Linkage Isomerism in Transition-Metal Complexes of Mixed (Arylcarboxamido)(arylimino)pyridine Ligands

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Supporting Information

ABSTRACT: The synthesis of a series of asymmetric mixed 2,6-disubstituted (arylcarboxamido)(arylimino)pyridine ligands and their coordination chemistry toward a series of divalent first-row transition metals (Cu, Co, and Zn) have been explored. Complexes featuring both anionic N,N,N″-carboxamido and neutral O,N,N′-carboxamide coordination have been prepared and characterized by X-ray crystallography, cyclic voltammetry, and UV-visible and EPR spectroscopy. Specifically, RLM(X) (M = Cu; X = Cl−, OAc−) and R(L)(H)MX2 (M = Cu, Co, Zn; X = Cl−, SbF6−) complexes that feature N,N,N″- or O,N,N′-coordination are presented. Base-induced linkage isomerization from O,N,N′-carboxamide to N,N,N″-carboxamido coordination is also confirmed by multiple forms of spectroscopy.

INTRODUCTION

In their doubly deprotonated form, bis(arylcarboxamido)pyridines 1 have been used as ligands to support nickel and copper complexes that exhibit novel properties. A unique anionic copper(II)−superoxide complex supported by 12− (R = iPr) acts as a nucleophile, in contrast to other such species supported by neutral N-donor ligands.1,2 Monoanionic nickel(II)− and copper(II)−hydroxide complexes supported by 12− (R = iPr or Me) undergo CO2 fixation reactions at exceptionally high rates3 and react with CH3CN in an unprecedented manner to yield cyanomethide complexes, [{12−}(CH3CN)]− (R = Me, M = Ni or Cu).4 In addition, one-electron oxidation of the copper(II)−hydroxide complexes yields thermally unstable Cu(III) species that rapidly oxidize dihydroanthracene via hydrogen atom abstraction (HAT).4,5 Among the various factors that underlie these unique observations, the dianionic nature and strong electron-donating properties of the supporting ligand 12− would appear to be key. As part of ongoing studies of these various influences, we asked: What would be the consequences of decreasing the negative charge of the supporting ligand while keeping the steric properties approximately constant?

As a first step toward addressing this question experimentally, we targeted ligands 2a−2c for synthesis and study of their coordination chemistry. These ligands may be viewed as a hybrid of the aforementioned 1 and bis(arylimino)pyridines like 3, which have been widely studied,5 including with Cu(II).7 Ligand 2b has been reported, but only as a product of an oxidation of a reduced Ni(II) complex of 3.8 A direct large-scale synthesis was not described, and 2a and 2c are new. Alkyl-substituted analogues 4, which, in deprotonated form, would be expected to be more basic than monoanionic versions 2a−2c, have been used to prepare Ni(II), Pd(II), and Fe(II) catalysts (e.g., for olefin polymerizations).9 Ligands 510 and 611 are noteworthy relatives of 2a−2c, insofar as they contain similar tridentate, mer, monoanionic N-donor sets.

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Herein, we report reproducible, large-scale synthetic routes to 2a−2c and the results of explorations of their ability to complex to divalent metal ions, with an emphasis on Cu(II). We found that metalations in the absence of base result in complexes that exhibit carboxamide $O,N,N'$-coordination and that subsequent treatment of these compounds with base induces isomerization to carboxamido $N,N',N''$-coordination. The structural and spectroscopic characterization of the complexes provides a foundation for future studies of biomimetic and/or catalytic reactivity.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Ligands and $N,N',N''$-Bound Complexes $^8$LClX (X = Cl−, OAc−). The report of $^{iPr}_2$L(H) (2b)$^8$ sparked our interest in arylcarboxamido(arylimino)pyridine ligands and motivated the development of a large-scale synthesis that could be modified to enable access to a series of related ligands with variable aryl substitution. We found that treatment of 6-acetylpicolinic acid with oxalyl chloride, followed by the desired aniline in the presence of NEt$_3$, yielded ketocarboxamide precursors 7 (Scheme 1). Addition of 7a or 7b to a preformed mixture of TiCl$_4$ and the second aniline provided $^8$L(H) (2a−2c) in a total yield of up to 47%. The indicated formulations for 7a, 7b and 2a−2c were supported by $^1$H and $^{13}$C NMR spectroscopy and, in the case of $^{Me}_2$L(H) (2c), X-ray crystallography. In the X-ray crystal structure of 2c, the amide, pyridine, and imine moieties are coplanar, but with the imine donor facing away from the putative metal ion binding pocket (Figure 1a and Table 1).

Treatment of $^8$L(H) (2a−2c) with sodium methoxide in the presence of CuCl$_2$ yielded complexes $^8$LClX (8a−8c) (Scheme 2). Related complexes $^8$LClOAc (9b, 9c) were synthesized by refluxing $^{iPr}_2$L(H) (2b) or $^{Me}_2$L(H) (2c), respectively, with Cu(OAc)$_2$·2H$_2$O in MeCN. The formulations of all of these compounds are supported by UV−vis and EPR spectroscopy, ESI mass spectrometry, and X-ray crystallographic data (8a, 8b, and 9b in Figure 1; 8c and 9c in Figure S2, Supporting Information). Similar $N,N',N''$-coordination of their arylcarboxamido(arylimino)pyridine ligands is apparent in all of the X-ray structures, each of which shows a tetragonal geometry for the Cu(II) ion. Disparate Cu−N bond distances within each complex are seen, with the trend Cu−N(pyridyl) < Cu−N(amide) < Cu−N(imine) reflected by the average distances of 1.927, 1.980, and 2.100 Å, respectively. The observation of the shortest Cu−N bond for the pyridyl group is consistent with previously reported structures of complexes of bis(arylcarboxamido)pyridine or diiminopyridine ligands 1 and 3.$^{12}$ Apparently, as a result of decreased steric bulk of its methyl-substituted aryl groups, the X-ray structure of $^{Me}_2$LCuCl (8a) is composed of polymeric repeating units resulting from axial coordination of the carboxamide carbonyl of one “monomer” to the copper center of a neighboring unit (8a; Cu1−O1′1 = 2.345(3) Å) (Figure 1c). Similar axial coordination, albeit intramolecular and involving an acetate ligand O atom, is observed in $^{iPr}_2$LCuOAc (9b; Cu1−O2 = 2.369(2) Å; Figure 1d) and $^{Me}_2$LCuOAc (9c; Cu1−O3 = 2.456(3) Å; Figure S6b, Supporting Information).
Table 1. Selected Interatomic Distances (Å) and Angles (deg) for the Indicated X-ray Crystal Structures$^a$

|                | $^{α}$L(MeCl)$_2$CuCl (8a) | $^{α}$LMeCuCl (8c) |
|----------------|----------------------------|-------------------|
| Cu(1)−N(1)    | 1.960(3)                  | 1.962(3)          |
| Cu(1)−N(2)    | 1.930(2)                  | 1.926(3)          |
| Cu(1)−N(3)    | 2.098(3)                  | 2.070(3)          |
| Cu(1)−Cl(1)   | 2.193(9)                  | 2.175(10)         |
| Cu(1)−N(4)    | 2.288(2)                  | 2.116(1)          |
| N(1)−Cu(1)−O(1)| 174.69(10)                | 174.09(10)        |
| O(3)−Cu(1)−N(3)| 117.31(10)                | 117.31(10)        |
| O(3)−Cu(1)−O(3)| 60.32(9)                  | 60.32(9)          |
| N(2)−Cu(1)−O(1)| 81.21(7)                  | 81.21(7)          |
| N(2)−Cu(1)−N(3)| 161.66(7)                 | 161.66(7)         |
| N(4)−Cu(1)−N(4)| 177.88(9)                 | 177.88(9)         |
| N(4)−Cu(1)−O(1)| 100.36(8)                 | 100.36(8)         |
| N(2)−Cu(1)−N(3)| 80.50(8)                  | 80.50(8)          |

X-band EPR spectra of solutions of $^{8}$LCuCl (8a−8c) and $^{8}$LCuOAc (9b,9c) in CH$_2$Cl$_2$/toluene (1:1 v/v) at 2−30 K exhibit rhombically distorted axial signals with resolved N-superhyperfine coupling (8a, 8b in Figure 2; 8c, 9b, 9c, in Figure S3, Supporting Information). Parameters from spectral simulations are listed in Table 2 (entries 1−5). These parameters compare favorably to those obtained for Cu(II) complexes of bis(arylcarboxamido)pyridine ligand 1, as illustrated by entries 6 and 7.$^4$ From the combined data, it appears that a $g_z$ value of $\sim$2.2, a large $A_{\parallel}$(Cu) $\sim$ 195 × 10$^{-4}$ cm$^{-1}$, and well-resolved N-superhyperfine features are signatures of $N,N'$-$N''$-coordination of the supporting ligand.

The only exception to this generalization is the smaller $A_{\parallel}$(Cu) value and lesser-resolved N-superhyperfine coupling for 8a. With the data in hand, we can only speculate that the outlier properties of 8a result from the reduced steric bulk of the aryl groups in this complex, perhaps enabling axial ligand interactions with the copper center (as seen in its X-ray structure) that perturb the EPR spectrum.

Cyclic voltammetry was performed on complexes $^{α}$LCl (8b) and $^{α}$LMeOAc (9b) to investigate the effect of the asymmetric ligand environment on the oxidation potential of neutral $^{α}$LX (X = Cl$^-$, OAc$^-$) complexes in comparison to previously studied anionic [(1)CuX]$^-$ (R = iPr, X = Cl$^-$).
A reversible oxidative wave was observed for $i$Pr$_2$LCuCl (8b) upon scanning anodically with $E_{1/2} = 0.760$ V vs Fc/Fc$^+$ and $\Delta E_p = 62$ mV (50 mV $s^{-1}$, 0.1 M Bu$_4$NPF$_6$ in acetone, Figure 3, red trace). In comparison to the analogous $[\text{(1)}CuCl]^{-}$ complex, the oxidation potential of $i$Pr$_2$LCuCl (8b) is larger by almost 0.5 V (Figure 3). Data for $i$Pr$_2$LCuOAc (9b) under identical conditions (0.1 M Bu$_4$NPF$_6$ in acetone) demonstrated a slightly lower oxidation potential of $E_{1/2} = 0.708$ V vs Fc/Fc$^+$ using scan rates of greater than 1000 mV $s^{-1}$; scan rates below 500 mV $s^{-1}$ resulted in an irreversible oxidative wave (Figure S5b, Supporting Information). The observed $\sim 0.5$ V larger oxidation potentials for $i$Pr$_2$LCuCl (8b) and $i$Pr$_2$LCuOAc (9b) relative to analogues supported by 1 support the hypothesis that installing the neutral imine donor into the ligand framework significantly raises the oxidation potential of N,N,N′-copper(II) complexes.

Table 2. EPR Parameters Derived from Simulations of Experimental X-Band Spectra$^a$

| entry | compound | $g_x$ | $g_y$ | $g_z$ | $A_x$(Cu) | $A_y$(N$_{av}$) | $A_z$(Cl) | ref |
|-------|----------|-------|-------|-------|------------|---------------|------------|-----|
| 1     | Me$_2$LcuCl (8a) | 2.08  | 2.05  | 2.23  | 165        | 12.5          | 12.5       | b   |
| 2     | $i$Pr$_2$LcuCl (8b) | 2.065 | 2.09  | 2.20  | 196        | 15            | 15         | b   |
| 3     | $i$Pr$_2$LcuCl (8c) | 2.06  | 2.045 | 2.185 | 197        | 15            | 15         | b   |
| 4     | $i$Pr$_2$LcuOAc (9b) | 2.037 | 2.072 | 2.21  | 190        | 15            |            | b   |
| 5     | $i$Pr$_2$LcuOAc (9c) | 2.07  | 2.055 | 2.20  | 194        | 15            |            | b   |
| 6     | (1$^+$)-Cu(CH$_3$CN) (R = iPr) | 2.027 | 2.064 | 2.190 | 199        | 15.6          | 15         | 1   |
| 7     | (1$^+$)-Cu(MeOH) (R = Me) | 2.028 | 2.055 | 2.189 | 193        | 15            | 4          | b   |
| 8     | $^{[\text{1L(H)}Cu(MeCN)]_{[\text{SbF}_6]_2}}$ (10) | 2.06  | 2.07  | 2.27  | 165        | 15            |            | b   |
| 9     | $^{[\text{1MeL(H)}Cu(MeCN)]_{[\text{SbF}_6]_2}}$ (11) | 2.06  | 2.07  | 2.27  | 165        | 15            |            | b   |
| 10    | $^{[\text{1MeL(H)}Cu(H_2O)(THF)]_{[\text{SbF}_6]_2}}$ (12) | 2.03  | 2.11  | 2.27  | 155        | 15            |            | b   |
| 11    | $^{[\text{1MeL(H)}CuCl_2}$ (13) | 2.14  | 2.14  | 2.14  | 15         | 15            |            | b   |

$^a$Measured in frozen solution at 2−30 K; units of $A$ are in $10^{-4}$ cm$^{-1}$. See the Experimental Section or indicated references for details. $^b$This work.
with bound solvent ligands were prepared by treatment of $[^{15}N]L(H)(2b)$ or $[^{18}N]L(H)(2c)$ with $[\text{Cu}(\text{MeCN})_5](\text{SbF}_6)_2$ (Scheme 3). X-ray crystal structures of the complexes

\begin{align*}
\text{Scheme 3}
\end{align*}

\begin{align*}
[^{15}N]L(H)\text{Cu(MeCN)}[(\text{SbF}_6)_2] (10, \text{Figure 5b}) \text{ and }[^{18}N]L(H)\text{Cu(OH}_2)(\text{THF})[(\text{SbF}_6)_2] (12, \text{Figure 5c}) \text{ revealed tetragonal copper ion geometries with } O,N,N' \text{-ligation at typical } Cu-O,N \text{ distances (Table 1). Metal–ligand bond distances (Table 1) are generally longer than those in the } N,N',N'' \text{-coordinated complexes, as expected for the differences in the protonation state of the ligands (neutral charge for } O,N,N' \text{- vs anionic for } N,N',N'' \text{-coordination). Longer axial interactions with counterions (water molecule, with } H(\text{water}) \text{ and/or solvent molecules (12, } Cu-O(\text{THF}) = 2.235(2) \AA \text{ are also present. Also in 12, two THF solvate molecules form hydrogen bonds to the bound water molecule, with } H(\text{water})-O(\text{THF}) \text{ distances of 1.788(9) and 1.802(11) } \AA \text{, respectively.}
\end{align*}

Consideration of the EPR spectra for complexes 10–12 reveals notable differences compared to the spectra for 8 and 9, which enable $N,N',N''$- and $O,N,N'$-coordination to be distinguished (Table 2 and Figure S3, Supporting Information). Notably, the complexes with $O,N,N'$-coordination display larger $g_z$ ($\sim 2.3$ vs $2.2$), decreased rhombicity ($g_x \sim g_y$), and smaller $A_J (\text{Cu})$ values (160 vs $\sim 190 \times 10^{-4}$ cm$^{-1}$). In addition, N-superhyperfine coupling is not observed for any of the $O,N,N'$-copper(II) complexes. These differences are illustrated in Figure 4, in which data and simulations for $[^{15}\text{Me}_2\text{L}\text{CuOAc}} (9c)$ and $[^{18}\text{Me}_2\text{L}(\text{Cu}(\text{MeCN})_5)](\text{SbF}_6)_2] (11)$ are directly compared.

Additional complexes exhibiting $O,N,N'$-coordination included $[^{15}\text{Me}_2\text{L}](\text{MCl})_2 (\text{M} = \text{Cu, Co, Zn})$, which were generated through the combination of divalent metal ions with $[^{15}\text{Me}_2\text{L}](H)_2$ in the absence of added base (Scheme 3). For example, treatment of $[^{15}\text{Me}_2\text{L}](H)_2$ with MCl$_2 (\text{M} = \text{Cu, Co, Zn})$ yielded the neutral complexes 13–15. These complexes were characterized by UV–visible spectroscopy, ESI-MS, elemental analysis, and, in the cases of 14 (M = Co) and 15 (M = Zn), by X-ray crystallography. The X-ray structures of 14 and 15 are essentially isostructural, with five-coordinate geometries illustrating $O,N,N'$-binding of the protonated forms of the arylecarboxamido(arylimino)pyridine ligand (15 in Figure 5a; 14 in Figure S6c, Supporting Information). Coordination geometries intermediate between square-pyramidal and trigonal-bipyramidal are indicated by $\tau$ values of 0.566 (14) and 0.491 (15). Consistent with the solvent-labile cationic copper(II) metal–ligand bond distances, those in 14 and 15 are elongated relative to those in the $N,N',N''$-coordinated complexes (Table 1). In both structures, solvent molecules in the crystal lattice propagate hydrogen-bonding networks through intermolecular interactions with the amide proton of the bound ligand $[^{15}\text{Me}_2\text{L}](H)_2$ (2c). In the absence of suitable crystals for structure determination by X-ray diffraction, the formulation of 13 (M = Cu) is supported by CHN analysis results and the presence of a peak envelope for $[^{15}\text{Me}_2\text{L}](\text{CuCl})_2$ in the ESI mass spectrum, which is consistent with the $[^{15}\text{Me}_2\text{L}](\text{MCl})_2$ peaks observed for 14 and 15.

$O,N,N'$-Carboxamido to $N,N',N''$-Carboxamido Linkage Isomerization. As described above, $O,N,N'$-bound complexes of L(H) or $N,N',N''$-bound complexes of L$^-$ may be accessed by performing the syntheses in the absence or presence of base. In addition, we have been able to demonstrate...
that addition of base can induce conversion of the former to the latter type. Such a linkage isomerization reaction was identified by monitoring reactions of PrMeL(H)CuCl2 (13) with NEt3 by EPR and UV–vis spectroscopy (Figures S7 and S8, Supporting Information). Preparation and analysis of a uniform series of independent frozen solutions (1:1, MeCN/toluene) samples of PrMeL(H)CuCl2 (13) after reaction with increasing amounts of NEt3 (ranging from 0 to 2 equiv of NEt3) by EPR spectroscopy allowed the reaction to be monitored incrementally. Interestingly, the EPR spectra of PrMeL(H)CuCl2 (13) exhibit an isotropic signal, which does not vary upon preparation in various solvents and analysis under a range of temperatures (2–30 K). While this signal deviates from the previously observed spectral features for the O,N,N′- and N,N′,N″-coordinated copper(II) series of compounds, related isotropic EPR signals have been reported for similar neutral O,N,N-coordinated CuX2 (X = Cl−, ClO4−, SCN−, NO3−) complexes.14 Upon reaction of PrMeL(H)CuCl2 (13) with NEt3, the isotropic EPR signal diminishes in intensity as features consistent with the axial signal of PrMeLCuCl (8c) appear. This axial signal displays g and A0(Cu) values in agreement with the EPR spectra of independently synthesized PrMeLCuCl (8c). Consistent with this result, the progressive addition of increasing amounts of NEt3 to a solution of PrMeL(H)CuCl2 (13) results in a color change from orange to dark green, which is characteristic of PrMeLCuCl (8c). The absorption features for the latter reached maximum intensity upon addition of ~1 equiv of NEt3. Also, single crystals isolated from THF solutions of PrMeL(H)CuCl2 (13) after reaction with NEt3 were determined to be isostructural to those obtained from independently synthesized PrMeLCuCl (8c) by X-ray diffraction analysis.

### CONCLUSIONS

In conclusion, we have developed a modular synthesis for the preparation of acrylcarboxamido(arilimino)pyridine ligands and demonstrated their abilities to coordinate a variety of metal(II) ions (Cu, Co, and Zn). Synthetic procedures for preparation of complexes featuring anionic N,N,N′-carboxamido or neutral O,N,N′-carboxamide ligation, as well as demonstration of linkage isomerization from O,N,N′- to N,N′,N″-coordination, have been established within these novel ligand frameworks. Extensive spectroscopic and structural characterization of a variety of metal(II) complexes in various coordination environments has provided an insight into how the asymmetric carboxamido(arilimino)pyridine framework influences the properties of these novel complexes. Ongoing investigations are focused on further establishing how these ligands support metal complexes in higher oxidation states and their potential reactivity.

### EXPERIMENTAL SECTION

#### General

All solvents and reagents were obtained from commercial sources and used as received unless otherwise stated. The solvents tetrahydrofuran (THF), diethyl ether (EtO2), toluene, pentane, and dichloromethane were passed through solvent purification columns (Glass Contour, Laguna, CA). Dichloromethane and acetonitrile were dried over CaH2 and then distilled under vacuum prior to use. THF was dried over sodium/benzophenone prior to use. Acetonitrile was dried over activated 3 Å molecular sieves and distilled under vacuum prior to use. Purified solvents were stored in a nitrogen-filled glovebox over either activated 3 Å molecular sieves or CaH2 and filtered through a 0.45 μm PTFE syringe filter immediately before use. All complexes were prepared under dry nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres inert atmosphere glovebox, unless otherwise stated. Cu(MeCN)3(SbF6)2 was synthesized according to published procedures.15 2,6-dibromopyridine was recrystallized from benzene/n-hexane and dried prior to use. The synthesis of 6-acetylpyridine-2-carboxylic acid was performed according to the literature,16 with slight modifications (see the Supporting Information for details).

### Physical Methods

UV–vis spectra were recorded with an HP8453 (190–1100 nm) diode array spectrophotometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc. (Parsippany, NJ) and Robertson Microlit Laboratory (Ledgewood, NJ). EPR spectra were recorded with a Bruker Continuum Wave EleXsys E500 spectrometer at either 2 or 30 K. EPR simulations were performed by using Bruker SimFonia software (version 1.2S). NMR spectra were recorded on either Varian V1-300 or VXR 300 spectrometers at room temperature. Chemical shifts (δ) for 13C and 1H NMR spectra were referenced to residual protium in the deuterated solvent (δH) or the characteristic solvent resonances of the solvent nuclei (δC). ESI-MS were recorded with a Bruker BIOTOF II instrument in positive ion mode. Cyclic voltammetry was performed in a three-electrode cell with a Ag/Ag+ reference electrode, a platinum auxiliary electrode, and a glassy carbon working electrode and analyzed with BASI Epsilon software. Tetrabutylammonium hexafluorophosphate (Bu4NPF6) was used as the supporting electrolyte. X-ray crystallography data collections and structure solutions were conducted by using either Siemens SMART or Bruker APEX II CCD instruments and the current SHELXTL suite of programs.17

#### 6-Acetyl-N-(2,6-diisopropylphenyl)picolinamide (7a).

6-Acetyl-2-pyridinocarboxylic acid (1.69 g, 10.3 mmol) was dissolved in toluene (100 mL), treated with oxalyl chloride (1.39 mL, 16.5 mmol), and refluxed 16 h under N2. The solvent was removed in vacuo after cooling the mixture to room temperature. The resulting brown solid and 2,6-diisopropyl aniline hydrochloride salt (1.1 equiv, 2.4 g, 11.3 mmol) were dissolved in THF (75 mL) and cooled to 0 °C under N2. Triethylamine (2.5 equiv, 3.6 mL, 25.7 mmol) was then added via syringe, resulting in the immediate formation of a white precipitate. After stirring for 15 min at 0 °C, the reaction mixture was warmed to room temperature and subsequently brought for reflux for 2 h. After cooling to room temperature, the reaction mixture was filtered and the resulting brown filtrate was concentrated by rotary evaporation. The resulting residue was then washed with hexanes to yield a brown solid and isolated via filtration. The brown solid was then dissolved in a 10:90 EtOAc:pentane solution and passed through charcoal. Evaporation of the resulting filtrate yielded a white solid (2.46 g, 74%).1H NMR (300 MHz, CD2Cl2): δ 8.35 (br s, 1H, NH2), 8.43 (d, 1H, J = 8.4 Hz, Py H), 8.23 (d, 1H, J = 7.5 Hz, Py H), 8.10 (t, 1H, J = 7.8 Hz, Py H), 7.37 (1H, J = 7.6 Hz, Ar H), 7.26 (2H, J = 7.2 Hz, Ar H), 3.14 (m, 2H, Ar CH(CH2)n), 2.77 (s, 3H, C(O)CH3), 1.22 (d, 12 H, J = 6.9 Hz, Ar CH(CH3)n).13C NMR (300 MHz, CD2Cl2): δ 123.9, 26.1, 29.5, 124.1, 124.6, 126.3, 128.9, 131.9, 139.5, 146.9, 149.7, 152.6, 163.4, 199.0. Anal. Calc. for C13H11N2O2: C 72.06, H 6.79, N 8.55.

#### 6-Acetyl-N-(2,6-dimethylphenyl)picolinamide (7b).

7b was synthesized following the identical procedure as was used for 7a, except with the substitution of 2,6-dimethylaniline for 2,6-diisopropyl aniline (1.92 g, 70%).1H NMR (300 MHz, CD2Cl2): δ 8.44 (d, 1H, J = 7.5 Hz, Py H), 8.22 (d, 1H, J = 7.8 Hz, Py H), 8.10 (t, 1H, J = 7.8 Hz, Py H), 7.17 (br s, 3H, Ar H), 2.78 (s, 3H, C(O)CH3), 2.31 (s, 6H, Ar CH(CH3)n).13C NMR (300 MHz, CD2Cl2): δ 128.3, 26.1, 29.5, 124.1, 124.6, 126.3, 128.9, 131.9, 139.5, 146.9, 149.8, 152.6, 163.4, 199.0. Anal. Calc. for C13H14N2O: C 72.62, H 7.46, N 8.64. Found: C 72.63, H 7.29, N 8.55.

#### 6-Acetyl-N(2,6-dimethylphenyl)picolinamide (2a).

2a was synthesized following the identical procedure as was used for 2b, except starting from 7b instead of 7a (1.43 g, 48%).1H NMR (300 MHz, CD2Cl2): δ 8.50 (br s, 1H, NH), 8.62 (4H, J = 7.8 Hz, Py H), 8.35 (d, 1H, J = 6.6 Hz, Py H), 8.07 (t, 1H, J = 7.8 Hz, Py H), 7.16–6.92 (6H, Ar H), 2.31 (s, 6H, Ar CH(CH3)n, N-carboxylamide), 2.23 (s, 3H, N=C(CH3)2), 2.04 (s, 6H, Ar CH(CH3)n, N-arylimine).13C NMR (300 MHz, CD2Cl2): δ 16.8, 18.2, 18.9, 123.7, 124.0, 124.4, 125.8, 127.7, 128.4, 128.6, 136.0, 138.7, 149.8, 152.6, 162.1, 199.0. Anal. Calc. for C13H14N2O: C 72.62, H 7.46, N 8.64. Found: C 72.63, H 7.28, N 8.56.
A solution of 2,6-disopropylaniline (3.7 mL, 19.8 mmol) was dissolved in 100 mL of toluene and cooled to 0 °C under N2. TiCl4 (0.36 mL, 3.3 mmol) was added via syringe, and the reaction mixture was stirred for 15 min. The reaction mixture was then filtered through Celite, and the brown-yellow filtrate was concentrated via rotary evaporation. The resulting brown-yellow solid was purified by column chromatography on silica gel (EtOAc/pentane (1:10); Rf = 0.36) to yield a yellow solid (2.02 g, 63%).

The H NMR and high-resolution ESI-MS of 2b are previously reported and correlate well with the current data. H NMR (300 MHz, CDCl3): δ 7.07, 6.92 (br s, 1H, NH), 8.61 (d, J = 7.8 Hz, Py H), 8.36 (d, J = 7.5 Hz, Py H), 8.08 (t, J = 7.8 Hz, Py H), 7.39–7.08 (m, 6H, Ar H), 3.17 (m, 2H, Ar CH(CH3)2), 2.76 (m, 2H, Ar CH(CH3)2-N-arylcarboxamide), 2.26 (s, 3H, NH=CHCl), 1.24–1.14 (m, 24 H, Ar CH(CH3)2), 0.95 (d, J = 6.9 Hz, Ar CH(CH3)2), 0.85 (s, 3H, NH=CHCl), 0.25 (s, 6H, Ar CH(CH3)2-N-arylcarboxamide). 13C NMR (300 MHz, CDCl3): δ 171.9, 23.5, 23.9, 28.9, 30.5, 103.3, 123.6, 124.1, 124.2, 124.5, 128.8, 131.2, 136.2, 138.8, 146.7, 146.9, 149.3, 153.5, 163.9, 166.4. Analytical data for C24H25N3O: C 77.60, H 6.78, N 11.31. A solution of 2,6-diisopropylaniline (3.7 mL, 19.8 mmol) in 40 mL of toluene was added to the reaction. The reaction mixture was then refluxed for 16 h. After cooling to room temperature, EtO (100 mL) was added and the reaction mixture was stirred for 15 min. The reaction mixture was then filtered through Celite, and the brown-yellow filtrate was concentrated via rotary evaporation. The resulting brown-yellow solid was purified by column chromatography on silica gel (EtOAc/pentane (1:10): Rf = 0.36) to yield a yellow solid (2.02 g, 63%).

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was stirred at room temperature for 30 min, resulting in an orange-brown solution. EtO (12 mL) was added to the solution, which was then cooled to −30 °C. The resulting orange-brown solid was collected by vacuum filtration, washed with pentane (3 × 10 mL), and dried under vacuum for 1 h (0.0624 g, 95%). MS (ESI+, CH₃OH): m/z = 523.27 [13 − Cl]⁺; UV−vis (MeCN) λmax (ε, M−1 cm−1): 400 (520), 450 (700), 750 (480) nm. EPR [9.45 GHz, MeCN/toluene (1:1), 30 K]: g = 2.14. Anal. Calc for C₁₉H₂₃Cl₂N₃O₂Cu: C 57.82, H 3.57, N 6.23. Found: C 57.78, H 3.78, N 6.31.

■ ASSOCIATED CONTENT

Supporting Information
Selected spectroscopic and ESI-MS data (PDF) and X-ray data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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