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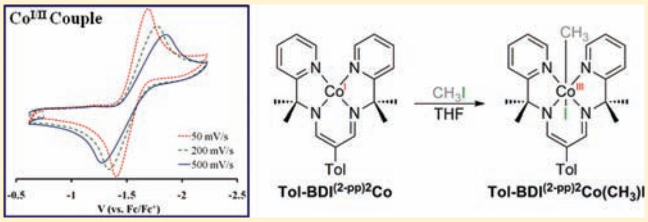
Synthesis and Reactivity of an Isolable Cobalt(I) Complex Containing a β-Diketiminate-Based Acyclic Tetradentate Ligand

Elodie E. Marlier, Bridget A. Ulrich, and Kristopher McNeill*,†

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States

Supporting Information

ABSTRACT: A model for cobalamin was synthesized using a new monoanionic tetradentate nitrogen donor ligand; 2-(4-tolyl)-1,3-bis(2-isopropylpyridyl)propenediimine (Tol-BDI$^{(2\text{-pp})2}$H) (**1**), which utilizes isopropylpyridines as pendant arms on a β-diketiminate (BDI) backbone. During the synthesis of **1**, the rearrangement product, Tol-BDI$^{(2\text{-pp})(4\text{-pp})}$H (**2**) was observed. Metalation of **1** with zinc iodide and cobalt chloride yielded the corresponding Tol-BDI$^{(2\text{-pp})2}$ZnI (**3**) and Tol-BDI$^{(2\text{-pp})2}$CoCl (**4**) complexes. The redox properties of **4** in comparison to cobalamin were examined through electrochemical studies. Electrochemical and bulk reduction of complex **4** gave a diamagnetic cobalt(I) complex, Tol-BDI$^{(2\text{-pp})2}$Co (**5**). Reactivity of **5** toward C-X bonds was investigated using methyl iodide and 1-iodo-2-(trimethylsilyl)acetylene, yielding Tol-BDI$^{(2\text{-pp})2}$Co(CH$_3$)I and Tol-BDI$^{(2\text{-pp})2}$Co(C$_2$Si(CH$_3$)$_3$)I respectively. Synthesis and characterization details for these complexes, including the crystal structure of **3**, are reported.



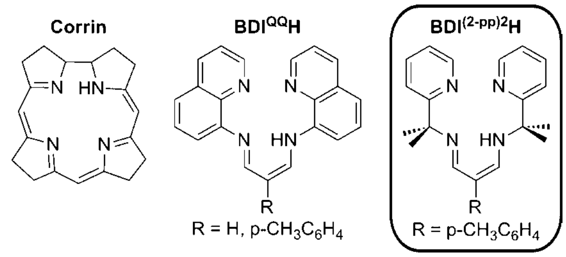
INTRODUCTION

Cobalamin complexes are cofactors that play a critical role in a variety of enzymes, including B$_{12}$-dependent isomerases, methyl transferases, and reductive dehalogenases.[1] To study the mechanism of these reactions, researchers have long employed structurally simpler model complexes, such as dimethylglyoxime- and porphyrin-containing complexes.[2] While such model complexes have proven useful in modeling the chemistry of cobalamin, there is room for improvement. In particular, the porphyrin and glyoxime-based systems mimic the tetraaza coordination environment of the cobalamin corrin, but do not match its monoanionic charge.

A more important shortcoming of the glyoxime- and porphyrin-based model compounds is the difficulty in preparing and isolating cobalt(I) complexes. While examples of Co(I) have been prepared in these systems, the complexity in synthesizing these compounds has hindered their use in further studies.[3] Researchers have opted instead to generate the Co(I) oxidation state in situ. This is unfortunate from the standpoint of studying reaction mechanisms, given that the Co(I) oxidation state can often play a central role. For example, Co(I) is the critical oxidation state in cobalamin-mediated dechlorination reactions.[4] In recent years, isolable cobalt(I) complexes have been supported by a variety of nitrogen donor ligands such as N$_2$P$_2$, bidentate BDI, and iminopyridine pincers.[5] With this in mind, we set out to prepare a ligand system that would allow for the isolation of a Co(I) complex that effectively models cobalamin.

Our approach to preparing a potentially improved structural model for the corrin has focused on using a β-diketiminate ligand with two pendant donor arms (Chart 1). This strategy has previously been employed by Roesky and co-workers with pendant trialkylamine donors and by Zatka et al. with pendant quinoline donors to create a variety of metal complexes.[6] Closely related examples include an unsymmetrical N$_4$−BDI complex reported by Chen and co-workers and a BDI ligand with two pendant ether donors reported by Chisholm and co-workers.[7] The initial attempts to prepare similar ligands with methylpyridine pendant arms prompted the discovery of a new route to pyridylpyrroles due to intramolecular cyclization of the ligand.[8] The cyclization is thought to occur through a nucleophilic attack by the carbon atom α to the pyridine on the neighboring ketone (or imine). To avoid the cyclization, we followed the lead of Zatka et al., and employed quinolines as pendant arms for the second generation ligand.[9] Subsequent study revealed that a ligand equipped with quinoline pendant arms was too rigid to accommodate the different oxidation states of cobalt.[10] This prompted the design of a more flexible ligand.

Chart 1. Tetradentate Monoanionic Ligands with the Ligand Reported Here Shown Boxed



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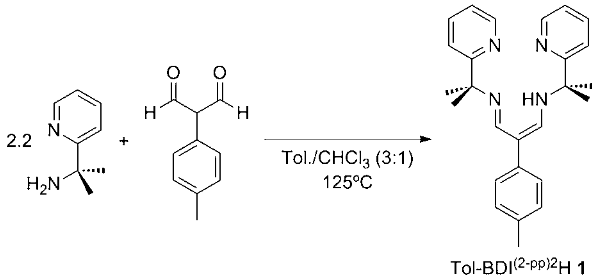
In this work, we report the synthesis and characterization of a new monoanionic tetradentate nitrogen donor ligand; 2-(4-tolyl)-1,3-bis(2-isopropylpyridyl)propenediimine (Tol-BDI$^{(2\text{-pp})2}$H) (**1**), which employs isopropylpyridines as pendant arms on a *β*-diketiminate backbone (Chart 1). Learning from prior work, greater flexibility was introduced by switching from an sp^2-hybridized carbon to an sp^3-hybridized carbon between the pyridyl group and the BDI backbone. Furthermore, gem-dimethyl substitution on the carbon atom *α* to the pyridine prevents pyrrole formation through intramolecular cyclization.

Compound **1** was used to prepare zinc iodide (**3**) and cobalt chloride (**4**) complexes. Most notably, we report the synthesis and characterization of an isolable cobalt(I) complex, Tol-BDI$^{(2\text{-pp})2}$Co (**5**) from the reduction of **4** with sodium amalgam. Lastly, the ability of compound **5** to model cobalamin was examined by exploring its reactivity toward carbon−halogen bonds. Substrates investigated were methyl iodide (**6**) and 1-iodo-2-(trimethylsilyl)acetylene (**7**). In addition, we report a ligand rearrangement product; Tol-BDI$^{(2\text{-pp})(4\text{-pp})}$H (**2**), which is formed during the synthesis of **1**.

RESULTS AND DISCUSSION

Ligand Synthesis. Compound **1** was prepared through the condensation of 2-(4-tolyl)-malondialdehyde and 2-amino-2-(2-pyridyl) propane (Scheme 1). The latter starting material was synthesized in four steps from published procedures.[11] The condensation to **1** was conducted in a toluene/chloroform solvent mixture heated to reflux for one week. This yielded a mixture of **1** and the intermediate monoimine, in which only one aldehyde had undergone reaction. Compound **1** was purified by flash chromatography and was isolated in 67% yield.

Scheme 1. Synthetic Route to Tol-BDI$^{(2\text{-pp})2}$H, 1



Compound **1** was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, electrospray ionization high-resolution mass spectrometry (ESI-HRMS), and UV−vis spectroscopy. The ^{1}H NMR spectrum shows a singlet at 11.6 ppm for the amine proton and seven resonances in the aromatic region including a singlet at 7.73 ppm belonging to the proton *α* to the imine on the *β*-diketiminate backbone (Figure 1). In the methyl region, a 1:4 ratio is observed between the tolyl methyl (2.31 ppm) and the isopropylpyridyl methyl resonances (1.70 ppm). This indicates that the two isopropylpyridine arms of compound **1** are symmetric on the NMR time scale.

Interestingly, a rearrangement is observed during the synthesis of **1** when the reaction concentration is above approximately 0.07 M. The ligand rearrangement product, **2**, only differs from **1**, in that one pendant arm contains a 4-pyridyl group instead of a 2-pyridyl group. Compound **2** was isolated from the flash chromatography purification of **1** in 14% yield.

Compound **2** was fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, ^{1}H/^{1}H COSY, and ESI-HRMS. The ^{1}H NMR spectrum of **2** does not contain a singlet for the proton *α* to the imine as is seen for **1** (Figure 2). Rather, it has two doublets (7.82 and 7.53 ppm) that share a 2.5 Hz coupling constant, confirmed by ^{1}H/^{1}H COSY. Furthermore, the isopropylpyridyl methyls give rise to two separate resonances (1.70 and 1.63 ppm), each integrating to 6H against the tolyl methyl proton signal (2.31 ppm, 3H). The assignment of a 4-pyridyl group comes from the two second-order doublets each integrating to 2H at 8.52 and 7.36 ppm.

Metal Complexes Synthesis. Metalation of compound **1** was achieved by deprotonation of the ligand with potassium bis(trimethylsilyl)amide, followed by the addition of the desired metal halide salt (Scheme 2). Zinc (**3**) and cobalt (**4**) complexes were synthesized in 29% and 98% yield using zinc iodide and cobalt chloride, respectively. We speculate that the large difference in isolated yield is due in part to the superior ability of compound **3** to form a zinc dimer, [Tol-BDI$^{(2\text{-pp})}$ZnI]$_2$ where the ligand has been partially hydrolyzed. The dimer was isolated from preparation of **3** in low nonquantified yields as a crystalline solid. Crystal structure and important crystallographic data of the zinc dimer are reported in the Supporting Information, Figure 1S, Tables 1S and 2S.

Compound **3** was characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, ESI-HRMS, UV−vis spectroscopy, cyclic voltammetry, and X-ray crystallography. The ^{1}H NMR spectrum is similar to that of compound **1**, apart from the disappearance of the amine proton and a downfield shift of the proton *α* to the imine which is now located at 8.16 ppm (Figure 3). A 1:4 ratio is still observed between the tolyl methyl (2.33 ppm) and the isopropylpyridyl methyl resonances (1.73 ppm). The UV−vis spectrum of **3** in CH_2Cl_2 showed three bands at 263, 297, and 393 nm which were also observed in the UV−vis absorbance spectrum of **1** in tetrahydrofuran (THF) at 210, 262, 279 (shoulder), and 344 nm (Supporting Information, Figure 2S). These transitions are likely ligand-based, as they resemble the transitions observed in the absorbance spectrum of **1**. X-ray quality crystals were grown from slow vapor diffusion of diethyl ether into a solution of **3** in CH_2Cl_2 (Figure 4). The geometry of compound **3** can be described as distorted square pyramidal with a τ value of 0.32.[12] We have previously reported two similar BDI zinc complexes which use quinolines for pendant arms.[9,10] The structures for these complexes are very similar with Zn−N bonds matching within 0.03 Å. Important crystallographic data for compound **3** can be found in the Supporting Information, Tables 1S and 2S.

Compound **4** was characterized by ^{1}H NMR spectroscopy, ESI-HRMS, and UV−vis spectroscopy. The ^{1}H NMR spectrum of **4** exhibits broadened resonances, which are expected for a paramagnetic cobalt(II) complex (Supporting Information, Figure 3S). The elemental composition of **4** (456. 1715 *m*/*z*) was checked by ESI-HRMS with a polyethylene glycol exact mass internal standard. The UV−vis spectrum of **4** showed four transitions at 211, 256, 287, and 355 nm (Figure 5). All four of these transitions are assigned as ligand-based transitions. The solution magnetic moment of **4** was found to be $\mu_{\text{eff}} = 3.64\ \mu_B$ by Evans' method. This is slightly smaller than the spin-only magnetic moment for an $S = 3/2$ state ($\mu_{\text{S.O.}} = 3.88\ \mu_B$), which leads to the assignment of a high-spin Co(II) center. While the geometry and coordination mode of **4** remains unknown, 4-coordinate and 5-coordinate cobalt(II) complexes with four

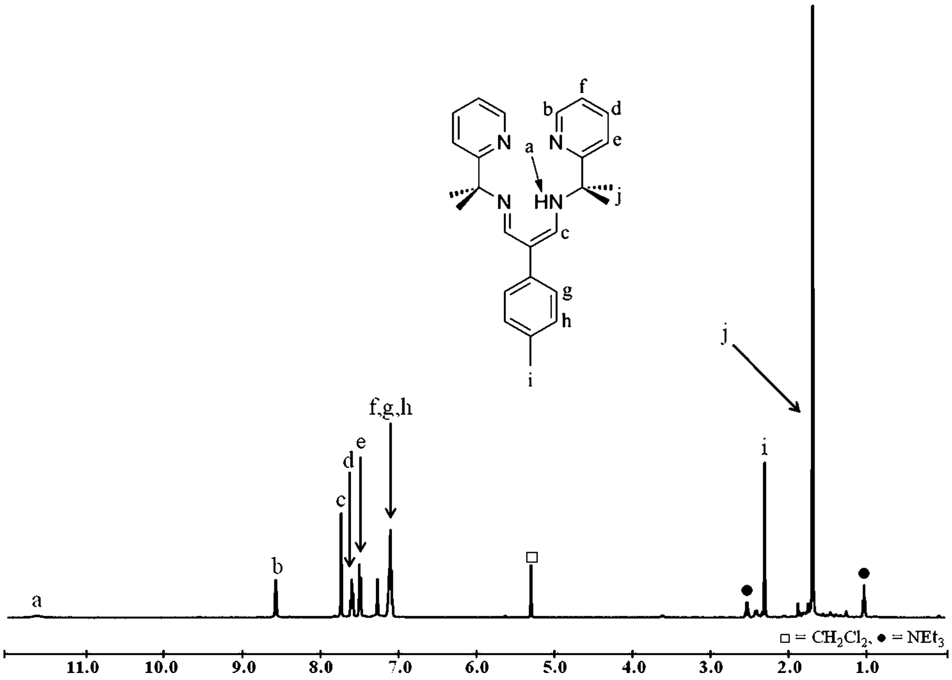


Figure 1. ^{1}H NMR spectrum of Tol-BDI$^{(2\text{-pp})2}$H, **1**, in CDCl$_3$.

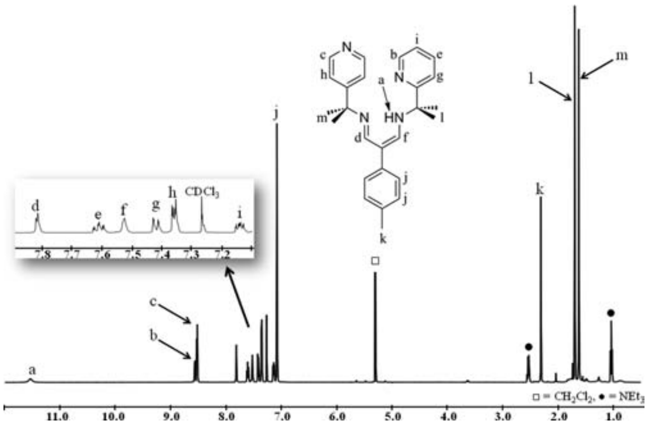
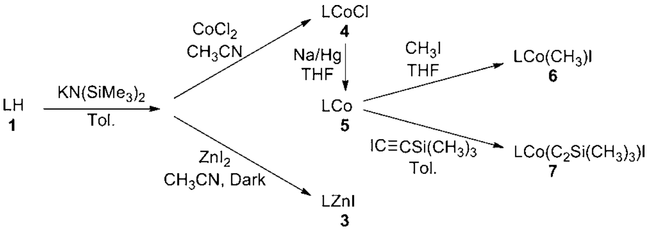


Figure 2. ^{1}H NMR spectrum of rearranged ligand, **2** (Tol-BDI$^{(2\text{-pp})(4\text{-pp})}$H), in CDCl$_3$.

Scheme 2. Synthetic Routes to Tol-BDI$^{(2\text{-pp})2}$ Zn and Co Complexes, 3–7 (L = Tol-BDI$^{(2\text{-pp})2}$)



nitrogen donors have been shown to support a variety of geometries and spin states.[13]

Reduction of compound **4** using sodium amalgam in THF yields the diamagnetic, cobalt(I) complex, Tol-BDI$^{(2\text{-pp})2}$Co(I) (**5**). Compound **5** was characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, UV–vis spectroscopy, and electron-impact high-resolution mass spectrometry (EI-HRMS). The ^{1}H NMR spectrum of **5** shows seven resonances in the aromatic region, while two resonances at 2.29 and 1.52 ppm can be observed in the methyl region belonging to the tolyl methyl and the pyridyl methyl groups (Figure 6). Compound **5** has a unique teal color. The UV–vis spectrum of **5** is similar to **4**. In addition to the four ligand-based transitions at 210, 257, 270, and 318 nm, a distinctive transition is observed at 610 nm (Figure 5). This transition is associated with a molar absorptivity of 5000 M^{-1} cm^{-1}. Transitions with molar absorptivities of similar magnitude have been observed for other square planar cobalt(I) complexes.[14]

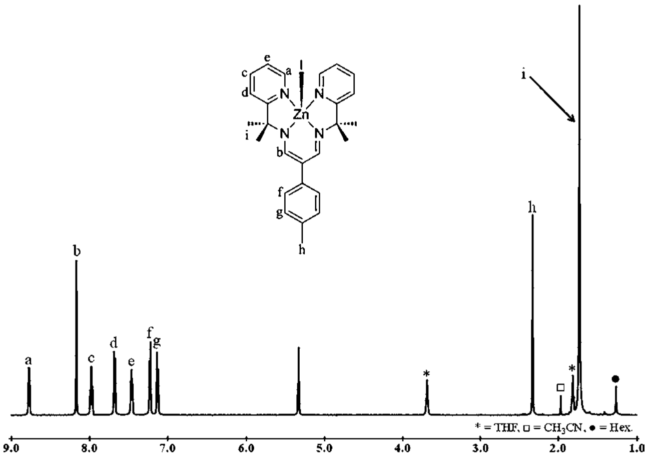


Figure 3. ^{1}H NMR spectrum of Tol-BDI$^{(2\text{-pp})2}$ZnI, **3**, in CD$_2$Cl$_2$.

There is some ambiguity of the oxidation state of the complex **5**, specifically whether it is truly a neutral ligand bound to Co(I) or a reduced ligand radical anion bound to Co(II). Such ligand radical cobalt complexes have been reported with a variety of ligands.[15] In this case, we do not have a crystal structure to make a definitive assignment, but we favor the Co(I) assignment based on the nucleophilicity demonstrated by the complex (vide infra).

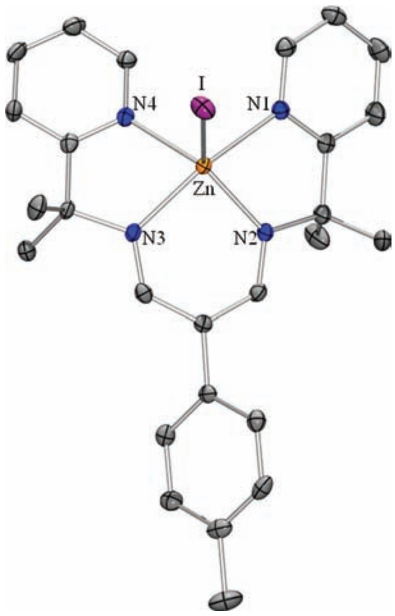


Figure 4. ORTEP diagram of Tol-BDI$^{(2\text{-pp})2}$ZnI, **3**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

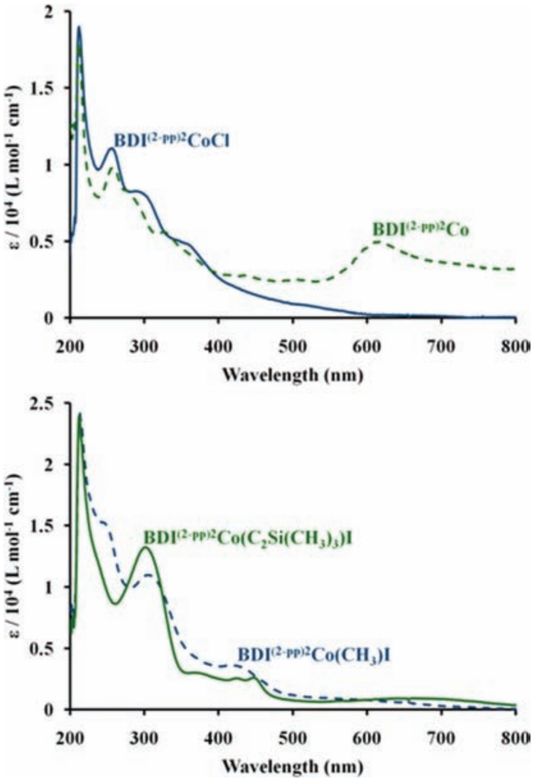


Figure 5. Electronic absorption spectrum of complexes **4**−**7**.

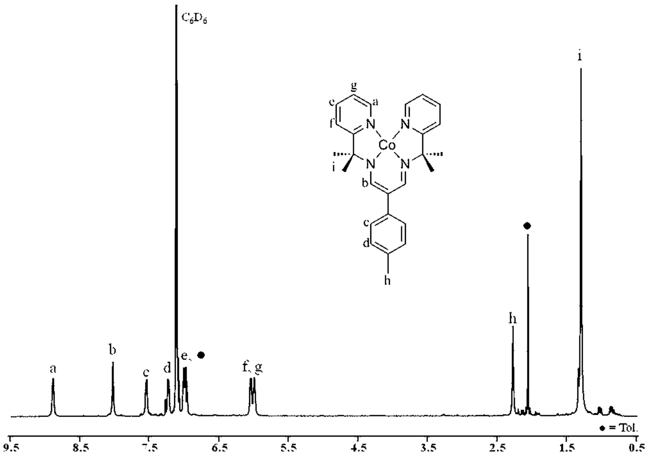


Figure 6. ^{1}H NMR spectrum of Tol-BDI$^{(2\text{-pp})2}$Co, **5**, in C_6D_6.

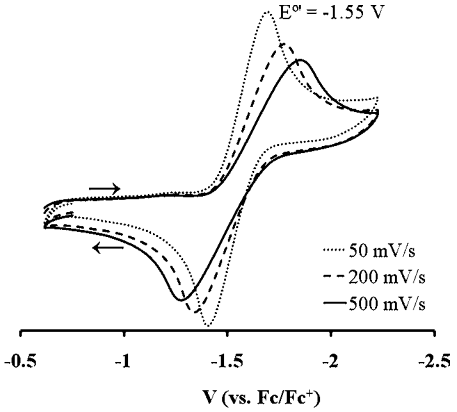


Figure 7. Cyclic voltammograms of **4** at various scan rates (50, 200, 500 mV/s; 0.1 M $[^n\text{Bu}_4\text{N}]\text{PF}_6$ in THF). Currents were multiplied by (scan rate)$^{-1/2}$.

Cyclic Voltammetry. Considering its Co$^{I/II}$ couple of −1.38 V (vs Fc/Fc$^+$), cobalamin is a strong reductant, capable of reducing difficult substrates, such as chlorinated organics.[2h,16] To investigate the reducing power of complex **5**, cyclic voltammetry experiments in 0.1 M $[^n\text{Bu}_4\text{N}]\text{PF}_6$ THF solution were performed on both **3** and **4** with the aim of finding the Co$^{I/II}$ couple. Full cyclic voltammograms of **3** and **4** can be found in the Supporting Information, Figure 4S. Although the cyclic voltammogram of **4** is complex, a quasi-reversible electron transfer wave was observed at −1.55 V with a peak-to-peak separation of 300 mV (vs Fc/Fc$^+$) when scanning at 50 mV (Figure 7). This separation increases to 600 mV, and the peak potential shifts slightly cathodically to −1.56 V at the faster rate of 500 mV/s. The reduction/oxidation wave centered at −1.55 V is assigned to the Co$^{I/II}$ couple. This is slightly lower than the Co$^{I/II}$ couple observed for cobalamin, indicating that **5** is a slightly stronger reductant than cob(I)alamin.[2h,16]

Reactivity of 5. In addition to being a strong reductant, nucleophilicity of the cobalt(I) center is believed to be important to its reactivity. The reaction of cobalt(I) with methyl iodide has previously been used to measure the nucleophilicity of the metal center.[17] For this reason, complex **5** was treated with methyl iodide, which produced an immediate color change from teal to green upon mixing. The product of this reaction was isolated and found to be the cobalt(III) methyl iodide complex, **6**, which was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, ESI-HRMS, and UV−vis spectroscopy. The ^{1}H NMR spectrum of **6** has the expected seven resonances in the aromatic region while three resonances in a 1:4:1 ratio are present in the alkyl region (Figure 8). While the resonances at 2.37 ppm and 1.85 ppm could be identified as belonging to the methyl of the tolyl group and the methyl groups on the pendant arms, respectively, the

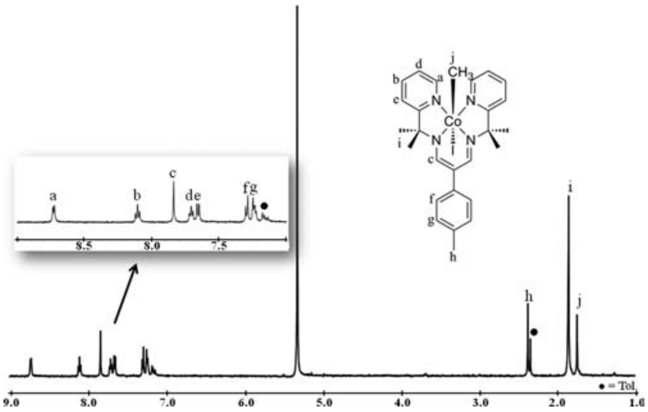


Figure 8. ^{1}H NMR spectrum of Tol-BDI$^{(2\text{-pp})2}$Co(CH$_3$)I, **6**, in CD$_2$Cl$_2$.

resonance at 1.74 ppm was tentatively assigned as the methyl bound to the cobalt center. This assignment was verified through the reaction of **5** with CD$_3$I and observation of the methyl resonance by ^{2}H NMR spectroscopy. The ^{2}H NMR spectrum showed two resonances: one at 2.17 ppm belonging to residual CD$_3$I and one at 1.74 ppm, verifying the shift of the cobalt-bound methyl. The shift of the methyl is notably downfield compared to those of methyl groups bound to cobalamin and cobaloxime, which have been reported at −0.12 ppm in D$_2$O and 0.82 ppm in CDCl$_3$, respectively.[18] For the assignment of the carbon resonance of the methyl cobalt, it was necessary to use ^{13}C-labeled methyl iodide, as the carbon shift could not be unambiguously assigned with unlabeled material. Using ^{13}CH$_3$I, the carbon resonance for the cobalt methyl was observed at −4.67 ppm. The UV−vis spectrum of **6** has a total of four transitions (Figure 5). These ligand-based transitions are similar to those in complexes **4** and **5**.

In addition to methyl iodide, complex **5** reacts with 1-iodo-2-(trimethylsilyl)acetylene to form complex **7** which was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, ESI-HRMS, IR and UV−vis spectroscopy. The ^{1}H NMR spectrum revealed five resonances in the aromatic region, integrating to a total of 14 protons and three resonances in the alkyl region in a 1:4:3 ratio (Supporting Information, Figure 5S). The methyl resonances from the trimethylsilyl group are shifted downfield from the starting material from 0.17 ppm to −0.24 ppm. Similarly, the IR spectrum shows a shift from 2099 cm^{-1} to 2046 cm^{-1} from starting material to complex **7** for the carbon−carbon triple bond stretching mode. In addition, a band at 840 cm^{-1} was observed and assigned to the C(methyl)-Si stretch. These values are similar to those reported for a [(PP$_3$)Co(H)-(C≡CSiMe$_3$]BPh$_4$ complex where bands at 2023 cm^{-1} and 851 cm^{-1} were reported for the C≡C and SiMe$_3$ groups.[19] In addition to having similar ligand-based transitions as the previously mentioned compounds, the UV−vis spectrum of **7** also has peaks at 425 and 447 nm. Through its reactivity toward methyl iodide and 1-iodo-2-(trimethylsilyl)acetylene, complex **5** has been shown to be nucleophilic and thus similar to cobalamin in this regard.

■ CONCLUSION

A monoanionic, tetraaza ligand was prepared in an effort to model the monoanionic corrin ligand in cobalamin. The ligand reported here, Tol-BDI$^{(2\text{-pp})2}$H, is a third-generation ligand that is the product of an iterative design process. The ligand is composed of a β-diketiminate backbone with isopropylpyridine pendant arms. It is both flexible enough to support the three important oxidation states of Co (I, II, III) and stable with respect to decomposition to pyridylpyrrole products. An isolable Co(I) complex of Tol-BDI$^{(2\text{-pp})2}$ was prepared and was found to be comparable to cobalamin(I) both in terms of its Co(I)/Co(II) redox couple and in its reactions as a nucleophile.

■ EXPERIMENTAL SECTION

General Considerations. Experiments were conducted under anhydrous and anaerobic (dinitrogen) conditions using a glovebox or Schlenk line at the exception of the ligand synthesis which was conducted in air. Reagents with the exception of 2-amino-2-(2-pyridyl) propane were purchased commercially and used without further purification. 2-Amino-2-(2-pyridyl) propane was synthesized in four steps from published procedures.[11] Solvents were purchased commercially and dried under standard procedures.[20] UV−vis absorbance data was collected with an OceanOptics CHEMUSB2 spectrophotometer using a quartz cuvette. Infrared (IR) spectra were collected with a Midac M series spectrometer. ^{1}H NMR and 2D NMR spectra were acquired on Varian Inova instruments at 300 and 500 MHz.^{13}C shifts were established from 2D HMQC (Heteronuclear Multiple Quantum Correlation) and HMBC (Heteronuclear Multiple Bond Correlation) NMR experiments. The assignment of the carbon shifts can be found in the Supporting Information, Table 3S. ^{13}C NMR spectrum for the ^{13}CH$_3$I experiment was acquired on a Varian Inova instrument at 75 MHz. ^{2}H NMR spectrum was acquired on a Varian Inova instrument at 300 MHz. Mass spectrometry (MS) data were acquired on a Bruker BioTOF ESI-MS under positive mode. Polyethylene glycol (PEG) and polypropylene glycol (PPG) standards were used for ESI-HRMS. Solution magnetic susceptibilities were determined by the Evans' method.[21] A Finnigan MAT 95 double-focusing mass spectrometer with BE-geometry was used to collect EI-HRMS with sample introduction using a solids probe. Perfluorokerosene (PFK) was used as an internal standard for EI-HRMS.

Tol-BDI$^{(2\text{-pp})2}$H (**1**). Under ambient atmosphere, 2-amino-2-(2-pyridyl) propane (0.200 g, 1.47 mmol) was dissolved in toluene (22 mL) in a round-bottom flask. 2-(4-Tolyl)-malondialdehyde (0.107 g, 0.66 mmol) was dissolved in CHCl$_3$ (7 mL) and was added to the solution of 2-amino-2-(2-pyridyl)propane. A concentration of 0.070 M was found to be optimal to prevent the formation of compound **2**. The reaction was heated to reflux with a bath temperature of 125 °C for one week. The reaction was cooled to room temperature, and solvent was removed using a rotoevaporator. A silica column (99:1 CH$_2$Cl$_2$:Et$_3$N eluent mixture) was used to separate compound **1** from the monocondensed intermediate, 2-(4-tolyl)-1-(2-isopropylpyridyl)propeneimine-3-aldehyde. A brown oil was isolated and dried under vacuum (0.176 g, 67%). UV (THF) $\lambda_{\max}$, nm (ε, L mol^{-1} cm^{-1}): 210, 262 (9200), 279 sh., 344 (4700). ^{1}H NMR (500 MHz, CDCl$_3$): δ ppm 11.62 (1 H, br. s, HN); 8.57 (2 H, d, J 4.0, pyr. CH); 7.73 (2 H, s, CH); 7.60 (2 H, ddd, J 2.0, 8.0 and 9.0, pyr. CH); 7.49 (2 H, d, J 8.0, pyr. CH); 7.12 (2 H, m, pyr. CH); 7.10 (2 H, m, tolyl CH); 7.10 (2 H, m, tolyl CH); 2.31 (3 H, s, tolyl CH$_3$); 1.70 (12 H, s, CH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ ppm 167.3, 150.3, 149.5, 138.7, 136.7, 134.1, 129.3, 125.5, 121.7, 120.4, 105.7, 61.7, 29.4, 21.0. ESI-TOF HRMS (MeOH) with PEG-400−600 m/z: [M + H]$^+$ calcd. for C$_{26}$H$_{31}$N$_4$, 399.2543; found, 399.2538; 1.25 ppm error.

Tol-BDI$^{(2\text{-pp})(4\text{-pp})}$H (**2**). Compound **2** was synthesized as a side product of the synthesis of compound **1**. Under high reaction concentration (approximately 0.1 M), compound **2** was observed. Compound **2** was isolated using a silica column (99:1 CH$_2$Cl$_2$:Et$_3$N eluent mixture). A brown oil was isolated and dried under vacuum (0.050 g, 14%). ^{1}H NMR (500 MHz, CDCl$_3$): δ ppm 11.54 (1 H, br. s, HN); 8.57 (1 H, d, J 3.5, pyr. CH); 8.52 (2 H, d, J 6.0, pyr. CH); 7.82 (1 H, d, J 2.5, CH); 7.61 (1 H, t, J 8.0, pyr. CH); 7.53 (1 H, d, J 2.5, CH); 7.42 (1 H, d, J 8.0, pyr. CH); 7.36 (2 H, d, J 6.0, pyr. CH); 7.15 (1 H, dd, J 5.0 and 7.0, pyr. CH); 7.09 (4 H, br s, tolyl CH); 2.31 (3 H, s, tolyl CH$_3$); 1.70 (6 H, s, CH$_3$); 1.63 (6 H, s, CH$_3$). ^{13}C NMR

(125 MHz, $CDCl_3$): δ ppm 166.5, 158.2, 153.6, 149.8, 148.7, 147.8, 138.6, 136.5, 134.5, 129.1, 125.3, 121.6, 121.3, 119.8, 105.6, 60.6, 59.7, 29.7, 29.1, 20.9. ESI-TOF HRMS (MeOH) with PPG-425 *m*/*z*: $[M + H]^+$ calcd. for $C_{26}H_{31}N_4$, 399.2543; found, 399.2544; 0.25 ppm error.

Tol-BDI$^{(2\text{-}pp)2}$ZnI (3). Under inert atmosphere, compound **1** (0.028 g, 0.07 mmol) was dissolved in toluene (10 mL). A solution of potassium bis(trimethylsilyl)amide was prepared by dissolving $KN(SiMe_3)_2$ (0.016 g, 0.08 mmol) into toluene (5 mL). Upon addition of $KN(SiMe_3)_2$, a slight color change from brown to reddish brown was observed. After 10 min of stirring, a solution of ZnI_2 (0.026 g, 0.08 mmol) was prepared in the dark by dissolving ZnI_2 in CH_3CN (5 mL) and was added dropwise to the deprotonated ligand solution. The solution became orange when left stirring overnight. The solvent was removed under vacuum. The residue was extracted into minimal CH_3CN and was placed in the freezer overnight. The solids precipitated and were dried under vacuum (0.012 g, 29%). X-ray quality crystals were grown from vapor diffusion of diethyl ether into a solution of **3** in CH_2Cl_2. UV (CH_2Cl_2) λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 263, 297, 393 (8500). ^1H NMR (500 MHz, CD_2Cl_2): δ ppm 8.77 (2 H, d, *J* 5.0, pyr. CH); 8.16 (2 H, s, CH); 7.97 (2 H, dt, *J* 1.5 and 8.5, pyr. CH); 7.67 (2 H, d, *J* 8.5, pyr. CH); 7.46 (2 H, t, *J* 6.0, pyr. CH); 7.22 (2 H, d, *J* 8.0, tolyl CH); 7.12 (2 H, d, *J* 8.0, tolyl CH); 2.33 (3 H, s, tolyl CH_3); 1.73 (12 H, s, CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ ppm 166.9, 156.8, 147.3, 141.5, 139.6, 133.2, 129.5, 125.9, 123.4, 123.1, 104.6, 61.6, 31.1, 21.2. ESI-TOF HRMS (CH_3CN) with PEG-400−600 *m*/*z*: $[M - I]^+$ calcd. for $C_{26}H_{29}N_4Zn$, 461.1684; found, 461.1680; 0.87 ppm error.

Tol-BDI$^{(2\text{-}pp)2}$CoCl (4). Under inert atmosphere, compound **1** (0.389 g, 0.98 mmol) was dissolved in toluene (50 mL). A solution of potassium bis(trimethylsilyl)amide was prepared by dissolving $KN(SiMe_3)_2$ (0.187 g, 0.94 mmol) into toluene (25 mL). Upon addition of $KN(SiMe_3)_2$, a slight color change from brown to reddish brown was observed. After 10 min of stirring, a solution of $CoCl_2$ (0.129 g, 0.99 mmol) was prepared by dissolving it in CH_3CN (25 mL) and was added dropwise to the deprotonated ligand solution. No visible change of color was observed. The reaction was left stirring overnight. The solvent was removed on a Schlenk line, and the residue was extracted using toluene, THF, and CH_3CN. The extraction solutions were filtered and evaporated to dryness. The residues were combined and dried under vacuum (0.473 g, 98%). UV (THF) λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 211 (21000), 256 (12000), 287 (8700), 355 (5300). ^1H NMR (300 MHz, CD_3CN): δ ppm 15.67, 12.24, 11.44, 11.12, 7.98, 7.19, 5.44, 2.32, 1.63, −2.87. Evans' method ($CDCl_3$/$CHCl_3$, 300 MHz): μ_{eff} = 3.64 μ_B. ESI-TOF HRMS (CH_3CN) with PEG-400−600 *m*/*z*: $[M - Cl]^+$ calcd. for $C_{26}H_{29}N_4Co$, 456.1724; found, 456.1715; 1.97 ppm error.

Tol-BDI$^{(2\text{-}pp)2}$Co (5). Under inert atmosphere, compound **4** (0.069 g, 0.14 mmol) was dissolved in THF (30 mL). Sodium amalgam was created by adding elemental mercury (1.093 g, 5.45 mmol) to sodium metal (0.013 g, 0.57 mmol). The solution of compound **4** was added to the sodium amalgam and was left stirring overnight. The brown solution became teal. The THF solution was filtered, and filtrate was dried under vacuum. The residue was extracted using toluene, and the extraction solution was dried under vacuum (0.046 g, 72%). UV (THF) λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 210, 257 (10000), 270 sh., 318 (5900), 610 (5000). ^1H NMR (500 MHz, d_8-THF): δ ppm 9.02 (2 H, d, *J* 3.5, pyr. CH); 7.77 (2 H, s, CH); 7.56 (2 H, t, *J* 7.0, pyr. CH); 7.11 (2 H, d, *J* 6.5, tolyl CH); 7.02 (2 H, d, *J* 6.5, tolyl CH); 6.72 (2 H, d, *J* 7.0, pyr. CH); 6.57 (2 H, t, *J* 8.0, pyr. CH); 2.29 (3 H, s, tolyl CH_3); 1.52 (12 H, s, CH_3). ^{13}C NMR (125 MHz, d_8-THF): δ ppm 173.4, 150.5, 149.5, 142.4, 136.7, 132.7, 129.3, 125.5, 121.7, 120.4, 112.1, 71.3, 29.4, 21.0. EI-HRMS (70 eV) with PFK *m*/*z*: $[M]^+$ calcd. for $C_{26}H_{29}N_4Co$, 456.1724; found, 456.1700; 5.26 ppm error.

Tol-BDI$^{(2\text{-}pp)2}$Co(CH$_3$)I (6). Under inert atmosphere, compound **5** (0.010 g, 0.02 mmol) was dissolved in THF (5 mL). While stirring, methyl iodide (13 μL, 0.02 mmol) was added dropwise. The solution changed color immediately to green. The solution was stirred for 1 h before being filtered and dried under vacuum (0.012 g, 94%). UV (THF) λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 212, 236, 304 (9800), 418 (3600). ^1H NMR (500 MHz, CD_2Cl_2): δ ppm 8.73 (2 H, dd, *J* 1.0 and 5.5, pyr. CH); 8.11 (2 H, dd, *J* 1.0 and 8.0, pyr. CH); 7.84 (2 H, s, CH); 7.71 (2 H, dd, *J* 1.0 and 7.0, pyr. CH); 7.65 (2 H, dd, *J* 1.0 and 8.0, pyr. CH); 7.29 (2 H, d, *J* 8.5, tolyl CH); 7.24 (2 H, d, *J* 8.0, tolyl CH); 2.37 (3 H, s, tolyl CH_3); 1.85 (12 H, s, CH_3); 1.74 (3 H, s, $CoCH_3$). The ^1H NMR shift of the methyl bound to the cobalt was verified by reacting compound **5** with CD_3I. ^2H NMR (300 MHz, CH_3CN): δ ppm 1.74 (s, $CoCD_3$). ^{13}C NMR (125 MHz, CD_2Cl_2): δ ppm 173.1, 151.9, 151.1, 139.4, 137.9, 135.9, 130.0, 126.8, 124.9, 122.2, 112.8, 75.5, 31.7, 29.4, 21.2. The resonance for the methyl bound to the cobalt was not observed when using CH_3I; however, the use of $^{13}CH_3I$ allowed for its observation. ^1H NMR (500 MHz, CD_3CN): δ ppm 1.76 (d, J_{CH} 141, $Co^{13}CH_3$). ^{13}C NMR (125 MHz, CD_3CN): δ ppm −4.7. ESI-TOF HRMS (CH_3CN) with PPG-425 *m*/*z*: $[M - I]^+$ calcd. for $C_{27}H_{32}N_4Co$, 471.1959; found, 471.1957; 0.42 ppm error.

Tol-BDI$^{(2\text{-}pp)2}$Co(C$_2$Si(CH$_3$)$_3$)I (7). Under inert atmosphere, compound **5** (0.010 g, 0.02 mmol) was dissolved in toluene (7 mL). While stirring, a solution of 1-iodo-2-(trimethylsilyl)acetylene (10 μL, 0.07 mmol) in toluene (3 mL) was added dropwise to the solution of compound **5**. The solution changed color immediately to red brown. The solution became green after stirring for an hour. It was filtered and dried under vacuum. The residue was washed heavily with hexanes to remove starting material and was dried under vacuum (0.013 g, 86%). UV (THF) λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 205 (3900), 301 (13000), 367 (3200), 425 (2800), 447 (2800). IR $°\upsilon_{max}$/cm^{-1}: 2046 (C≡C), 840 (Si-CH_3) (Nujol Mull). ^1H NMR (500 MHz, CD_2Cl_2): δ ppm 8.96 (2 H, br. d, pyr. CH); 7.97 (2 H, t, *J* 7.0, pyr. CH); 7.49 (2 H, t, *J* 6.0, pyr. CH); 7.45 (2 H, d, *J* 7.0, pyr. CH); 7.30 (2 H, s, CH); 7.28 (2 H, d, *J* 7.5, tolyl CH); 7.19 (2 H, d, *J* 7.5, tolyl CH); 2.35 (3 H, s, tolyl CH_3); 1.87 (12 H, s, CH_3), −0.23 (9 H, s, $Si(CH_3)_3$). ^{13}C NMR (125 MHz, CD_2Cl_2): δ ppm 173.0, 152.2, 152.0, 139.0, 138.8, 134.5, 129.8, 126.0, 124.2, 121.7, 118.8, 108.7, 89.6, 75.8, 33.4, 22.1, 1.2. ESI-TOF HRMS (CH_3CN) with PEG-400−600 *m*/*z*: $[M - I]^+$ calcd. for $C_{31}H_{38}N_4CoSi$, 553.2198; found, 553.2205; 1.27 ppm error.

Electrochemistry. Cyclic voltammetry experiments were performed inside a glovebox with a CHInstruments Model 600D potentiostat/galvanostat. A single-chamber cell was set up with a glassy carbon working electrode (3 mm diameter), a Pt wire as the auxiliary electrode, and a reference electrode consisting of a silver wire in 10 mM $AgNO_3$ solution (0.1 M $[^nBu_4N]PF_6$ in CH_3CN). The measurements were taken in a 0.1 M $[^nBu_4N]PF_6$ THF solution. The background cyclic voltammograms of the electrolyte solution were taken prior to the addition of the sample. All measurements were calibrated to an internal ferrocene standard.

X-ray Crystallography. A single crystal of **3** was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer for data collection at 173(2) K. The data collection was carried out using Mo Kα radiation (graphite monochromator). The data intensity was corrected for absorption and decay (SADABS). Final cell constants were obtained from least-squares fits of all measured reflections. The structure was solved using SHELXS-97 and refined using SHELXL-97.[22] A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Crystallographic data for complex **3** is summarized in Supporting Information, Table 1S and 2S.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

ORTEP diagram for zinc dimer, crystallographic information for zinc dimer and **3**, UV−vis of **1** and **3**, cyclic voltammograms of **3** and **4**, ^1H spectrum of **7**, ^{13}C assignments for **1**−**7**, and CIF file for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kris.mcneill@env.ethz.ch.

Present Address

†Department of Environmental Sciences, ETH Zurich, Switzerland.

Notes

The authors declare no competing financial interest.

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