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Syntheses and Reactivity Studies of Square-Planar Diamido–Pyridine Complexes Based on Earth-Abundant First-Row Transition Elements

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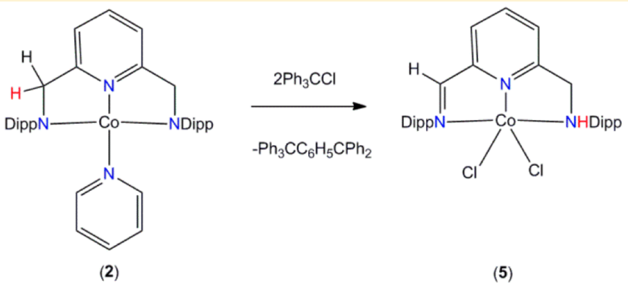
Supporting Information

ABSTRACT: The new square-planar complexes M[NNN](pyridine) (M = Fe (**1**), Co(**2**); NNN = 2,6-bis(2,6-diisopropylphenylamidomethyl)pyridine) were synthesized and fully characterized to investigate small molecule activation on this platform and also associated ligand innocence. The equatorial pyridine solvent moiety could not be removed; a new bis-ligand species Co[NNN.H]$_2$ (**3**) was synthesized in low yield while attempting to make the base-free derivative. Attempts to prepare the Ni analogue of **1** and **2** instead yielded crystals of a di-imino–pyridine complex Ni[PDI]Cl (**4**) (PDI = 2,6-bis(2,6-diisopropylphenyliminomethyl)pyridine), following loss of methylene backbone hydrogen atoms. Structural analysis indicates that the PDI ligand is a mono-anionic radical. This susceptibility of the ligand to oxidative dehydrogenation was also shown when the reaction of **2** with 2 equiv of trityl chloride yielded a new complex with an asymmetric imino–amino pyridine ligand Co[NNN′]Cl$_2$ (**5**) (NNN′ = 2-(2,6-(diisopropylphenyliminomethyl)-6-(diisopropylphenylamidomethyl)-pyridine) in good yield.



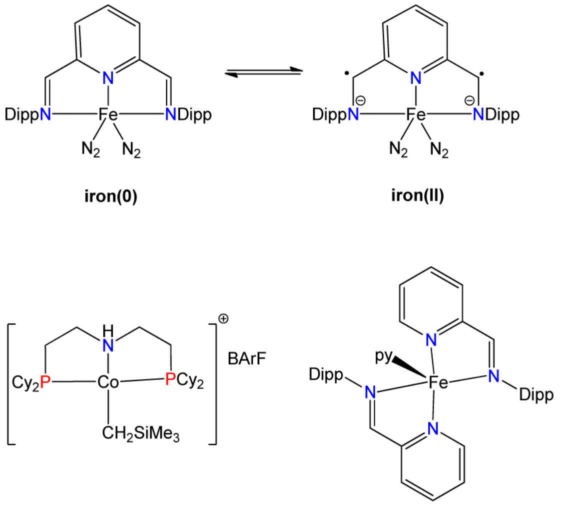
■ INTRODUCTION

The replacement of precious metal catalysts with those based on earth-abundant elements, such as the first-row transition metals Fe, Co, and Ni, is a prerequisite for the development of a sustainable chemical industry and also has clear impact on mitigating industrial costs and environmental impact. Development of these catalysts with respect to those based on precious metals meanwhile has been impeded by their often paramagnetic nature, which frustrates analysis with NMR techniques and by their preponderance toward one-electron reactivity, which demands a subtly different approach in terms of ligand design and reaction conditions.

Recent research focused on this area has shown remarkable advances in the performance of these types of catalysts in olefin polymerizations, hydrogenations, and hydroborations[1−10] using a variety of ligands that promote either metal- or ligand-based redox chemistry, or via cooperative substrate activation without redox chemistry. This array of mechanistic facility is possibly owing to the diminished role of purely metal-based redox in the first- versus second- and third-row transition elements and currently highlights our lack of fundamental understanding of the behavior of these complexes.

Our approach includes using pincer ligands with amide donors (Scheme 1), in particular, those that can promote a reactive square-planar geometry with possible bifunctional behavior. With this in mind, we chose to investigate first-row transition metal derivatives of the diamino–pyridine ligand, which has been employed for a relatively limited number of transition metals (e.g., Ti, Zr, Re, Ru, Pd)[11−18] and theoretically allows for square-planar coordination with a monodentate coligand, in both neutral (protonated) and dianionic forms. This ligand is closely related to the successful di-imino–pyridine ligand, which is well-known to be redox-active, and the

Scheme 1. Examples of Active First-Row Transition Metal Catalysts Supported by Nitrogen Donor Pincer Ligands



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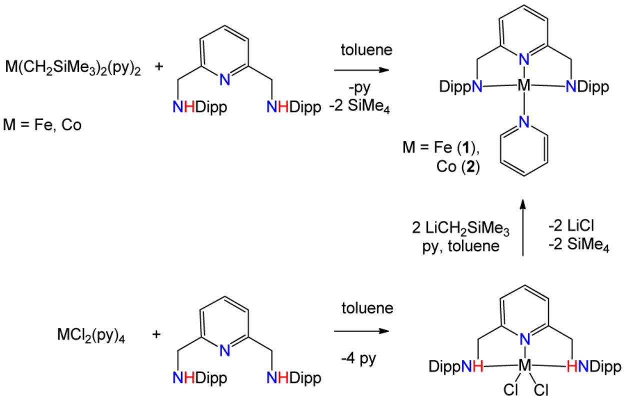
bis(arylcarboxamido) pyridine ligand, assumed to be redox and chemically innocent.[19−22]

■ RESULTS AND DISCUSSION

Because of the complications of handling the unstable [NNN]Li_2 salt,[23] the aminolysis route to "M[NNN]"-type complexes was chosen (NNN = 2,6-bis(2,6-diisopropylphenylamido-methyl)pyridine). The reaction between M$(CH_2SiMe_3)_2(py)_2$ (M = Fe, Co; py = pyridine)[24,25] and [NNN.H_2] yielded the new complexes M[NNN](py) (M = Fe (**1**) and Co(**2**)) as dark purple and red crystalline solids, respectively, in moderate to good yields (**1**: 65%, **2**: 86% yield; Scheme 2). **1** and **2** were found to be highly air- and moisture-sensitive. Further experimentation revealed that an easier route could be accessed by the addition of 2 equiv of $LiCH_2SiMe_3$ as a base to "MCl_2[NNN.H_2]$(py)_x$" (formed in situ from $MCl_2(py)_4$ (M = Fe, Co) and [NNN.H_2]—this material was not characterized, although the iron compound is known)[26] with similar isolated yields of **1** and **2**. Reaction with 1 equiv of $LiCH_2SiMe_3$ yielded an equimolar mixture of the doubly deprotonated complex (**1** or **2**) and starting material, rather than a complex of the type MCl[NNN.H].

Scheme 2. Two Synthetic Routes to Square-Planar Diamido−Pyridine Complexes 1 and 2



The ^{1}H NMR spectra (C_6D_6) of **1** and **2** both show broadened and shifted resonances, consistent with paramagnetic metal centers. Magnetic susceptibility measurements using Evans method yielded $\mu_{eff} = 3.71\ \mu_B$ for **1** and $\mu_{eff} = 1.59\ \mu_B$ for **2** consistent with two unpaired ($S = 1$) and single unpaired electron ($S = 1/2$) configurations, respectively. This would also be consistent with intermediate-spin d^6 and low-spin d^7 metal centers in square-planar geometry, respectively. In the case of **1**, the value $\mu_{eff} = 3.71\ \mu_B$ is between spin-only values of $S = 1$ ($\mu_{spin\text{-}only} = 2.83\ \mu_B$) and $S = 2$ ($\mu_{spin\text{-}only} = 4.90\ \mu_B$). This anomaly has been well-documented for similar Fe(II) porphyrin and phthalocyanine complexes,[27] which share the same D_{4h} symmetry supported by N donors, and is owing to an orbitally degenerate triplet ($S = 1$) ground state (^3E_g for iron(II) phthalocyanine,[27b] which gives $\mu_{eff} \approx 3.8\ \mu_B$ at $T = 100$ to 300 K[27a]). Recently an unsupported high-spin square-planar Fe(II) complex was reported by Veige et al.[28]

Unequivocal structural characterization of these molecules was obtained via single-crystal X-ray diffraction. **1** and **2** were both found to crystallize in the triclinic space group $P\bar{1}$, with two molecules in the unit cell and three molecules of toluene solvent. The structures reveal that in both cases the ligands are bound in a tridenate fashion, with approximately square-planar geometry at the metal centers and a pyridine bound directly trans to the pyridine donor of the NNN ligand (Figure 1). The pyridine fragment is rotated toward the plane of the aryl ring of the adjacent groups of 2,6-di-isopropylphenyl (Dipp), presumably due to attractive forces between the π systems. The pyridine nitrogen atoms are almost colinear with the metal center (∠N(py)−M−N(py) = 179.17(10) and 176.71(10) for **1**; 179.6(3) and 177.8(3) for **2**), whereas there is a slight distortion from ideal square-planar coordination with the binding of the amide donors (∠N(amide)−M−N(amide) N(1) = 164.85(9) and 165.71(10) for **1**; 167.4(2) and 168.3(3) for **2**). M−N(amide) distances are typical (average (av) 1.902 Å for **1**; 1.865(6) Å for **2**). We observe that the pyridine component of the pincer ligand system is bound slightly closer than the other pyridine molecule, as expected for a chelating ligand (e.g., in **2**, Co−N(py-NNN) av 1.851(5) and 1.843(6) Å vs Co−N(py) 1.913(6) and 1.912(6) Å).

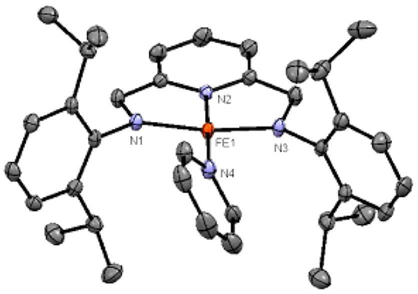


Figure 1. Thermal ellipsoid plot of the structure of one molecule in unit cell of [$\mathbf{2}_2$.$(C_7H_8)_3$]; isopropyl groups and hydrogen atoms omitted for clarity, except for pincer backbone hydrogens, ellipsoids at 50% probability.

These are the first reported structures containing a diamido−pyridine ligand bound to a four-coordinate metal center, and they show a great deal of similarity to related di-imino−pyridine ligated species with the exception of the C−C−N angles and distances (as would be expected).[19,20] The methylene protons were located crystallographically, with angles consistent with the anticipated sp^3 hybridized carbon atoms (av ∠C(o-py)−C(methylene)−N(amide) 109.8(6)°), and the C(methylene)−N(amide) and C(*o*-py)−C(methylene) distances are consistent with single bonds (av 1.455(9) and 1.491(10) Å, respectively).

To increase reactivity of these species for small-molecule activation chemistry and catalysis, we attempted to synthesize base-free complexes of the type M[NNN]. The (nonpincer ligand) pyridine coligand within **1** and **2** is strongly bound and could not be removed using typical desolvation procedures (heat and/or high vacuum), nor could it be readily displaced by other solvents, for example, tetrahydrofuran (THF). Therefore, the syntheses of these complexes were attempted in the absence of coordinating solvents. When $CoCl_2$ was used in the place of $CoCl_2(py)_4$, in the absence of coordinating solvents, instead of the intended three-coordinate complex, the four-coordinate bis-ligated species Co[NNN.H]$_2$ (**3**) was obtained in 21% yield (Scheme 3). Similar reactions with $FeCl_2$ did not yield tractable products.

Complex **3** displays paramagnetically broadened resonances within the ^{1}H NMR spectrum, and a distinctive N−H stretch was found in the IR spectrum at 3350 cm^{-1} (in addition to strong features at 2850−3100 cm^{-1} that overlap with the

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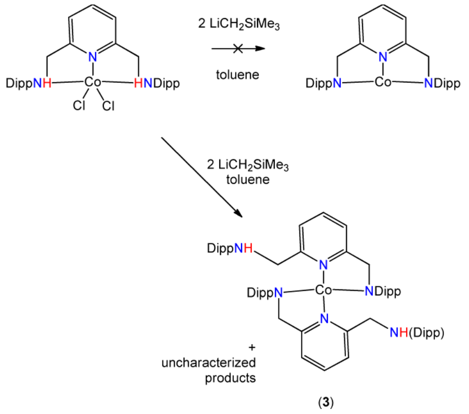
Scheme 3. Unexpected Synthesis of Bis-Ligand Complex 3 from $CoCl_2[NNN.H_2]$



pyridine stretches). The crystal structure of **3** was solved in triclinic space group $P\bar{1}$ and exhibits a distorted tetrahedral geometry at the four-coordinate Co center. Each ligand is bound through one amide and one pyridine nitrogen atom, and the remaining dangling amine arm is found to be protonated (Figure 2). Bond distances and angles are typical for those

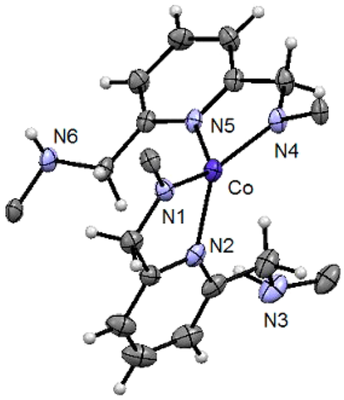
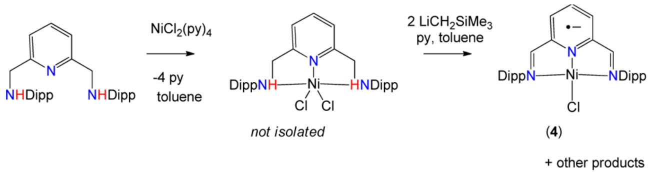


Figure 2. Thermal ellipsoid plot of the core structure of **3**; Dipp groups omitted for clarity, ellipsoids at 40%.

expected for this type of complex.[29] Given the low yield and the unbalanced reactant stoichiometry, it is evident that **3** cannot be the sole product of this reaction, but we could not isolate any other compounds from this reaction; the paramagnetism of the materials precluded useful NMR studies.

Expanding the chemistry to nickel, following identical synthetic protocols as used for **1** and **2** did not yield the expected nickel(II) diamido–pyridine complex. The reaction between $Ni(CH_2SiMe_3)_2(py)_2$[30] and $[NNN.H_2]$ gave metallic Ni (mirror) and uncharacterized decomposition products. The reaction between "$NiCl_2(py)_x.[NNN.H_2]$" and 2 equiv of $LiCH_2SiMe_3$ meanwhile gave a mixture of products, including a di-imino–pyridine species Ni[PDI](Cl) (**4**), which was obtained as a component of a homogeneous mixture of dark purple crystals (Scheme 4; PDI = 2,6-bis(2,6-diisopropylphenyliminomethyl)pyridine). The mechanism of the formation of this species is unclear, but it involves additional loss of two methylene hydrogen atoms, presumably with a strong driving force toward the formation of a conjugated π system. The ^1H NMR spectrum of this solid showed a multitude of peaks, which suggests that although it

Scheme 4. Synthesis of Di-Imino–Pyridine Complex 4 from Diamino–Pyridine Starting Materials



was isolated in a crystalline form, it is not a pure, single compound. Unfortunately, further attempts to purify this material failed. The continuous wave (CW) electron paramagnetic resonance (EPR) spectrum showed two peaks centered at $g = 2.001$ and $g = 2.216$ (see Figure S1 in Supporting Information); the former is likely an organic radical impurity, whereas the latter is very similar in appearance to the feature found for $Ni[2,6\text{-}\{(Dipp)N{=}CMe\}_2C_5H_3N]Cl$ and is likely attributable to **4**.[31] This peak was assigned as an indicator of radical anion character of the di-imino–pyridine ligand.

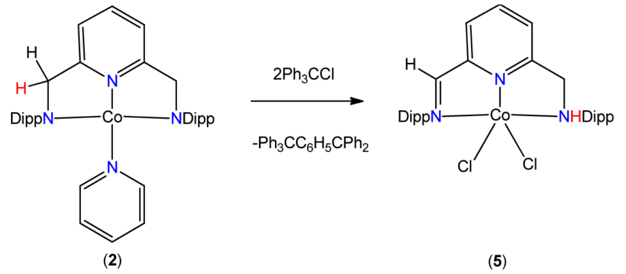
The crystal structure of **4** was solved in monoclinic space group $P2_1/n$, with one molecule of cocrystallized toluene per Ni complex. In a manner similar to **1** and **2**, the metal center is four-coordinate with a terdentate ligand; the equatorial chloride ligand is found to be displaced further out of the Ni-[NNN] plane compared with the equatorial pyridine ligands in **1** and **2**, leading to a more distorted square-planar geometry. The most significant structural parameters of **4** are the C(*o*-py)–C(methylene)–N(amide) angles and C(methylene)–N(amide) distances of the pincer arms, which average 115.6(5)° and 1.320(7) Å, respectively, and are approximately consistent with an imine functionality. Close inspection reveals that the $C_{im}{=}N_{im}$ distances are in fact slightly elongated compared with the neutral PDI ligand—although still significantly shorter than a single bond—and further indicate radical anion character.[31]

Deprotonation at the backbone methylene center has been reported for similar phosphine–pyridyl [PNP] and [PN] and amine–dipyridyl [NNN] pincer ligands—in these cases, the resulting anionic charge is localized on the pyridine nitrogen atom rather than the α-carbon.[32,33] Complete oxidative dehydrogenation to an imine, as observed herein, is also well-known for similar ligand systems and is performed by a base/oxidant combination.[34] In many cases, transition metal centers function as the oxidant; therefore, we propose that a component of the product mixture is a reduced Ni species, perhaps metallic Ni(0).

Given the outcome of the nickel reaction, we were curious as to whether the diamino–pyridine ligand in the square-planar complexes **1** or **2** could be converted into a di-imino–pyridine fragment with the addition of an external oxidant. The cobalt complex was chosen for this experiment, and trityl chloride was chosen as an oxidant as it was speculated that the reaction with complex **2** could logically yield $Co[PDI]Cl_2$ plus 2 equiv of Ph_3CH. Instead, the reaction gave a new species $Co[NNN']Cl_2$ (**5**) (NNN′ = 2-(2,6-(diisopropylphenylimino-methyl)-6-(diisopropylphenylamidomethyl)-pyridine) plus an equivalent of the Gomberg dimer $Ph_3CC_6H_5CPh_2$ as detected by ^1H NMR spectroscopy (Scheme 5). **5** displays a unique, paramagnetically shifted ^1H NMR spectrum, consistent with the presence of a Co^{2+} center.

5 contains an oxidatively rearranged, asymmetric imino–amino–pyridine ligand, which is found to be protonated at the

Scheme 5. Synthesis of 5 from 2



amine nitrogen and is overall charge neutral. This structure was revealed via X-ray diffraction methods and was solved in monoclinic space group $P2_1/n$. The molecule exhibits a five-coordinate metal complex as shown in Figure 3. The asymmetry of the complex is clearly apparent—although equivalent in the parent complex **2**, the Co(1)−N(1) 2.299(4) Å and Co(1)−N(3) 2.171(4) Å distances indicate different donor properties and are longer than the Co−N(amide) distances found in **2**. The N3−C19 distance of 1.281(6) Å and N3−C13−C18 angle of 118.0(4)° are consistent with an imine functionality, whereas the N1−C13 distance 1.495(5) Å and N1−C13−C14 angle 112.1(4)° are consistent with an amine/amide. The latter was confirmed as a protonated amine by crystallographic location of the hydrogen atom, in conjunction with the longer Co−N1 distance and the nonplanar geometry at the nitrogen center (i.e., sp^3 rather than sp^2 hybridized). IR spectroscopy revealed a distinctive N−H stretch at 3335 cm^{-1}.

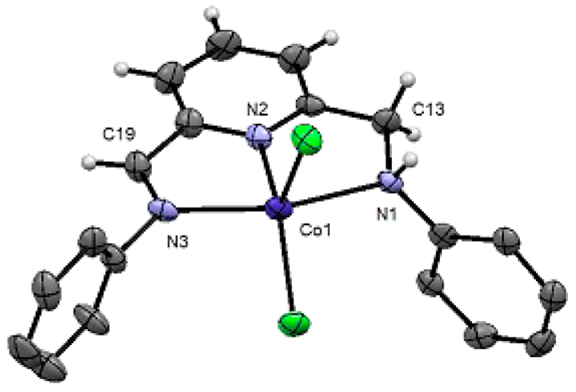


Figure 3. Thermal ellipsoid plot of the structure of **5**; isopropyl groups and hydrogen atoms of Dipp substituents omitted for clarity, ellipsoids at 50% probability.

This type of asymmetric imino−amino−pyridine ligand is known and has been used to stabilize a variety of metal centers in its neutral form, for example, Mn, Fe, and Co.[26,35] These complexes have been found to be moderately active catalysts for olefin polymerization. The ligands used in these studies are typically accessed via 1,2-addition reactions from the di-imino−pyridine ligand,[36] as opposed to the reaction found here, where oxidation of a bound diamino−pyridine ligand has led to a rearrangement of a methylene proton.

CONCLUSION

In summary, we have synthesized two new square-planar complexes **1** and **2** based on the ostensibly “innocent” diamido−pyridine ligand. However, this ligand framework has been shown to be susceptible to chemical oxidation: we observe conversion into a di-imino−pyridine ligand on a Ni center during a salt metathesis reaction, and into an asymmetric imino−amino−pyridine on a Co center by additional of trityl chloride to a well-defined diamido−pyridine complex.

Although the conditions reported herein are dramatically different from those found in catalytic applications,[26] this work shows that catalysts based on the diamido−pyridine ligand may not be chemically resistant to oxidation under certain conditions. It would be expected that alkyl substitution at the methylene linker would prevent oxidation of the C−N bond, for example, with the use of disubstituted pincer 2,6-bis(2,6-diisopropylphenylamido-2-isopropyl)pyridine.[18]

EXPERIMENTAL SECTION

Unless noted otherwise, all operations were performed under a purified argon atmosphere in a standard MBraun UniLab drybox or under an argon atmosphere using high-vacuum and Schlenk techniques. Anhydrous hydrocarbon solvents were purchased from Sigma-Aldrich and further dried over activated 4 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratory and dried over 4 Å molecular sieves. Unless noted, chemicals were purchased from commercial sources and used without further purification. $[NNN]H_2$,[37] $CoCl_2(py)_4$,[25] $Co(CH_2SiMe_3)_2(py)_2$,[25] $FeCl_2(py)_4$,[24] $Fe(CH_2SiMe_3)_2(py)_2$,[24] $NiCl_2(py)_4$,[30] and $Ni(CH_2SiMe_3)_2(py)_2$[30] were prepared according to the literature. All NMR spectra were recorded using a Bruker 400 Ultra Shield spectrometer. ^1H NMR spectra were referenced to solvent residual peaks (δ 7.15 ppm for C_6D_6, δ 1.72 and 3.58 ppm (compound **5**) for THF-d_8). Infrared spectra were measured as KBr discs using a PerkinElmer Spectrum Two FTIR spectrometer. Solution magnetic susceptibilities were calculated using the Evans method.[38] Elemental analyses were performed by Midwest Microlab (Indianapolis, IN) or UC Berkeley Microanalytical Laboratory. The CW EPR spectra were collected on a Bruker model E500 (Bruker BioSpin, Billerica, MA) operating in the X-band microwave frequency range equipped with a Bruker SHQE resonator. The CW spectra were collected at room temperature. Spectra were acquired using a modulation amplitude of 10 G, a frequency modulation of 100 kHz, an optimum microwave power of 1 mW, a conversion time of 163 ms, and a resolution of 1024 points. Minimal background signals were observed for an empty tube.

Preparation of Fe[NNN](py) (1) Method A. A solution of $Fe(CH_2SiMe_3)_2(py)_2$ was prepared in situ by reaction of $FeCl_2(py)_4$ (299 mg, 0.67 mmol) and 2 equiv of $LiCH_2SiMe_3$ (127 mg, 1.34 mmol) stirred in cold hexane (−30 °C) and allowed to warm to room temperature overnight. The solution was filtered, and the solvent was removed in vacuo. The red oily material was redissolved in cold toluene (−30 °C), and to this was added 0.9 mol equiv of $[NNN]H_2$ (277 mg, 0.61 mmol) in cold toluene (−30 °C), whereupon the solution immediately changed to a dark purple color. After the solution was stirred overnight, the solvent was removed in vacuo, and the product was recrystallized from a minimal quantity of toluene (ca. 5 mL) at −30 °C. The compound was isolated as a highly crystalline dark purple solid (234 mg, 0.40 mmol, 65% yield). ^1H NMR (C_6D_6) δ (ppm) −21.08, −16.27, −11.65, 4.80, 7.44, 16.17, 20.84, 47.83 (broad). μ_{eff} (benzene-d_6) = 3.74 μ_B. Anal. Calcd. (%) for $C_{36}H_{46}N_4Fe$ (found) C 73.20 (72.91) H 7.85 (7.95) N 9.49 (9.12).

Method B. A solution of $FeCl_2(py)_4$ (387 mg, 0.88 mmol) and $[NNN]H_2$ (400 mg, 0.88 mmol) was stirred in toluene, producing a yellow precipitate. After 30 min, the solution was cooled to −30 °C and 2 equiv of $LiCH_2SiMe_3$ (164 mg, 1.76 mmol) in cold toluene (−30 °C) was added, whereupon the solution immediately changed to a dark purple color. After the solution was stirred overnight, the solvent was removed in vacuo, and the product redissolved in a minimal quantity of toluene (ca. 5 mL) and filtered (diatomaceous earth). The compound was recrystallized from this solution at −30 °C and isolated as a highly crystalline dark purple solid (384 mg, 0.65 mmol, 74% yield).

Preparation of Co[NNN](py) (2) Method A. A solution of $Co(CH_2SiMe_3)_2(py)_2$ was prepared in situ by reaction of $CoCl_2(py)_4$ (300 mg, 0.67 mmol) and 2 equiv of $LiCH_2SiMe_3$ (127 mg, 1.34 mmol) stirred in cold hexane (−30 °C) and allowed to warm to room temperature overnight. The solution was filtered and solvent removed in vacuo. The green oily material was redissolved in cold toluene (−30 °C) and to this was added 0.9 mol equiv of $[NNN]H_2$ (277 mg, 0.61 mmol) in cold toluene (−30 °C), whereupon the solution immediately changed to a dark blood red color. After the solution was stirred overnight, the solvent was removed in vacuo, and the product recrystallized from a minimal quantity of toluene (ca. 5 mL) at −30 °C. The compound was isolated as a highly crystalline dark red solid (310 mg, 0.52 mmol, 86% yield). ^1H NMR (C_6D_6) δ (ppm) −4.94, 0.42, 4.75, 18.37, 19.61 (broad); μ_{eff} (benzene-d_6) = 1.59 μ_B. Anal. Calcd. (%) for $C_{36}H_{46}N_4Co$ (found) C 72.82 (72.99) H 7.81 (8.07) N 9.44 (9.26).

Method B. A solution of $CoCl_2(py)_4$ (392 mg, 0.88 mmol) and $[NNN]H_2$ (400 mg, 0.88 mmol) was stirred in toluene, producing a bright blue precipitate. After 30 min, the solution was cooled to −30 °C, and 2 equiv of $LiCH_2SiMe_3$ (164 mg, 1.76 mmol) in cold toluene (−30 °C) was added, whereupon the solution immediately changed to a dark blood red color. After the solution was stirred overnight, the solvent was removed in vacuo, and the product was redissolved in a minimal quantity of toluene (ca. 5 mL) and filtered (diatomaceous earth). The compound was recrystallized from this solution at −30 °C and isolated as a highly crystalline dark red solid (381 mg, 0.64 mmol, 73% yield).

Preparation of Co[NNN.H]$_2$ (3). A solution of $CoCl_2$ (85 mg, 0.66 mmol) and $[NNN]H_2$ (300 mg, 0.66 mmol) was stirred in toluene, producing a bright blue precipitate. After 30 min, the solution was cooled to −30 °C, and 2 equiv of $LiCH_2SiMe_3$ (123 mg, 1.32 mmol) in cold toluene (−30 °C) was added, whereupon the solution immediately changed to a dark green color. After the solution was stirred overnight, the solvent was removed in vacuo, and the product was redissolved in a minimal quantity of hexane (ca. 10 mL) and filtered (diatomaceous earth). The compound was recrystallized from this solution at −30 °C and isolated as a highly crystalline dark green solid (132 mg, 0.14 mmol, 21% yield). ^1H NMR (C_6D_6) δ (ppm) 1.25, 3.54, 4.25 (broad); IR (KBr, selected) 3350 cm^{-1} (N−H stretch). Anal. Calcd. (%) for $C_{62}H_{84}N_6Co$ (found) C 76.58 (76.62) H 8.71 (8.89) N 8.65 (8.98).

Preparation of Ni[PDI](Cl) (4). A solution of $NiCl_2(py)_4$ (146 mg, 0.33 mmol) and $[NNN]H_2$ (150 mg, 0.33 mmol) was stirred in toluene, producing a cream colored precipitate. After 30 min, the solution was cooled to −30 °C, and 2 equiv of $LiCH_2SiMe_3$ (62 mg, 0.66 mmol) in cold toluene (−30 °C) was added, whereupon the solution immediately changed to a dark purple color. After the solution was stirred overnight, the solvent was removed in vacuo, and the product was redissolved in a minimal quantity of hexane (ca. 5 mL) and filtered (diatomaceous earth). The compound was recrystallized from this solution at −30 °C and isolated as an impure crystalline dark purple solid from which single crystals of the product were obtained for structural analysis.

Preparation of Co[NNN′]Cl$_2$ (5). To a solution of **2** (122 mg, 0.21 mmol) in THF, 2 equiv of Ph_3CCl was added (115 mg, 0.42 mmol), whereupon the solution immediately changed from red to an emerald green color. After the solution was stirred overnight, the solvent was removed in vacuo, and the remaining solid was washed with hexane to leave the product in an analytically pure form (110 mg, 0.19 mmol, 89% yield). ^1H NMR analysis of the yellow hexane washings after removal of volatiles showed pure $Ph_3CC_6H_5CPh_2$. ^1H NMR (d_8-THF) δ (ppm) −31.4, −18.47, −4.44, 4.01, 7.71, 31.9, 34.9, 41.7 (broad); IR (KBr, selected) 3335 cm^{-1} (N−H stretch). Anal. Calcd. (%) for $C_{31}H_{43}N_3CoCl_2$ (found) C 63.37 (63.79) H 7.38 (7.93) N 7.15 (7.04).

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format and tables of bond distances for **1**, **2**, **3**, **4** and **5**, and the EPR spectrum of **4**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00779.

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Notes

The authors declare no competing financial interest.

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