemental analysis facility at the University of Rochester. Solid-state magnetometry was carried out on an Alfa Aesar Magnetic Susceptibility balance, model mk1 c = 1.029. EPR spectra were recorded on a Bruker EMX EPR spectrometer with a dual-mode cavity and Oxford Cryosystems ESR900 cryostat. DFT calculations were performed using the Gaussian09 suite on the Temple University Owlsnest HPC cluster.

**Synthesis.** *α*-*Cyano-2-pyrroleacrylate* (2). 2-Pyrrolecarboxaldehyde is protected by conversion to a cyanoacrylate protecting group using a Knoevenagel condensation, Scheme 1.<sup>15</sup> A solution of 2pyrrolecarboxaldehyde (15 g, 158 mmol), ethyl cyanoacetate (26 g, 226 mmol), and diethylamine (1.2 g, 16 mmol) in toluene (250 mL) was prepared in a 500 mL round-bottom flask. The solution was refluxed for 2.5 h using a Dean–Stark trap to remove water during the reaction. The mixture was then cooled to room temperature and allowed to stand at 2 °C overnight. The pinkish-yellow precipitate was collected via vacuum filtration, washed with ~300 mL of diethyl ether, and air dried to yield 10.06 g (34% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 9.88 (br s, N–H), 8.02 (s), 7.24 (m), 6.95 (m), 6.42 (m), 4.32 (q, CH<sub>2</sub>), 1.38 (t, CH<sub>3</sub>).

Ethyl  $\alpha$ -Cyano-5-formyl-2-pyrroleacrylate (3). An aldehyde group can now be added to the protected 2 through a Vilsmeier–Haack reaction<sup>16</sup> under an inert atmosphere. A suspension of phosphoryl





oxychloride in dichloroethane (9.73 g, 63.43 mmol) was added dropwise over 20 min to cooled, stirred N,N-dimethylformamide (4.64 g, 63.43 mmol) in a 250 mL two-neck round-bottom flask connected to a reflux condenser. The temperature was maintained between 10 and 20 °C during the addition. The pink solution was allowed to stir for 15 min without cooling before 1,2-dichloroethane (30 mL) was added. The stopper on the second neck of the flask was removed such that inert N<sub>2</sub> gas purged through the flask, preventing air from entering the opened neck. On the side, a stirred suspension of  $\alpha$ -cyano-2pyrroleacrylate (10.05 g, 52.86 mmol) in 45 mL of 1,2-dichloroethane was prepared in a 100 mL beaker. The opaque pink mixture was cooled to 0-5 °C and maintained at this temperature during the 30 min dropwise addition of the stirred suspension using a needleless syringe. The second neck was resealed with a stopper, and the mixture was then refluxed for 15 min, during which HCl gas evolved. The dark orange solution was cooled to room temperature, and 4 M sodium acetate (82 mL) was added slowly over 10 min. The mixture was refluxed for an additional 15 min and allowed to cool to room temperature. After standing overnight at 2  $\,^{\circ}\mathrm{C}$  the precipitate was filtered and washed with DI water to yield 8.8 g (76%) of a greenishbrown powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 10.5$  (br s, N–H), 9.69 (s, CHO), 8.14 (s, =CH), 7.20 (m), 7.05 (m), 4.38 (q, CH<sub>2</sub>), 1.37 (CH<sub>3</sub>).

*Pyrrole-2,5-dicarboxaldehyde (4).* The aldehyde is deprotected via alkaline hydrolysis. Ethyl α-cyano-5-formyl-2-pyrroleacrylate (8.8 g, 40.5 mmol) was added to a 3 M aqueous solution of sodium hydroxide (108 mL) and refluxed for 2 h. The mixture was then cooled below 20 °C and acidified with 2 M sulfuric acid before passing through a filter, removing a black powdery byproduct. An ethyl acetate extraction (3 × 55 mL) was concentrated to yield nearly pure pyrrole-2,5 dicarboxaldehyde (4.9 g, 39.8 mmol, 98%) This crude material was used without further purification. The dialdehyde can be purified further by recrystallization from water. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 10.2 (br s, N–H), 9.75 (s, CHO), 6.99 (s, pyrrole H).

(*Mes*<sub>2</sub>*pyr*)*H* (5). Pyrrole dicarboxaldehyde 4 (0.98 g, 8.02 mmol) was dissolved in dry EtOH (25 mL). 2,4,6-Trimethylaniline (2.17 g, 16.04 mmol) was added to the stirred solution along with catalytic formic acid (~5 drops). The solution was stirred under a nitrogen atmosphere for 48 h at RT. The solution was concentrated to yield a dark brown powder. This residue was filtered, washed with cold ethanol, dried, and dissolved in a minimal amount of DCM. The ligand was recrystallized by vapor diffusion with pentane to yield a yellow crystalline solid (2.23 g, 6.26 mmol, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.693 (s, imine C–H), 6.927 (d, Mes C–H), 6.482 (s, pyrrole C–H), 2.304 (s, Mes-*p*-Me), 2.179 (s, Mes-*o*-Me). Unit Cell (XRD): monoclinic *P*, *a* = 8.1829(14) Å, *b* = 34.929(6) Å, *c* = 8.2568(15) Å,  $\beta$  = 118.462(4)°.

(*Mes*<sub>2</sub>*pyr*)*CoCl*<sub>2</sub> (Mes<sub>2</sub>*pyr*)H (40 mg, 0.112 mmol, 1 equiv) was dissolved in 15 mL of THF. Anydrous CoCl<sub>2</sub> (14.52 mg, 0.112 mmol, 1 equiv) was added to the stirred solution. The solution was refluxed for 8 h open to air. The solution was dried under vacuum, and Co(Mes<sub>2</sub>*pyr*) was recrystallized from cold (-40 °C) DCM/pentane to yield 36.8 mg of green crystals (0.076 mmol, 68% yield). Anal. Calcd for C<sub>24</sub>H<sub>26</sub>Cl<sub>2</sub>CoN<sub>3</sub>·0.4 (CH<sub>2</sub>Cl<sub>2</sub>): C, 56.326; H, 5.192; N, 8.076. Found: C, 56.134, H, 5.520; N, 7.839. Unit Cell (XRD): monoclinic *P*, *a* = 16.453(2) Å, *b* = 11.3132(17) Å, *c* = 15.240(2) Å, *β* =

108.344(3)°. UV-vis (dichloromethane):  $\lambda_{max}$  [nm] ( $\varepsilon \times 10^{-3}$ ) 276 (10.8), 342 (7.5), 421 (22.9). ATR-FTIR:  $\lambda_{max}$  [cm<sup>-1</sup>] 2800-3100 (Me C-H stretch), 1630 (imine C=N stretch, unbound), 1570 (imine C=N stretch, metal bound) 1290 (pyrole C-N stretch), 1000-1010 (M-N stretch).

**Quantification by EPR.** A calibration curve for signal intensity vs concentration was prepared by EPR analysis of differing concentrations of  $[\text{CoCl}_4]^{2^-}$ . Calibration solutions of  $\text{CoCl}_2$  in concentrated HCl were prepared with concentrations of 38, 63, 95, and 190, and 380  $\mu$ M, prepared by serial dilution. A 0.25 mL amount of these solutions was analyzed by X-band EPR spectroscopy in the range of 500–5000 G. A calibration curve (Figure S5) was prepared by plotting intensity (double integration in the region of 500–3500 gauss) vs concentration. The concentration of S = 3/2 species within a 0.21 mM sample of Mes<sub>2</sub>pyr)CoCl<sub>2</sub> was then determined from this calibration curve to be 0.028 mM.

**Density Functional Theory.** Density functional theory calculations  $(B3LYP)^{82,83}$  were carried out using Gaussian09 R.C.01.<sup>84</sup> In Gaussian, structures were first minimized using the 3-21G basis set<sup>85–89</sup> and the resulting coordinates used as the input file for higher level basis sets. For the calculation of  $(Mes_2pyr)H$ , the basis set was 6- $31G^{*,90-99}$  and for the calculations on  $(Mes_2pyr)CoCl_2$ , a mixed pseudopotential basis set, 6- $311g(d,p)^{93,100,101}$  (C, H, N, Cl) and TZVP,  $^{102,103}$  (Co) was used. Minimum energy structural optimizations were also run using the B3LYP<sup>82,83</sup> functional and the basis set 6- $31G^{*90-99}$  on all atoms with pseudopotentials used to define core electrons for cobalt (LANL2DZ).

**Solid State Magnetometry.** A vibration sample magnetometer (Microsense, LLC) was used to capture the temperature-dependent susceptibility by using temperature dependence mode at a small magnetic field of 100 Oe. A 23.4 mg amount of powered sample was filled into a quartz tube and sealed for the measurement. The temperature was controlled by a model 9700 temperature controller (Kelvin Technology Ltd.) from 83 to 293 K at a step of 5 K and a rising speed of ~0.8 K/min. When the temperature reached each point, 1 min of waiting time is needed before the capture of the signal. The diamagnetic signal is deducted by the recorded calibration file in the software.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02898.

IR and UV–vis spectra, details of density functional theoretical calculations, EPR spin quantitation, solid state magnetometry, crystallographic tables (PDF) Crystallographic tables (CIF)

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#### Notes

The authors declare no competing financial interest.

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