

Catalytic hydrogen evolution from a covalently linked dicobaloxime

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A dicobaloxime in which monomeric Co(III) units are linked by an octamethylene bis(glyoxime) catalyzes the reduction of protons from *p*-toluenesulfonic acid as evidenced by electrocatalytic waves at -0.4 V vs. the saturated calomel electrode (SCE) in acetonitrile solutions. Rates of hydrogen evolution were determined from catalytic current peak heights ($k_{app} = 1100 \pm 70 \text{ M}^{-1} \text{ s}^{-1}$). Electrochemical experiments reveal no significant enhancement in the rate of H_2 evolution from that of a monomeric analogue: The experimental rate law is first order in catalyst and acid consistent with previous findings for similar mononuclear cobaloximes. Our work suggests that H_2 evolution likely occurs by protonation of reductively generated $\text{Co}^{\text{II}}\text{H}$ rather than homolysis of two $\text{Co}^{\text{III}}\text{H}$ units.

hydrogen evolving catalysts | solar fuel

Efficient catalytic reduction of protons to dihydrogen is a requirement for one half of a functional solar water splitting system (1, 2). Progress has been made recently in identifying catalysts capable of producing hydrogen from acidic media using either small molecule mimics of hydrogenase active sites or other synthetic systems (3–11).

Our work has focused on difluoroboryl-bridged Co^{II} -diglyoxime complexes that catalyze hydrogen evolution at low overpotentials (12–15). With these complexes, hydrogen evolution is initiated upon reduction to Co^{I} , which then reacts with a proton donor to form a $\text{Co}^{\text{II}}\text{H}$ -hydride ($\text{Co}^{\text{II}}\text{H}$). The $\text{Co}^{\text{II}}\text{H}$ intermediate can either undergo subsequent protonation to release H_2 and a Co^{III} species that is reduced to regenerate the catalyst (heterolytic route) or react with another $\text{Co}^{\text{II}}\text{H}$ to eliminate H_2 by a homolytic route. Alternatively, $\text{Co}^{\text{II}}\text{H}$ can be reduced further to form $\text{Co}^{\text{I}}\text{H}$, which can react via similar heterolytic or homolytic routes (16). Digital simulations of electrocatalytic waves performed by Hu et al. (17) indicated that the bimolecular homolytic $\text{Co}^{\text{II}}\text{H}$ route is the dominant pathway for hydrogen evolution. Our analysis of electron transfer rates in the catalytic cycle confirmed that the barriers to H_2 evolution associated with this pathway are more favorable than that for protonation of $\text{Co}^{\text{II}}\text{H}$ (17, 18). Recent work in our group examining the mechanism of hydrogen evolution from a photogenerated hydridocobaloxime suggests that hydrogen evolution via protonation of $\text{Co}^{\text{II}}\text{H}$ is favored under certain conditions ($\text{Co}^{\text{II}}\text{H}$ in low concentrations with reducing equivalents in excess) (16). Computational studies reported by Hammes-Schiffer (19, 20) and Muckerman (21) suggest that $\text{Co}^{\text{II}}\text{H}$ protonation is a very favorable reaction pathway and that relative fluxes through the homolytic $\text{Co}^{\text{II}}\text{H}$ and heterolytic $\text{Co}^{\text{II}}\text{H}$ channels depend on experimental conditions (relative concentrations of acid and catalyst).

In the low-barrier homolytic mechanism, two $\text{Co}^{\text{II}}\text{H}$ species must diffuse together in solution in order to react and release H_2 . It follows that immobilization onto an electrode surface would disfavor this pathway (7, 22, 23). It is of interest in this context that binuclear analogues of many catalysts that rely on bimetallic interactions show enhanced activity when compared to monomeric species, examples include certain Ru and Os diporphyrin H_2 evolving catalysts with cofacial orientation (24, 25). In one noteworthy case, Jones and coworkers (26, 27) showed that a “bisalen” analogue of Jacobsen’s Co-(salen) catalyst for hydro-

lytic kinetic resolution of racemic epoxides (a reaction that also shows a second-order dependence on catalyst concentration) maintained activity when linked to a solid support, whereas the immobilized monomer was essentially inactive (26–28). Because one of our goals is construction of a catalytic cobaloxime-modified electrode for water reduction, we have investigated the reactivity of a covalently-linked dicobalt complex.

Results and Discussion

An octamethylene-linked bis(glyoxime) ligand, tetradecane-2,3,12,13-tetraone tetraoxime (LH_4), was synthesized by a method similar to the procedure of Busch and coworkers (Scheme 1) (29). Reaction of the ligand with 2 eq. diphenylglyoxime (dpgH_2) and 2 eq. cobalt(II) dichloride in ethanol, followed by addition of 4 eq. pyridine under aerobic conditions, yielded a mixture of products including the desired binuclear $\text{Co}^{\text{III}}\text{Cl}$ complex **1**, mononuclear $\text{ClCo}^{\text{III}}(\text{dpgH})_2\text{py}$, and the singly metalated ligand, $\text{ClCo}^{\text{III}}(\text{dpgH})(\text{LH}_3)\text{py}$. Product purification difficulties prevented us from isolating the analogous binuclear species with a dimethylglyoxime (dmgH_2) ligand.

The reaction mixture was separated via column chromatography and **1** was isolated in 10% yield. The oxime-linking hydrogen atoms of **1** were replaced by bridging BF_2 groups, which enhance stability and shift reduction potentials to more positive values (17), by reflux with excess boron trifluoride in acetonitrile. Under these conditions, the axial pyridine is displaced by acetonitrile yielding the desired binuclear cobaloxime **2**.

As a mononuclear analogue of **2**, $\text{ClCo}^{\text{III}}(\text{dmgH})(\text{dpgH})\text{py}$ was synthesized according to Gupta (30–32), and reaction with boron trifluoride diethyl etherate afforded $\text{ClCo}^{\text{III}}(\text{dmgBF}_2)(\text{dpgBF}_2)(\text{CH}_3\text{CN})$ (**3**).

The cyclic voltammogram of **2** (see *SI Text*, Fig. S1) measured in 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ acetonitrile solution reveals an irreversible reduction at approximately 0.2 V vs. the saturated calomel electrode (SCE) attributed to one-electron Co^{III} reduction accompanied by the loss of an axial chloride and a reversible redox process at -0.37 V vs. SCE assigned to the $\text{Co}^{\text{II/I}}$ couple. Electrochemical measurements of **3** under similar conditions also show an irreversible $\text{Co}^{\text{III/II}}$ couple at approximately 0.2 V vs. SCE and the $\text{Co}^{\text{II/I}}$ couple at -0.37 V vs. SCE (see *SI Text*, Fig. S2). The virtually identical $\text{Co}^{\text{II/I}}$ reduction potentials for **2** and **3** are due to the similarity in electronic properties of the respective ligands. The methyl and alkyl substituents of dimethylglyoxime and tetradecane-2,3,12,13-tetraone tetraoxime have similar electron-donating properties, and the redox potentials of the mixed dioxime complexes **2** and **3** fall, unsurprisingly, between the corresponding $\text{Co}^{\text{II/I}}$ potentials of $\text{Co}(\text{dpgBF}_2)_2(\text{CH}_3\text{CN})_2$ and

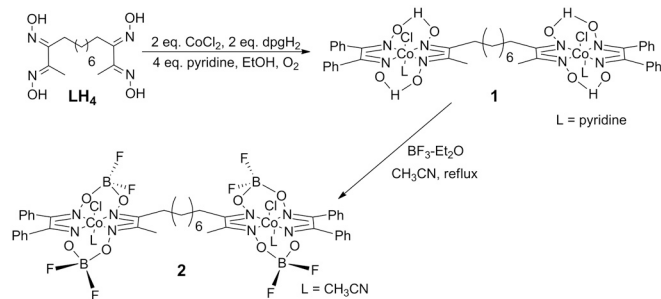
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Scheme 1.

$\text{Co}(\text{dmgBF}_2)_2(\text{CH}_3\text{CN})_2$, which appear at -0.28 and -0.55 V vs. SCE, respectively (17, 33). The $\text{Co}^{\text{II/I}}$ reductions of **2** and **3** are well-defined with peak separations similar to that of the reference Fc^+/Fc^0 couple (approximately 70 mV) even at low scan rates, and the peak current is linear with the square root of scan rate (see *SI Text*, Figs. S3 and S4) consistent with a reversible one-electron transfer process at each metal site with no electronic communication between the two cobalt centers (34, 35). The diffusion coefficients for **2** and **3** were estimated from the scan rate dependence of the $\text{Co}^{\text{II/I}}$ peak current in the absence of acid (see *SI Materials and Methods*). As expected, bulkier **2** has a substantially smaller diffusion coefficient ($2.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) (Fig. S3) than the mononuclear complex **3** ($8.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) (Fig. S4).

Upon addition of *p*-toluenesulfonic acid monohydrate ($\text{TsOH} \cdot \text{H}_2\text{O}$) to solutions of **2** or **3** in an inert atmosphere, catalytic waves were observed at a potential slightly negative of the formal reduction potential, $E^\circ(\text{Co}^{\text{II/I}})$ of the species indicating catalytic hydrogen evolution (Fig. 1). Based on the standard

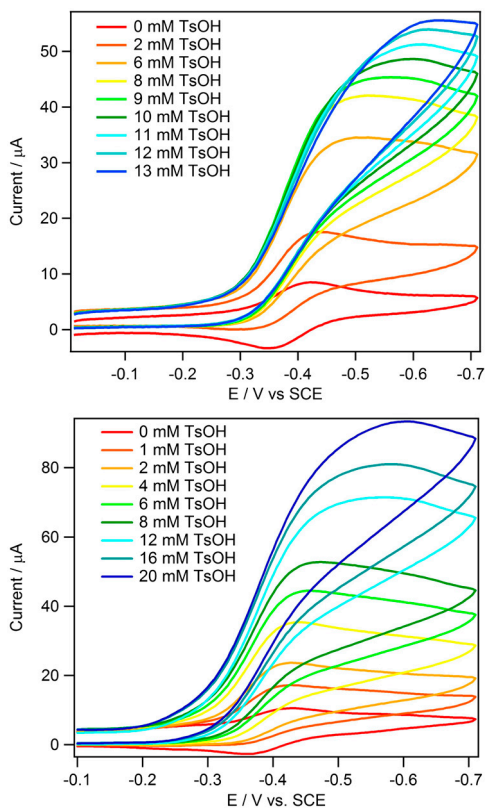


Fig. 1. Cyclic voltammograms of 0.372 mM **2** (Top) and 0.524 mM **3** (Bottom) in the absence (red curve) and presence (all other colors) of *p*-toluenesulfonic acid monohydrate ($\text{TsOH} \cdot \text{H}_2\text{O}$). Samples were measured at a scan rate of 100 mV s^{-1} in 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ CH_3CN solution.

potential for hydrogen evolution for $\text{TsOH} \cdot \text{H}_2\text{O}$ in CH_3CN ($E^\circ(\text{HA}/\text{H}_2) = -0.27$ V vs. SCE) (36), **2** and **3** operate at an overpotential of approximately 100 mV. Similar to the electrocatalytic behavior of $\text{Co}(\text{dpgBF}_2)_2(\text{CH}_3\text{CN})_2$ and $\text{Co}(\text{dmgBF}_2)_2(\text{CH}_3\text{CN})_2$, catalytic waves at low acid concentrations exhibit peak-like shapes indicative of a process wherein catalysis occurs rapidly enough that current is controlled by diffusion of acid to the electrode surface.

At higher acid-to-catalyst ratios, the catalytic waves approach a plateau. Under these conditions, acid concentration is not depleted in the reaction region and catalytic current plateau indicates that the rate of reduction of the catalytic species at the electrode is equivalent to the rate of its reoxidation by the acid. The plateau currents of **2** and **3** follow a first-order dependence on the concentration of acid (Fig. 2), but tend toward saturation at high catalyst concentrations, possibly indicating a change in rate-limiting step (Fig. 3). An analysis similar to that of Hu et al. (17) was used to calculate the overall rate constant for H_2 evolution (*vide infra*).

The overall rate constant for H_2 evolution was estimated from the height of the catalytic plateau current as a function of acid concentration for **2** and **3**. For a reaction that is first order in catalyst and acid, the current in the plateau region (i_c , in A) is related to the concentrations of catalyst per metal atom ($[\text{Co}]$, in mol cm^{-3}) and acid ($[\text{TsOH} \cdot \text{H}_2\text{O}]$ in M) by

$$i_c = nFA[\text{Co}](Dk[\text{TsOH} \cdot \text{H}_2\text{O}])^{1/2} \quad [1]$$

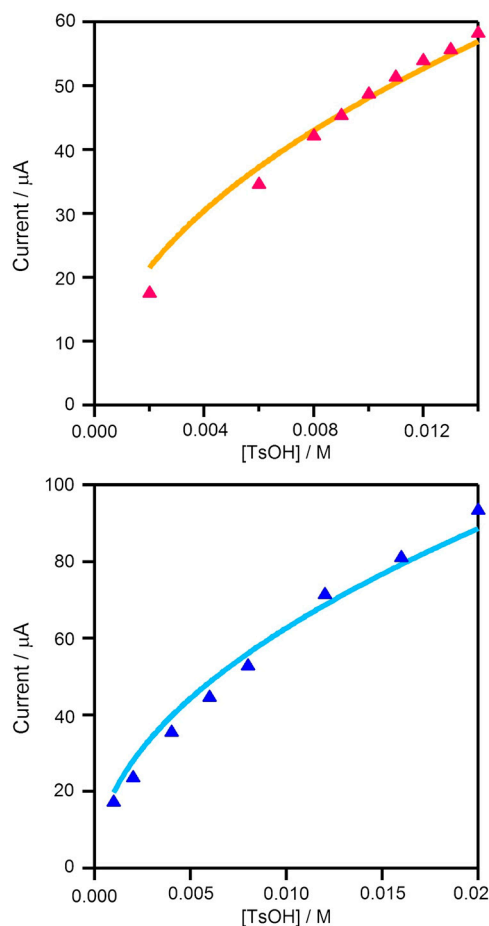


Fig. 2. Dependence of catalytic plateau current on acid concentration for 0.372 mM **2** (Top) and 0.524 mM **3** (Bottom). Data were fit to the function $i_c = b[\text{TsOH}]^{1/2}$ as suggested by Eq. 1. For **2**: $b = 4.8 \times 10^{-4} \text{ A M}^{-1/2}$, for **3**: $b = 6.3 \times 10^{-4} \text{ A M}^{-1/2}$. Samples were measured at a scan rate of 100 mV s^{-1} in 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ CH_3CN solution.

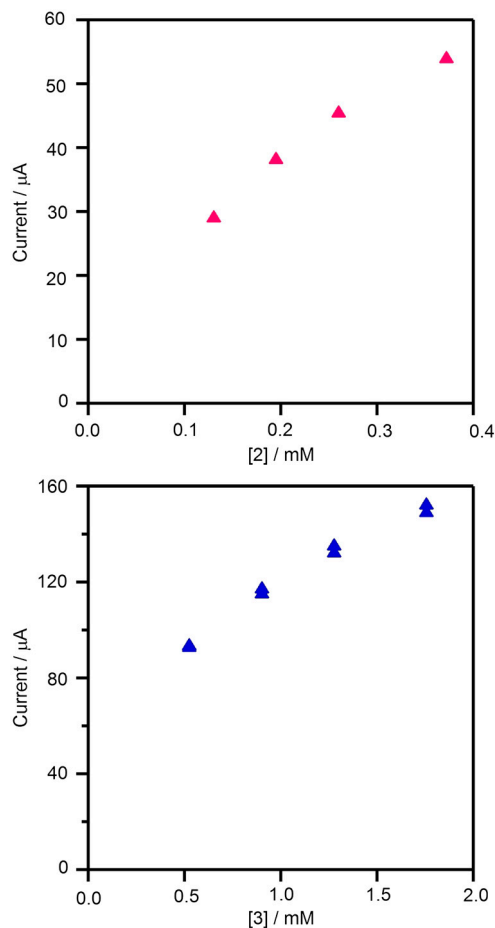


Fig. 3. Dependence of catalytic plateau current on catalyst concentration for **2** with 12 mM *p*-toluenesulfonic acid monoydrate (*Top*) and **3** with 20 mM *p*-toluenesulfonic acid monoydrate (*Bottom*). Samples were measured at a scan rate of 100 mV s⁻¹ in 0.1 M [nBu₄N][PF₆] CH₃CN solution.

where n is the number of electrons ($n = 2$), F is Faraday's constant (96,485 C mol⁻¹), A is the area of the electrode surface (cm²), D is the diffusion coefficient (cm² s⁻¹), and k is the reaction rate constant (M⁻¹ s⁻¹) (37, 38). There is no obvious increase in the apparent rate constant for **2**, 1,100 M⁻¹ s⁻¹, compared to that for **3**, 900 M⁻¹ s⁻¹, and both lie between the measured values for Co(dpgBF₂)₂(CH₃CN)₂ and Co(dmgBF₂)₂(CH₃CN)₂ (Table 1). Overall, the electrocatalysis of hydrogen evolution by **2** and **3** is closely analogous to that observed for Co(dmgBF₂)₂(CH₃CN)₂ (17).

If the homolytic reactivity of two Co^{III}H species were the rate-limiting step for hydrogen evolution, the rate law would have a second-order dependence on the concentrations of Co^I and acid as well as an inverse second-order dependence on the concentration of the conjugate base. Hence, an enhancement in rate would be expected for **2**, which is not what we observed. We conclude

that [Co^{III}H] homolysis is less favorable than protonation of reductively generated Co^{II}H under the conditions employed for hydrogen production catalyzed by dicobaloxime **2**.

Materials and Methods

General Procedures. All synthetic procedures and electrochemical measurements were performed under anaerobic and anhydrous conditions under an atmosphere of argon or nitrogen with the exception of the preparation of the ligand. Dry acetonitrile was prepared by passing commercially available dry solvent over an activated alumina column and was stored on 4 Å sieves under nitrogen. Tetrabutylammonium hexafluorophosphate was recrystallized from ethanol before use. All other reagents were purchased from chemical suppliers and used as received. ClCo(dmgH)(dpgH)py (dmgH₂ = dimethylglyoxime, dpgH₂ = diphenylglyoxime, and py = pyridine) was prepared by the method of Gupta et al. (32).

¹H and ¹⁹F NMR measurements were recorded on a Varian Mercury 300 MHz spectrometer and analyzed using MestReNova (version 6.1.1). ¹H NMR spectra were referenced to internal solvents and ¹⁹F spectra were referenced using an external C₆F₆ standard.

Electrospray high resolution mass spectrometry measurements were recorded on a Finnigan LCQ ion trap mass spectrometer. High resolution mass spectrometry (FAB) measurements were recorded using a JEOL JMS-600H high resolution mass spectrometer.

Electrochemical measurements were made with a Pine Instruments WaveNow potentiostat and the data were processed using Igor Pro 5.01 (WaveMetrics). Electrochemical analysis was carried out in a three-electrode cell consisting of a glassy carbon working electrode (surface area = 0.07 cm²), a platinum wire counter electrode, and a freshly prepared Ag/AgNO₃ (0.01 M) reference electrode filled with 0.1 M [nBu₄N][PF₆] acetonitrile solution. All potentials were referenced to Fc⁺/Fc⁰ as an internal standard and converted to SCE (E°(Fc⁺/Fc⁰) = 0.380 V vs. SCE).

Tetradecane-2,3,12,13-Tetraone 3,12-Dioxime Synthesis. Under an argon atmosphere, sodium metal (1.5 g, 65 mmol) was dissolved in 100 mL of absolute ethanol. Ethyl acetoacetate [8.28 mL (8.45 g), 65 mmol] was syringed into the stirring solution and allowed to react. After 10 min, the yellow solution was heated to reflux followed by the addition of 1,8-dibromooctane (8.02 g, 29.5 mmol) and exposure to atmosphere. The solution was allowed to react for 12 h until neutral followed by the removal of solvent via rotary evaporation to yield a viscous oil containing a white precipitate (NaBr). Enough water was added to the product to dissolve the precipitate, and the product was extracted with ether. The ether layers were combined and dried over anhydrous magnesium sulfate, and the ether was removed via rotary evaporation. To the resulting clear oil, an aqueous solution of potassium hydroxide (4.51 g, 80 mmol) was added, and hydrolysis was effected for 3 h at room temperature producing a cloudy, bright yellow solution. The mixture was cooled to 0 °C followed by the addition of sodium nitrite (4.26 g, 62 mmol) and then 10% sulfuric acid was added dropwise until an aliquot of the yellow solution turned the color of a potassium iodide:starch test dark blue for 15 min. Aqueous potassium hydroxide was added until the mixture became homogeneous, followed by extraction with ether to remove residual starting materials. The yellow mixture was cooled and 4 M sulfuric acid was added until the solution was acidified (pH ≈ 5). The resulting solid was extracted with ether, washed with water and a saturated sodium carbonate solution, and dried over MgSO₄. Ether was removed via rotary evaporation to yield a cream solid (2.4 g, 28%). ¹H NMR (300 MHz, (CD₃)₂CO): δ 10.4 (s, 2 H, oxime), δ 2.48 (t, 4 H, J = 7.3 Hz, α-CH₂), δ 2.26 (s, 6 H, CH₃), and δ 1.5–1.25 (m, 12 H, CH₂) ppm.

Tetradecane-2,3,12,13-Tetraone Tetraoxime (LH₄) Synthesis. Tetradecane-2,3,12,13-tetraone 3,12-dioxime (2.4 g, 8.4 mmol), hydroxylamine hydrochloride (2.3 g, 33.5 mmol), and sodium carbonate (2.45 g, 17.7 mmol) were

Table 1. Reduction potentials, apparent rate constants, and diffusion constants for cobaloxime complexes

Complex	E°(Co(III/II))	E°(Co(II/I))	k _{app} (M ⁻¹ s ⁻¹)	D (cm ² /s)
Co(dmgBF ₂) ₂ (CH ₃ CN) ₂ [*]	~0.2 [†]	-0.55	7,000	8.0 × 10 ^{-6‡}
Co(dpgBF ₂) ₂ (CH ₃ CN) ₂ [*]	~0.3 [†]	-0.28	200	1.4 × 10 ^{-6‡}
2	~0.2 [†]	-0.37	1,100 ± 70	2.0 × 10 ^{-6§}
3	~0.2 [†]	-0.37	900 ± 80	8.0 × 10 ^{-6§}

^{*}Reference (17).

[†]Irreversible couple.

[‡]Diffusion constant determined by simulation of cyclic voltammogram in absence of acid (17).

[§]Diffusion constant determined from scan rate dependence of the Co(II/I) peak current in the absence of acid.

suspended in ethanol (100 mL). Water was added slowly (20 mL) until all solids dissolved and the solution was refluxed for 14 h. The white precipitate that formed was collected, washed with water until chloride was no longer detected in the filtrate, and dried (1.65 g, 63%). ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 10.46 (s, 2 H, oxime_a), δ 10.41 (s, 2 H, oxime_b), δ 2.60 (t, 4 H, $J = 7.5$ Hz, $\alpha\text{-CH}_2$), δ 1.96 (s, 6 H, CH_3), and δ 1.41–1.30 (m, 12 H, CH_2) ppm. Electrospray MS (50:50 MeOH:H₂O), m/z calculated for $\text{C}_{14}\text{H}_{26}\text{N}_4\text{O}_4$: 314.2. Found: 315.0 (M), 296.9 (M–OH).

ClCo(dpgH)₂py-LH₂-ClCo(dpgH)₂py (LH₄ = Tetradecane-2,3,12,13-Tetraone Tetraoxime, py = Pyridine and dpgH₂ = Diphenylglyoxime) (1) Synthesis. Under an argon atmosphere, anhydrous pyridine (0.79 g, 10 mmol) was added by syringe to a refluxing solution of cobalt(II) chloride (0.45 g, 1.9 mmol), diphenylglyoxime (0.49 g, 2.0 mmol), and tetradecane-2,3,12,13-tetraone tetraoxime (0.3 g, 0.9 mmol) in degassed ethanol (50 mL). The heterogeneous mixture was cooled to room temperature, and air was bubbled through the solution for at least 6 h. The solvent was removed via rotary evaporation to yield a brown solid. This brown mixture was dissolved in a minimal amount of chloroform and loaded onto a silica gel column preeluted with chloroform. Three bands were observed with 1:9 ethyl acetate:chloroform. The first band, corresponding to the monomeric species ClCo(dpgH)₂py (as determined by ^1H NMR), eluted with 1:9 ethyl acetate:chloroform, and the second and third bands eluted together with 1:1 ethyl acetate:chloroform. The second band corresponds to the half-metalated ligand, ClCo(dpgH)(LH₃)py (as determined by ^1H NMR), and the third to the desired product. Solvent was evaporated from this mixture and the resulting solid was dissolved in minimal chloroform. The two products were separated on a silica gel column with 15:85 ethyl acetate:chloroform to yield the desired product as a brown crystalline solid (0.11 g, 10%). ^1H NMR (300 MHz, CD_3CN): δ 18.5 (s, 4 H, -OHO-), δ 8.29 [m, 4 H, py CH(2,6)], δ 7.86 [m, 4 H, py CH(3,5)], δ 7.39 [m, 2 H, py CH(4)], δ 7.4–7.1 (m, 20 H, Ph), δ 2.85 (m, 4 H, $\alpha\text{-CH}_2$), δ 2.39 (s, 6 H, CH_3), and δ 1.55–1.05 (m, 12 H, CH_2) ppm. HRMS (FAB+), m/z calculated for $\text{C}_{52}\text{H}_{56}\text{Cl}_2\text{Co}_2\text{N}_{10}\text{O}_8$: 1,136.23. Found: 1137.24 (M + H), 1022.3 (M – Cl – pyridine), 979.3 (M – C₆H₅ – pyridine – 2H) 907.3 (M – 2Cl – 2pyridine + H, M – 3 C₆H₅ – H), 783.2 (M – 4 C₆H₅ – Cl – CH₃), 704.2 (M – 4 C₆H₅ – CH₃ – Cl – pyridine), and 668.2 (M – 4 C₆H₅ – CH₃ – 2Cl – pyridine – H).

ClCo(dpgBF₂)(CH₃CN)-L(BF₂)₂-ClCo(dpgBF₂)(CH₃CN) (LH₄ = Tetradecane-2,3,12,13-Tetraone Tetraoxime and dpgH₂ = Diphenylglyoxime) (2) Synthesis. Under an atmosphere of argon, boron trifluoride diethyl etherate (0.153 g, 1.1 mmol) was syringed into a brown, refluxing solution of **1** (0.15 g, 0.13 mmol) in dry acetonitrile (25 mL). The solution turned red-brown and was allowed to reflux for 1 h, then the solvent was evaporated to yield a red-brown solid that was recrystallized from acetonitrile and diethyl ether (0.15 g, 91%). ^1H NMR (300 MHz, CD_3Cl): δ 7.4–7.2 (m, 20 H, Ph), δ 3.08 (m, 4 H, $\alpha\text{-CH}_2$), δ 2.67 (s, 6 H, CH_3), and δ 1.7–1.3 (m, 12 H, CH_2) ppm. ^{19}F NMR (300 MHz, CD_3CN): δ –151 (s) ppm.

ClCo(dmgBF₂)(dpgBF₂)(CH₃CN) (dmg = Dimethylglyoxime and dpg = Diphenylglyoxime) (3) Synthesis. Under an atmosphere of argon, ClCo(dmgH)(dpgH)₂py (0.24 g, 0.455 mmol) was dissolved in dry acetonitrile (15 mL). Boron trifluoride diethyl etherate (0.646 g, 4.55 mmol) was syringed into the brown solution. The resulting red solution was heated to reflux for 1 h then allowed to stir at room temperature for 3 h. The solvent was evaporated, and the resulting red oily solid was redissolved in acetonitrile (4 mL). Diethyl ether (15 mL) was added until a white solid crashed out. The solution was filtered, and the solvent was removed from the red-brown solution. The oily solid was dissolved in ethyl acetate (8 mL) and washed with water (2 mL) then dried over MgSO₄. The solvent was evaporated to yield a red-brown solid (0.079 g, 30%). ^1H NMR (300 MHz, CD_3CN): δ 7.5–7.3 (m, 10 H, Ph), δ 2.68 (s, 6 H, CH_3) ppm. ^{19}F NMR (300 MHz, CD_3CN): δ –151 (s) ppm. HRMS (FAB+), m/z calculated for $\text{C}_{20}\text{H}_{19}\text{BClCoF}_4\text{N}_5\text{O}_4$: 585.06. Found: 585.06 (M), 566.05 (M – F), 509.03 (M – C₆H₅), 490.03 (M – F – C₆H₅), 461.04 (M – C₆H₅ – BF₂ + H), and 442.01 (M – C₆H₅ – BF₂ – F + H).

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