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Ligand Noninnocence in Cobalt Dipyrrin–Bisphenols: Spectroscopic, Electrochemical, and Theoretical Insights Indicating an Emerging Analogy with Corroles

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Supporting Information

ABSTRACT: Three cobalt dipyrrin-bisphenol (DPPCo) complexes with different meso-aryl groups (pentafluorophenyl, phenyl, and mesityl) were synthesized and characterized based on their electrochemistry and spectroscopic properties in nonaqueous media. Each DPPCo undergoes multiple oxidations and reductions with the potentials, reversibility, and number of processes depending on the specific solution conditions, the specific macrocyclic substituents, and the type and number of axially coordinated ligands on the central cobalt ion. Theoretical calculations of the compounds with different coordination numbers are given in the current study in order to elucidate the cobalt-ion oxidation state and the



innocence or noninnocence of the macrocyclic ligand as a function of the changes in the solvent properties and degree of axial coordination. Electron paramagnetic resonance spectra of the compounds are obtained to experimentally assess the electron spin state. An X-ray structure of the six-coordinate complex is also presented. The investigated chemical properties of DPPCo compounds under different solution conditions are compared to those of cobalt corroles, where the macrocycle and metal ion also possess formal 3- and 3+ oxidation states in their air-stable forms.

INTRODUCTION

The free-base dipyrrin-bisphenols (DPPH₃; Chart 1), an emerging class of hybrid pyrrole-based ligands, are of interest

Chart 1. Structures of Free-Base Dipyrrin-Bisphenol and **Corrole Ligands**



for a variety of reasons,¹⁻⁹ perhaps most notably for the fact that several DPPM derivatives ($\hat{M} = Co_1^{1,2} Ni_1^{1} Cu_3^{3} \text{ or } Pt^4$) have been found to exist as metal-radical assemblies, i.e., as (DPP^{•2-})M^{II}, as opposed to (DPP³⁻)M^{III}. In terms of both their formally trianionic character and their propensity to yield noninnocent metal-radical assemblies, DPPH₃ ligands resem-

ble free-base corroles ($CorH_3$; Chart 1), a class of tetrapyrrole ligands whose chemistry has grown dramatically over the last two decades.^{10–13} Herein we report a detailed electrochemical, spectroscopic, and quantum-chemical study of DPPCo complexes that provides strong support for a DPP-corrole analogy, indeed a simple case of an isolobal analogy,¹⁴ which in time may prove to be a significant driver of new discoveries in the DPP field.

Until now, there have been two major studies of fourcoordinate (abbreviated as 4c) DPPCo derivatives.^{1,2} The authors of one paper,¹ Thomas and co-workers, formulated the neutral cobalt dipyrrin-bisphenols as (DPP^{•2-})Co^{II} and the corresponding singly oxidized complex as (DPP⁻)Co^{II} (both reasonable formulations, in our view), while in another paper,² the authors mainly focused on the catalytic reactivity of the DPPCo complexes. These authors, however, did not characterize the ionized states of the compounds after oxidation or

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reduction, nor did they explore the axial ligation chemistry of the complexes. As part of this work, we have synthesized three DPPCo derivatives, 1-3, as four-coordinate complexes in the solid state and investigated their electrochemical and spectroscopic properties in four different nonaqueous solvents, one of which is noncoordinating [dichloromethane (CH₂Cl₂)] and three of which are coordinating [benzonitrile (PhCN), dimethyl sulfoxide (DMSO), and pyridine]. The three compounds are depicted in Chart 2 and referred to hereafter

Chart 2. Structures of the Investigated DPPCo Complexes 1-3



as (F_5Ph)DPPCo (1), (Ph)DPPCo (2), and (Mes)DPPCo (3), where F_5Ph , Ph, and Mes refer to the pentafluorophenyl, phenyl, and mesityl groups at the *meso*-position of the DPP ligand, respectively. By examining three different DPPCo derivatives under different solution conditions, we are able to document the rich coordination chemistry of the DPPCo complexes, which have previously been examined only in one noncoordinating solvent, CH_2Cl_2 .¹

Like cobalt porphyrins^{15,16} and corroles,^{12,17,18} the DPPCo complexes examined are expected to undergo several reduction and oxidation processes involving the Co center, the DPP π system or a combination of both. Here we have used a comprehensive set of UV–visible spectroelectrochemical measurements to characterize the neutral, cationic, and anionic states of the complexes. The measurements underscore the importance of axial ligands, which greatly influence whether a given redox process occurs in a metal- or ligand-centered manner. Density functional theory (DFT) calculations with three different exchange-correlation functionals on 2 (Chart 2) were also carried out and provide additional details on the nature of the low-energy states of the complex for the various charge and coordination states.

Our results indicate extensive parallels between the lowenergy states of the DPPCo and CorCo complexes.^{19,20} These similarities may foreshadow important applications of the DPP derivatives in areas where metallocorroles already play a significant role, for examples, in catalytic group-transfer chemistry²¹ (such as epoxidations,^{22,23} aziridinations,^{24,25} and cyclopropanations²⁶) and chemical sensing of small molecules such as carbon monoxide (CO)^{27–29} or nitrite.³⁰

RESULTS AND DISCUSSION

Synthesis and Characterization. The DPP complexes 1–3 were synthesized via modification of a previously reported protocol.² The synthetic route is shown in Scheme 1. The acid-catalyzed condensation of 2-(2-methoxyphenyl)pyrrole and aldehyde in methylene chloride, followed by subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, afforded the dipyrrin precursor.³¹ Deprotection of the phenol moieties with boron tribromide (BBr₃) then quantitatively afforded the free-base dipyrrin–bisphenol precursors (DPPH₃).⁶ The target DPPCo complexes 1–3 were prepared by the reaction of DPPH₃ with Co(OAc)₂·4H₂O.

¹H NMR spectra (Figures S1–S3) and mass spectrometry (MS) measurements (Figures S4–S9) were carried out to confirm the structures reported in Chart 2. A perfect match was observed between the experimental high-resolution MS (HR-MS) spectra (Figures S4–S6) of compounds 1–3 and the simulated ionic patterns. Electrospray ionization (ESI)-MS spectra have also been registered in the presence of pyridine or NH₃·H₂O (Figures S7–S9). In both cases, the molecular peaks corresponding to the six-coordinate species (e.g., bis-py and bis-NH₃ species) are clearly observed, proving that the DPPCo complexes 1–3 can also lead to six-coordinate species in the presence of NH₃ or pyridine, as previously reported in the case of cobalt corrole complexes.

UV–Visible Spectroscopy. Before the redox reactions were carried out, the UV–visible spectrum of each neutral compound 1-3 was measured in one noncoordinating solvent (CH₂Cl₂) and three coordinating solvents (PhCN, DMSO, and pyridine). Examples of the obtained spectra are given in Figure 1 for a 10^{-3} M solution of compounds 1-3 in four solvents containing 0.1 M tetrabutylammonium perchlorate (TBAP), and a summary of the spectral data under these conditions is given in Table 1.

Each spectrum is characterized by an intense band at 311– 329 nm, two to three intense overlapping bands at 554–693 nm, and one less intense band at wavelengths between these two major absorption peaks. For example, all three investigated







Figure 1. UV-visible spectra of 1-3 (~ 10^{-3} M) in four solvents containing 0.1 M TBAP.

Table 1. UV–Visible Spectral Data for $1-3 (\sim 10^{-3} \text{ M})$ in CH₂Cl₂, PhCN, DMSO, or Pyridine Containing 0.1 M TBAP

			$\lambda_{\rm max}$ nm ($\varepsilon \times 10^{-4}$, M ⁻¹ cm ⁻¹)				
solvent	<i>meso-</i> substituent	compd	Soret region	visible region			
CH_2Cl_2	F ₅ Ph	1	316 (1.6)	596 (1.2), 624 (1.2)			
	Ph	2	320 (1.8)	574 (1.1), 603 (1.2)			
	Mes	3	311 (1.8)	572 (1.4), 602 (1.6)			
PhCN	F ₅ Ph	1	316 (1.5), 434 (0.5)	602 (1.1), 633 (1.4)			
	Ph	2	319 (1.4), 414 (0.5)	580 (0.9), 607 (1.3)			
	Mes	3	312 (1.5), 414 (0.5)	580 (1.2), 607 (1.7)			
DMSO	F ₅ Ph	1	315 (1.5), 471 (0.5)	645 (1.1), 670 (1.1)			
	Ph	2	321 (1.6), 445 (0.5)	587 (0.7), 627 (1.1)			
	Mes	3	313 (1.5), 443 (0.5)	587 (0.8), 627 (1.3)			
Ру	F ₅ Ph	1	329 (1.4), 473 (0.7)	649 (0.9), 693(1.2)			
	Ph	2	325 (1.5), 461 (0.7)	613 (0.8), 658 (1.2)			
	Mes	3	323 (1.4), 461 (0.6)	613 (0.7), 658 (1.2)			

compounds have bands at 414–473 nm in PhCN, DMSO, or pyridine, but this band is not seen in the noncoordinating CH_2Cl_2 solvent. In addition, the major visible bands of compounds 1–3 in the three coordinating solvents are redshifted compared to the corresponding bands in CH_2Cl_2 . The magnitude of the wavelength shift compared to that in CH_2Cl_2

is 4–9 nm in PhCN, 13–49 nm in DMSO, and 39–69 nm in pyridine. The first intense band is at similar wavelengths in CH₂Cl₂, PhCN, and DMSO (around 316, 320, and 312 nm for compounds 1–3, respectively), but this band is red-shifted by 5–13 nm in pyridine compared to the other solvents. Considering the known solvent-binding ability of the Co metal center in similar compounds, $1^{7,18,32}$ those red shifts and the appearance of the additional band might correspond to the axial coordination of a solvent molecule at the Co center in the DPPCo complex.

Moreover, as seen in Figure 1, the UV–visible spectra of compounds 2 and 3, which have *meso*-phenyl and mesityl groups, are almost identical with each other in the same solvent. These spectra differ from that of 1, which has a highly electron-withdrawing *meso*- F_s Ph group and is characterized by visible bands that are 21–43 nm red-shifted compared to compounds 2 and 3, with the exact value depending on the specific solvent.

In order to investigate the possible binding of the solvent molecules to DPPCo, the UV-visible spectral changes of 3 in CH2Cl2 were measured during titration with DMSO and pyridine. The binding constants were calculated as $\log K_1$ = 1.51 and 6.55, respectively, for the addition of a single solvent molecule using nonlinear curve fitting (Figures S10 and S11). A second set of spectral changes were not observed under the experimental conditions on the time scale of both titrations. As seen in Figures S10a and S11a, the major absorption bands of the DPP derivatives in the neat solvents (627 nm in DMSO and 658 nm in pyridine) are red-shifted compared to those of the last spectra during the titration (18 nm shift from 609 nm in the DMSO titration and 54 nm shift from 604 nm in the pyridine titration). This contrasts with that seen in neat PhCN (at 607 nm), where the major absorption band at the end of the titration is the same as that in neat PhCN. This indicates

that five-coordinate (abbreviated as 5c) species are the major derivatives of DPPCo compounds in PhCN and in the solution mixture at the end of both titration experiments, while sixcoordinate (abbreviated as 6c) species can exist in neat DMSO and neat pyridine.

Interestingly, when measuring the UV-visible spectrum of compounds 1-3 in pyridine, a slow transformation was observed to occur between two different forms of the DPPCo complexes. To study the kinetics of this transformation, the UV-visible spectral changes of compounds 1-3 in pyridine were recorded as a function of time and kinetic plots were constructed in order to determine the reaction order of the transformation. Examples of the spectral changes and corresponding plots are given in Figure 2.



Figure 2. (a) UV-visible spectral changes of **3** ($\sim 10^{-5}$ M) in pyridine, from *t* = 0 (assigned as 5c) to 90 min (assigned as 6c), after dissolution of the compound in solution. (b) Plot of the absorbance at 607 and 658 nm versus time (min). (c) Correlation between the natural logarithm of the concentration of the initial 5c compound **3** versus time (min).

As seen in Figure 2a, the initial spectrum of 3 when dissolved in pyridine has two major bands at 580 and 607 nm, but after 90 min, the most intense band has shifted from 607 to 658 nm while the less intense band has disappeared. The initial spectrum is assigned as a 5c form of DPPCo and the final spectrum as a 6c form. Well-defined isosbestic points can be seen at 506 and 624 nm in Figure 2, which indicate the absence of a spectrally detectable intermediate between the 5c and 6c forms on the time scale of the measurement. The changes in absorbance at 607 nm for state 5c and at 658 nm for state 6c are plotted versus time in Figure 2b, while Figure 2c shows a plot of ln [5c] versus time, which was calculated from the absorbance band at 607 nm. As shown in Figure 2c, there is a linear relationship between the natural logarithm of the calculated concentration of the 5c reactant versus time, with a slope of -0.07. The linearity of the slope indicates that this transformation process involves a first-order chemical reaction. Similar transformations also can be seen for compounds 1 and 2, and a summary of the spectral data under different solution conditions is given in Table 2, along with the calculated rate constants for conversion between two states of compounds 1-3.

Table 2. Spectral Data for Compounds $1-3 \ (\sim 10^{-5} \text{ M})$ in Pyridine and a $CH_2Cl_2/Pyridine$ Mixture and Slopes of the Kinetic Plots

			$\lambda_{ m ma}$	λ_{\max} nm		
compd	solution condition	CN ^a	Soret region	visible region	$slope = -k^b$	
(F ₅ Ph) DPPCo (1)	CH ₂ Cl ₂ /2000 equiv of Py	5c	316, 464	600, 627		
	neat Py (initial)	5c	316, 464	604, 632		
	neat Py (final)	6c	329, 473	649, 693	-0.18	
(Ph)DPPCo (2)	CH ₂ Cl ₂ /2000 equiv of Py	5c	320, 435	575, 604		
	neat Py (initial)	5c	320, 435	583, 608		
	neat Py (final)	6c	325, 461	613, 658	-0.24	
(Mes)DPPCo (3)	CH ₂ Cl ₂ /2000 equiv of Py	5c	312, 430	575, 604		
	neat Py (initial)	5c	312, 430	580, 607		
	neat Py (final)	6c	323,	613, 658	-0.07	

^{*a*}CN = coordination numbers of 5c and 6c. ^{*b*}Conversion between two forms only occurs in neat pyridine (Py).

As shown in Table 2 and Figure 2, the major visible bands of 1-3 are red-shifted by 50 to 61 nm during the transformation from 5c to 6c. Red shifts are also seen for the other bands. The reaction rate constant for compound 3, which has an electron-donating (mesityl) group on the meso position, is 0.07, which is much smaller than the 0.24 value for compound 2 (Ph) and the 0.18 value for compound 1 (F₅Ph). The electron-donating group decreases the rate of the transformation processes.

Considering the possible equilibrium between $(DPP^{\bullet 2-})Co^{II}$ and $(DPP^{3-})Co^{III}$, the slow conversion from 5c to 6c can be proposed to involve a change of the electronic configurations, as shown in Scheme 2. The 5c form can be assigned to the complex $(DPP^{\bullet 2-})Co^{II}(Py)$, while the 6c form corresponds to the complex $(DPP^{3-})Co^{III}(Py)_2$. All of the data suggest the reactions in Scheme 2.

Scheme 2. Transformations among the 4c-6c Forms of Compounds 1-3



To confirm the axial ligation of two pyridine molecules on the DPPCo complexes, TGA (Figure S12) and ¹H NMR spectroscopy (Figure S1) were measured for the chemically synthesized bis(pyridine)-ligated $(F_5Ph)DPPCo(Py)_2$ [1(Py)₂]. According to TGA, the measured weight loss (Δm) of the bis-ligated compounds was 21.0% compared to the calculated value 22.3% for two pyridine molecules. More evidence is given in the following DFT Calculations section of the manuscript.

Notably, 6c species can also partially exist in neat DMSO as mentioned above. However, the complete transformation from 5c (with one axial DMSO molecule) to 6c (with two axial DMSO molecules) species was not observed either in neat DMSO or during the titration of DMSO in CH_2Cl_2 . A transformation from 5c to 6c was also not observed on the experimental time scale during titration with pyridine.

Electrochemistry. The first step in characterizing the electrochemistry of compounds 1-3 was to obtain cyclic voltammograms in the coordinating and noncoordinating solvents and then to relate changes in the observed redox potentials to changes in the spectroscopic properties of the neutral, electroreduced, and electrooxidized forms of the compounds. As described on the following pages, two major reductions and two major oxidations can be observed for DPP derivatives, as schematically shown in Scheme 3.





The DPPCo complex with *tert*-butyl groups was reported earlier to undergo two reversible oxidations and one reversible reduction in CH_2Cl_2 containing 0.1 M TBAP, all three of which were assigned to electron transfers at the DPP ligand.¹ However, the currently examined DPPCo complexes 1-3show three or four oxidations and several reductions, with the exact number depending on the specific electrochemical solvent. An example of the cyclic voltammograms for compound 1 in the four utilized solvents is given in Figure 3, and a summary of measured potentials for the major redox reactions of these three complexes is given in Table 3.

Table 3. Half-Wave or Peak Potentials ($E_{1/2}$ or $E_{p'}$ V vs SCE) of DPPCo Complexes 1–3 in Four Solvents Containing 0.1 M TBAP

			potential (V vs SCE)					
solvent	<i>meso-</i> substituent	compd	Ox 2	Ox 1	Red 1	Red 2		
CH_2Cl_2	F ₅ Ph	1	1.10	0.65	0.13	-1.40 ^{<i>a</i>}		
	Ph	2	1.00	0.57	0.08	-1.46 ^{<i>a</i>}		
	Mes	3	1.04	0.56	0.07	-1.52^{a}		
PhCN	F ₅ Ph	1	1.03	0.56 ^b	0.05	-1.37		
	Ph	2	1.01	0.51 ^b	0.04	-1.51		
	Mes	3	1.02	0.51 ^b	0.02	-1.55		
DMSO	F ₅ Ph	1	0.92	0.46	-0.10	-1.30		
	Ph	2	0.85	0.44	-0.13	-1.43		
	Mes	3	0.83	0.41	-0.13	-1.46		
Ру	F ₅ Ph	1		0.54	-1.02 ^{<i>a</i>}	-1.40		
	Ph	2		0.48	-1.12 ^a	-1.52		
	Mes	3		0.49	-1.16^{a}	-1.55		
$a_{\mathbf{D}}$, $b_{\mathbf{D}}$, $b_{$								

"Peak potentials (E_{pc}) for irreversible redox processes. "Potentials were taken from multiple scans at a scan rate of 500 mV s⁻¹.

Solvent Effect on the Redox Potentials. As shown in Figure 3, the first reduction of compound 1, labeled as Red 1, shifts from $E_{1/2} = 0.13$ V in CH₂Cl₂ to 0.05 V in PhCN and then to -0.10 V in DMSO. Similar positive shifts of the potentials are also seen for two major oxidations of compound 1 as well as for the related redox reactions of compounds 2 and 3. As seen in Figure 3, the cyclic voltammogram of compound 1 in



Figure 3. Cyclic voltammograms of compound 1 for the redox reactions in (a) CH₂Cl₂, (b) PhCN, (c) DMSO, and (d) pyridine containing 0.1 M TBAP.



Figure 4. Cyclic voltammograms of compound 1 (~10⁻³ M) under different solution conditions: (a) at room temperature (r.t.), (b) at -60 °C in CH₂Cl₂, (c) at r.t. in PhCN containing 100 equiv of added CH₃I; (d) in PhCN without CH₃I.



Figure 5. UV-visible spectral changes of compound 1 during the (a) first oxidation, (b) first reduction, and (c) second reduction in four different solvents.

pyridine is quite different from the cyclic voltammograms in the other three solvents; namely, there is one reversible oxidation at $E_{1/2} = 0.54$ V, one irreversible reduction at $E_p = -1.02$ V, and one reversible reduction at $E_{1/2} = -1.40$ V. The earlier described spectroscopic data of compounds 1-3 in pyridine suggest the binding of two Py axial ligands and a proposed electron configuration of $(DPP^{3-})Co^{III}(Py)_2$. This is consistent with the electrochemical behavior of the three compounds in this solvent.

Effect of Meso-Substituents. In all four solvents, compound 1 is easier to reduce and harder to oxidize than compounds 2 and 3 because of the highly electron-withdrawing F_5Ph- group on the *meso*-position of the dipyrrin ligand. For example, in CH₂Cl₂, $E_{1/2}$ for the first reduction is shifted positively by 50 mV compared with the same electrode reactions of compound 2, while an 80 mV positive shift is seen for the first oxidation of compound 1. The substituent effect is even larger for the second reduction in all four solvents. The difference in $E_{1/2}$

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Scheme 4. Proposed Mechanism for Redox Reactions of the DPPCo Complexes 1-3 in Different Solvents (S = PhCN or DMSO for 5c Complexes and Pyridine for 6c Complexes)



Figure 6. Spin-density plots for selected states of 4c 2: (a) state C; (b) state D; (c) state F; (d) state I; (e) state J. The states, indicated in capital letters, are defined in Table 4.

between the second reductions of compounds 1 and 2 ranges from 60 to 130 mV depending on the solvent.

"Extra" Reductions in CH_2Cl_2 . Unlike in other solvents, the second reduction of compounds 1-3 in CH_2Cl_2 is irreversible, and an additional irreversible reduction is observed at more negative potential. A similar irreversibility is also seen upon reduction of cobalt(II) porphyrins^{15,33} and electrogenerated cobalt(II) corroles³⁴ in CH_2Cl_2 , and this was explained by a chemical reaction between the low-oxidation-state electron-reduction product and the CH_2Cl_2 solvent.

Cyclic voltammograms illustrating the reduction of compound 1 under different solution conditions are given in Figure 4. As seen in the figure, an extra reduction is not observed at -60 °C in CH₂Cl₂ compared to that seen at room temperature, and it is also not observed in PhCN where the doubly reduced dipyrrin complexes are stable. The cyclic voltammogram at -60 °C in CH₂Cl₂ is quite similar to that in PhCN, providing evidence for a reaction of the doubly reduced species with the CH₂Cl₂ solvent.

Spectroelectrochemical Studies. The spectral changes that occurred during each redox reaction were monitored by UV–visible spectroelectrochemistry in the different solvents.

Examples of the time-resolved spectral changes for compound 1 are given in Figure 5, and the proposed mechanism for all major redox reactions of this compound is given in Scheme 4.

Although spectra of the neutral compounds vary with a change of the solvent, the spectra of the one-electron-reduced species (Figure 5b) are almost independent of the solvent and are characterized by bands at 626–639 and 362–374 nm. The similarity in the UV–visible spectra after the first electron addition of each compound under different solution conditions indicates that the electrophilic properties (binding properties) of the four investigated solvents have little to no effect on the one-electron-reduced species. According to the previous study on a related cobalt dipyrrin complex,¹ the reactant in the first reduction can be assigned as (DPP^{•2–})Co^{II}, which would then be reduced to (DPP^{3–})Co^{II}, as shown in Scheme 4.

The spectra of the two-electron-reduced species (Figure 5c) are also identical with each other in PhCN, DMSO, and pyridine but not in CH_2Cl_2 , where, as indicated by the cyclic voltammetry curves, a chemical reaction occurs between the doubly reduced DPP derivatives and the solvent. During the second reduction, the intense visible bands of the one-electron-reduced species at 626–639 nm decrease in intensity while

Table 4. Selected DFT Results for the 4c-6c States of 2

					all-electron occupations $(\alpha//\beta)$				$E_{\rm rel}~({\rm eV})$	с			
state	CN ^a	point group	q	S	a ₁	a ₂	b ₁	b ₂		description ^b	OLYP	B3LYP	B3LYP- D3
Α	4c	$C_{2\nu}$	0	0	54//54	8//8	39//39	17//17	LS Co(II	I)	0.136	0.707	0.704
В			0	0	54//53	8//9	39//39	17//17	LS $d_{z^{2^1}}$ C	o(II), L(•2–); antiferro	0.180	0.033	0.033
<u>C</u>			0	1	54//53	9//8	39//39	17//17	LS $d_{z^{2^1}}$ C	o(II), L(•2–); ferro	0.043	0.000	0.000
D			0	1	54//54	9//8	39//39	17//16	IS Co(III), L(3–)	0.000	0.100	0.098
Е			0	2	54//53	9//8	40//39	17//16	IS Co(II)	, L(●2–); ferro	0.662	0.361	0.363
<u>F</u>			1	$^{1}/_{2}$	54//54	8//8	39//39	17//16	IS Co(III), L(•2–); antiferro	6.031	6.345	6.342
G			1	$^{1}/_{2}$	54//53	8//8	39//39	17//17	LS $d_{z^{2^1}}$ C	o(II), doubly oxidized L(-	-) 6.027	6.198	6.160
Н			1	$^{3}/_{2}$	54//53	9//8	39//39	17//16	IS Co(III), L(●2−); ferro	6.462	6.643	6.638
I			-1	$^{1}/_{2}$	54//54	9//8	39//39	17//17	LS d_{π}^{-1} C	o(II), L(3–)	-2.489	-2.673	-2.653
J			-1	$^{1}/_{2}$	54//53	9//9	39//39	17//17	LS $d_{z^{2^1}}$ C	o(II), L(3–)	-2.322	-2.714	-2.712
K			-1	$^{1}/_{2}$	54//54	9//9	39//39	17//16	LS $d_{\pi'}^{1}$ C	o(II), L(3–)	-1.947	-2.392	-2.391
						all-electro	n occupation $\alpha//\beta)$	IS				$E_{\rm rel}~({\rm eV})^c$	
state	CN	<i>a</i> point gro	oup	9	S	a′	a′′	_	des	cription ^b	OLYP	B3LYP	B3LYP-D3
L	5c	C_s		0	0	83//83	56//56	LS	Co(III)		0.442	0.441	0.343
<u>M</u>				0	0	84//83	55//56	LS o	$d_{z^{2^{1}}}$ Co(II), 1	L(●2−); antiferro	0.208	0.054	0.076
N				0	1	84//83	56//55	LS o	$d_{z^{2^{1}}}$ Co(II), 1	L(•2–); ferro	0.000	0.000	0.000
0				0	2	84//82	57//55	HS	Co(II), L(•	2–); ferro	0.482	0.188	0.217
Р				1	¹ / ₂	83//83	56//55	LS	Co(III), L(•	2–)	6.026	6.232	6.149
Q				1	¹ / ₂	84//83	55//55	LS	$d_{z^{2^{1}}}$ Co(II),	doubly oxidized L(-)	5.692	5.897	5.904
R				1	³ / ₂	84//82	56//55	IS C	Co(III), L(•2	2–); ferro	5.984	6.229	6.227
<u>s</u>				-1	¹ / ₂	84//83	56//56	LS o	$d_{z^{2^{1}}}$ Co(II), 1	L(3-)	-2.070	-2.486	-2.489
						all-ele	ectron occupa	ations (α /	$ \beta)$			$E_{\rm rel}~({\rm eV})^c$	
state	CN ^a	point grou	р	9	s	a ₁	a ₂	b_1	b ₂	description ^b	OLYP	B3LYP	B3LYP-D3
Т	6c	$C_{2\nu}$	0		0 71	l//71	12//12	42//42	35//35	LS Co(III), L(3–)	0.069	0.000	0.000
<u>U</u>			0		1 72	2//71	12//11	42//42	35//35	IS Co(III), L(3–)	0.000	0.306	0.387
V			1		¹ / ₂ 71	l//71	12//11	42//42	35//35	LS Co(III), L(•2–)	5.426	5.518	5.528
W			-	-1	$1/_{2}$ 72	2//71	12//12	42//42	35//35	LS $d_{z^{2^{1}}}$ Co(II), L(3–)		-1.957	-1.728
^a CN		dination nu	mbor	bforro	- forror	nagnotica	lly coupled	antiforr	o – ontifor	romagnatically coupled	^c The oper	mi zoro los	al for each

 a CN = coordination number. b ferro = ferromagnetically coupled; antiferro = antiferromagnetically coupled. c The energy zero level for each molecule and each functional is indicated in boldface.

new bands grow in at 511–515 nm. The decrease in the intensity of the major absorption bands indicates a loss of conjugation in the DPP ligand upon the second electron addition. At the same time, new bands at 803–809 nm are seen in the spectra when measured in PhCN, DMSO, or pyridine, and those bands can be considered to be diagnostic criteria for a redox reaction involving the ligand.

DFT Calculations. Spin-unrestricted DFT calculations were undertaken for 2 to aid in the assignment of the neutral, cationic, and anionic states, as well as to evaluate the issue of ligand noninnocence and potential similarities with cobalt corroles. Three different, well-tested methods were employed: OLYP, B3LYP, and B3LYP-D3. Appropriate symmetry constraints were used for the 4c form $(C_{2\nu})$, monopyridine-ligated 5c form (C_s) , and bis(pyridine)-ligated 6c form $(C_{2\nu})$ so as to allow for an examination of different electronic configurations with different numbers of electrons in each irreducible representation. The results allow for a number of insights, which are shown in Figures 6–8, Table 4, and Figures S13–S15.

The calculations clearly indicate S = 1 states as the key contenders for the ground state of the neutral 4c complex, viz., a low-spin Co(II) state with a ferromagnetically coupled DPP^{•2-} radical (state C, Figure 6a) and an intermediate-spin Co(III) state with an antiferromagnetically coupled DPP^{•2-} radical (state D, Figure 6b). The reader may note that low-spin

Co(II) states are easily discernible in the spin-density plots by a d_{z^2} -shaped blob on the Co center. Note also the characteristic bond distance alternations on the ligand in states with DPP^{•2-} radicals (Figure S13).

For the 4c cationic complex, the calculations suggest two possible candidates for the ground state. The first is a low-spin Co(II) state with a doubly oxidized DPP ligand (state G). The second is an intermediate-spin Co(III) state with a $d_{xy}^2 d_z^{2^2} d_{xz}^{-1} d_{yz}^{-1}$ configuration with some spin delocalization to the ligand (state F, Figure 6c). The reader may verify that a dimple in the z direction at the Co atom in the spin-density plot is consistent with the absence of an unpaired electron in the Co d_{x^2} orbital.

For the neutral 5c complex, the calculations indicate a ferromagnetically coupled, $S = 1 \text{ Co}^{II}\text{DPP}^{\bullet 2-}$ state with a high degree of certitude (based on the mutual consistency of the three DFT methods), with the corresponding antiferromagnetically coupled state a couple of tenths of an electronvolt higher (state N, Figure 7a). An analogous electronic configuration, albeit with antiferromagnetic coupling, has also been considered plausible for 5c cobalt corrole monopyridine adducts (state M, Figure 7b). The preference for ferromagnetic coupling in the present compound is thought to be a reflection of the relative orthogonality of the Co 3d orbitals and the ligand highest occupied molecular orbital.



Figure 7. Spin-density plots for selected states of 5c 2(Py): (a) state N; (b) state M; (c) state Q; (d) state S. The states, indicated in capital letters, are defined in Table 4.

For the cationic Sc complex, the different calculational methods also proved mutually consistent, predicting a Co(II) center in association with a doubly oxidized ligand, a possibility that has also been entertained for Sc cobalt corrole cations (albeit without explicit computational support; state Q, Figure 7c).

For the 6c complex, the calculations unsurprisingly predict a low-spin Co(III) center for the neutral state (state U, Figure 8a) and a low-spin Co(III) center associated with a ligand radical for the cation (state U, Figure 8b). Thus, binding of a second pyridine results in a major electronic reorganization from a $(DPP^{\bullet 2-})Co^{II}$ state to a low-spin Co(III) state, which may explain the slow spectral change observed upon dissolution of the 4c complex in pyridine.

For the anionic 4c complex, the calculations indicate two potential contenders for the ground state, both of which may be described as low-spin Co(II) (states I and J, Figure 6d,e). In one of the them, the unpaired electron resides in the $Co(d_z^2)$ orbital (state J, Figure 6e), whereas in the other, the unpaired electron occupies an a_2 -symmetry Co d_{π} orbital (state J, Figure 6e). For the 5c and 6c anions (states S and W), in contrast, the calculations exhibit a much clearer preference for a low-spin Co(II) state with the unpaired electron in the Co d_z^2 orbital. B3LYP-D3 calculations do, however, indicate significantly elongated Co $-N_{py}$ bond distances of 2.228 Å for the 5c anion (Figure S14d for B3LYP) and 2.323 Å for the 6c anion, compared with a distance of 1.989 Å for the 6c, low-spin Co(III) neutral state (with the corresponding B3LYP distances for the three states being 2.309, 2.460, and 2.010 Å, respectively). There is thus a good chance that pyridines are essentially detached in the anionic 6c state and a 4c or 5c lowspin $d_{z^{2^{1}}}$ Co(II) state is the dominant anionic form under experimental conditions, in agreement with our conclusions based on UV-visible spectroelectrochemical measurements.



Figure 8. Spin-density plots for selected states of 6c $2(Py)_2$: (a) state U; (b) state V. The states, indicated in captal letters, are defined in Table 4.

In view of the difficulty of describing long-range chargetransfer excitations in metallocorroles with time-dependent DFT calculations, we have refrained from undertaking such calculations in the present study. However, the presence of a significant quantity of spin density at the *meso*-C in several of the DPPCo states examined is qualitatively consistent with our finding that meso substituents indeed have a significant influence on the UV-visible spectra.

EPR Spectroscopy. In order to directly assess the electronic spin state, EPR experiments were run at 293 and 100 K in dichloromethane (Figure S16) for 3. At 293 K, compound 3 gave an almost silent spectrum (Figure S16a), indicating that the cobalt complex is either in a diamagnetic Co(III) form or that it has an S = 0 spin state due to a strong antiferromagnetic coupling between Co(II) and the anion radical in the cobalt(II) corrole(2•–) formalism. After cooling to 100 K (Figure S16b), a radical-like pattern centered at g = 2.012 appears with a large broadening and a multiline morphology due to the hyperfine coupling of the single electron with the Co center. At least 7 of the 8 theoretical expected lines ($I_{\rm Co} = 7/_2$) are observed. Then it seems clear that the cobalt(II) corrole(2•–) formalism is favored with an electron delocalization over both the ligand and metal center.

After the addition of pyridine, a spectral shape typical of a radical complex centered at g = 2.004 is obtained (Figure S16c), with a small broadening of the single line (fwhh ≈ 7 G). This central line is probably assigned to a radical impurity because of overoxidation of 3 in the presence of strong axial donors like pyridine, with the six-coordinate $3(Py)_2$ being more oxidizable than the four-coordinate 3. In addition, this line is flanked by one broad signal with a low intensity at the left side of the radical signal, which is assigned to the excited triplet state, with the second transition band being overlapped by the more intense radical line. The low intensity of the triplet state agrees with a large singlet-triplet gap, inducing a weak

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thermally accessible excited triplet state. This result is confirmed by recording the EPR spectrum at 100 K that shows a very low intensity of the lines assigned to the triplet state (Figure S16d).

Crystal Structure Analysis. Single clear dark-violet needle-shaped crystals of 1 were recrystallized from a mixture of chloroform and heptane with 1 drop of aqueous NH_4OH by slow evaporation. An X-ray diffraction experiment was carried out to determine the crystallographic structure (Figure 9). As



Figure 9. ORTEP view of compound 1. Thermal ellipsoids are depicted at 50% probability. The water molecule and disordered chloroform are omitted for clarity.

seen in the figure, 1 was crystallized in a C2/c centrosymmetric group with a water molecule and a disordered chloroform molecule (Figure S16). The six-coordinate DPPCo complex was found to coordinate with both the N and O atoms of the DPP unit and two axial ammonia ligands, which are in the apical position. Detailed information for the crystallographic data collection and refinement are given in the Supporting Information.

As shown in Figure 9, the octahedral geometry is similar to that reported in a previous publication for bis(ammonia)coordinated cobalt corrole complexes,³² and this gives additional evidence that DPP is an analogue to the corrole ligand. In order to make this comparison in detail, the geometric parameters of both structures, $(F_5Ph)DPPCo-(NH_3)_2$ in this work and $(o_io-Cl_2Ph)_3CorCo(NH_3)_2$ in the previous publication,³² are given in Table 5. Despite structural differences between the two ligands (dipyrrinbisphenol and corrole), the distances and bond angles in the two cobalt complexes are of the same order of magnitude as those seen in the table. DPP is shown to be an excellent analogue of corrole, and it is thus expected to form some similar metal complexes.

EXPERIMENTAL SECTION

Chemicals. Dichloromethane (CH₂Cl₂, 99.8%) from EMD Chemicals Inc. was used for electrochemistry without further purification. Benzonitrile (PhCN) was purchased from Sigma-Aldrich Chemical Co. and distilled over P_2O_5 under vacuum prior to use. Dimethyl sulfoxide (DMSO), pyridine (Py; HPLC), and tetra-*n*butylammonium perchlorate (TBAP), used as the supporting electrolyte, were purchased from Sigma-Aldrich Chemical Co.

Instrumentation. Cyclic voltammetry was carried out with an EG&G model 173 potentiostat/galvanostat. A homemade threeelectrode electrochemistry cell was used, consisting of a glassy carbon working electrode (diameter = 0.3 mm), a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity, which contained the solvent/supporting electrolyte mixture. All potentials measured by cyclic voltammetry were referenced to the SCE.

Spectroscopically monitored titrations with acid or base were carried out in a 1.0 cm glass cell. Thin-layer UV–visible spectroelectrochemical experiments were carried out with the Honeycomb spectrochemical cell by Pine Research Instrumentation. Potentials were applied and monitored with an EG&G PAR model 173 potentiostat. Time-resolved UV–visible spectra were recorded with a Hewlett-Packard model 8453 diode-array spectrophotometer. High-purity N₂ from Trigas was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroscopic experiment.

CDCl₃ and C₆D₆ were used as solvents for the ¹H NMR spectra, which were recorded on a Bruker AVANCE III spectrometer (500 MHz). The measurements were made at the PACSMUB-WPCM technological platform, which relies on the Institut de Chimie Moléculaire de l'Université de Bourgogne and Welience TM, a Burgundy University private subsidiary. Chemical shifts were expressed in parts per million. NH₃·H₂O was added to enhance the resolution of the spectra. MS spectra were recorded on a Bruker Ultraflex Extreme MALDI Tandem TOF mass spectrometer using DCTB as the matrix or on a LTQ Orbitrap XL (Thermo) instrument in the ESI mode (for the HR-MS spectra). Low-resolution MS (LRMS) spectra were recorded on a Thermo Scientific MSQ Plus single quadrupole mass spectrometer equipped with an ESI source. All LRMS spectra were recorded in the positive mode (ESI⁺) using the following parameters: full scan, 250-1250 amu; data type, centroid; needle voltage, 3.0 kV; detector voltage, 1100 V; probe temperature, 350 °C; cone voltage, 10 or 75 V; scan time, 1 s. Sample preparation: cobalt dipyrrins were prepared in tetrahydrofuran (THF) and were directly analyzed by ESI-MS (direct infusion mode with a syringe pump; cone voltage, 75 V). To assess the chelation of NH₃ and pyridine molecules, 2 μ L of an aqueous NH₃ solution (25% in water, v/v) or pyridine was added to a dilute sample prior to injection through a direct infusion mode (cone voltage, 10 V). Thermogravimetric analyses (TGA) were recorded using a Netzsch STA 409 PC thermal analyzer. The samples were heated from 298 to 1273 K with a heating rate of 10 K min⁻¹ under a flow of nitrogen (30 mL min⁻¹) and oxygen (10 mL min⁻¹). The measurements were made at the PACSMUB-WPCM technological platform. Continuous-wave EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer. The instrument was equipped with a 4122 SHQE/0405 X-band resonant cavity operating at 9.43 GHz, a X-band high-power dual gun-oscillator bridge, and a quartz cryostat. The experiments were run at 293 or 100 K with a stream of nitrogen. The temperature was regulated with an ER 4131VT accessory. All apparatuses as well as the data acquisition were controlled using Xepr software. The magnetic field was swept from 250 to 360 mT through 2048 points. Spectra were recorded at 6 mW power, 100 kHz frequency modulation, 0.5 mT modulation amplitude, 10 ms time constant, and 40 ms conversion time. Samples were dissolved in dichloromethane and spectra recorded in both liquid (293 K) and frozen (100 K) solutions, before and after the addition of 1 drop of pyridine.

Synthesis of Compound 1. Compound 1 was prepared in 94% yield (44.0 mg, 80.0 µmol). Starting from free-base pentafluorophenyl-dipyrrin-bisphenol (42.1 mg, 85.2 µmol),⁶ triethanolamine $(34.4 \,\mu\text{L})$ and a solution of Co(OAc)₂·4H₂O (21.2 mg, 85.2 μ mol) in 5 mL of a mixture of methanol/chloroform (1:3) were mixed with 26 mL of a mixture of methanol/chloroform (1:3) at room temperature overnight. Then water was added (30 mL), and the product was extracted with chloroform, dried over MgSO4, and evaporated to dryness under vacuum. ¹H NMR (300 MHz, CDCl₃ + 1 drop of $NH_3 \cdot H_2O$: δ 7.53 (d, 2H, J = 7.0 Hz), 7.39 (d, 2H, J = 8.0 Hz), 7.13 (m, 4H), 6.81 (d, 2H, J = 4.0 Hz), 6.64 (t, 2H, J = 7.0 Hz), 1.75 (brs, 6H, 2NH₃). MS (MALDI-TOF, DCTB). Calcd for $C_{27}H_{12}CoF_5N_2O_2$: m/z550.01. Found: m/z 549.68 ([M]^{•+}). HR-MS (ESI). Calcd for $C_{27}H_{12}CoF_5N_2O_2$: m/z 550.0145. Found: m/z550.0129 ([M]^{•+}). MS (ESI, THF + 1 drop of NH₃·H₂O). Calcd for $C_{27}H_{13}CoF_5N_2O_2$: m/z 551.0 Found: m/z 551.1 ([M + H]⁺). Calcd

Table 5. Comparison of Selected Geometric Distances (Å) and Angles (deg) of Compound 1 and the Previous Cobalt Corrole $Complex^{32}$

Structures	æ				
Bond distances (Å)	bis-NH ₃ DPPCo		bis-NH ₃ cobalt corrole		
Co – Npyrrole	1.913(3)	1.909(3)	1.893(6)	1.908(6)	
Co – O / Npyrrole	1.919(2)	1.905(2)	1.868(6)	1.881(6)	
Average Co – Npyrrole / O	1.91	2(6)	1.888(17)		
Co – Nammonia	1.963(3)	1.938(3)	1.964(6)	1.974(6)	
Average Co – Nammonia	1.95	1(18)	1.969(7)		
Bond angles (°)	bis-NH ₃	DPPCo	bis-NH ₃ cobalt corrole		
O / Npyrrole – Co – Npyrrole	83.10(10)	91.82(11)	95.1(3)	91.5(2)	
Npyrrole / O – Co – Npyrrole / O	93.35(12)	83.10(10)	81.5(2)	91.9(3)	
Average O / Npyrrole – Co – Npyrrole	88	(6)	90(6)		
O / Neurrala Ca Nammania	89.17(11)	90.85(11)	89.3(3)	89.2(3)	
0 / Npyrrole – Co – Nammonia	88.54(11)	91.98(11)	92.9(2)	87.8(3)	
	88.79(13)	90.69(13)	90.2(2)	91.3(3)	
Npyrrole – Co – Nammonia	91.20(12)	88.84(12)	87.1(3)	92.4(3)	
Average Npyrrole / O – Co – Nammonia	90	(1)	90(2)		

for $C_{27}H_{13}CoF_5N_2O_2 \cdot 2NH_3$: m/z 585.2 ($[M + H + 2NH_3]^+$). Found: m/z 585.1. MS (ESI, THF + 1 drop of pyridine). Calcd for $C_{27}H_{12}CoF_5N_2O_2 \cdot 1py$: m/z 629.1. Found: m/z 629.1 ($[M + py]^{\bullet+}$). Calcd for $C_{27}H_{12}CoF_5N_2O_2 \cdot 2py$: m/z 708.1. Found: m/z 708.0 ($[M + 2py]^{\bullet+}$).

Synthesis of the $1(Py)_2$ Complex. Compound 1 (10 mg) was dissolved in dichloromethane (10 mL), 2 drops of pyridine were added, and the solution was evaporated. ¹H NMR (300 MHz, C₆D₆): δ 8.43 (brs, 4H, py), 7.96 (brs, 2H), 7.63 (brs, 2H), 7.31 (brs, 4H), 6.86 (brs, 2H), 6.71 (brs, 2H), 6.34 (brs, 2H, py), 6.08 (brs, 4H, py). Pyridine content determined by TGA (see Figure S11): Δm (calcd for 2 py ligated) = 21.0% (calcd 22.3%). $T_{onset} = 55$ °C. $T_{end} = 240$ °C.

Synthesis of Compound 2. Compound 2 was prepared in 86% yield (39.1 mg, 84.9 μmol), as described for 1, starting from free-base phenyl-dipyrrin-bisphenol (40.0 mg, 98.9 μmol)⁸ and Co(OAc)₂· 4H₂O (14.4 mg, 98.9 μmol). ¹H NMR (300 MHz, CDCl₃ + 1 drop of NH₃·H₂O): δ 7.50 (m, 7H), 7.39 (d, 2H, *J* = 7.5 Hz), 7.10 (m, 4H), 6.93 (m, 2H), 6.63 (m, 2H), 1.72 (brs, 6H, 2NH₃). MS (MALDI-TOF, DCTB). Calcd for C₂₇H₁₇CoN₂O₂: *m/z* 460.06. Found: *m/z* 459.69 ([M]^{•+}). HR-MS (ESI). Calcd for C₂₇H₁₇CoN₂O₂: *m/z* 460.0617. *m/z* 460.0609 ([M]^{•+}). MS (ESI, THF + 1 drop of NH₃· H₂O). Calcd for C₂₇H₁₇CoN₂O₂: *m/z* 460.1. Found: *m/z* 460.1 ([M]^{•+}). Calcd for C₂₇H₁₈CoN₂O₂·2NH₃: *m/z* 495.1. Found: *m/z* 495.0 ([M + H + 2NH₃]⁺). MS (ESI, THF + 1 drop of pyridine). Calcd for C₂₇H₁₇CoN₂O₂·1py: *m/z* 539.1. Found: *m/z* 539.0 ([M + py]^{•+}). Calcd for C₂₇H₁₇CoN₂O₂·2py: *m/z* 618.2. Found: *m/z* 618.2 ([M + 2Py]^{•+}).

Synthesis of Compound 3. Compound 3 was prepared in 94% yield (27.1 mg, 53.9 μ mol), as described for 1, starting from free-base

mesityl–dipyrin–bisphenol⁸ (25.5 mg, 57.7 μmol) and Co(OAc)₂. 4H₂O (24.6 mg, 57.7 μmol). ¹H NMR (300 MHz, CDCl₃ + 1 drop of NH₃:H₂O): δ 7.52 (d, 2H, *J* = 7.5 Hz), 7.35 (d, 2H, *J* = 8 Hz), 7.09 (m, 2H), 7.01 (d, 2H, *J* = 4.5 Hz), 6.96 (s, 2H), 6.73 (d, 2H, *J* = 4.5 Hz), 6.60 (t, 2H, *J* = 7.5 Hz), 2.37 (s, 3H), 2.07 (s, 6H), 1.78 (brs, 6H, 2NH₃). MS (MALDI-TOF, DCTB). Calcd for C₃₀H₂₃CoN₂O₂: *m/z* 502.11. Found: *m/z* 501.79 ([M]^{•+}). HR-MS (ESI). Calcd for C₃₀H₂₃CoN₂O₂: *m/z* 503.1. Found: *m/z* 503.0 ([M + H]⁺). Calcd for C₃₀H₂₄CoN₂O₂: *m/z* 503.1. Found: 536.9 ([M + 2NH₃]^{•+}). MS (ESI, THF + 1 drop of NH₃·H₂O). Calcd for C₃₀H₂₄CoN₂O₂: *m/z* 503.1. Found: 536.9 ([M + 2NH₃]^{•+}). MS (ESI, THF + 1 drop of Pyridine). Calcd for C₃₀H₂₄CoN₂O₂·1py: *m/z* 582.2. *m/z* 582.3 ([M + H + py]^{•+}). Calcd for C₃₀H₂₄CoN₂O₂·2py: *m/z* 661.2. Found: *m/z* 661.3 ([M + H + 2py]⁺).

Single-Crystal X-ray Diffraction. All experimental data are detailed in the Supporting Information. CCDC 1880078 for compound 1, containing the supplementary crystallographic data for this paper, can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ cif.

CONCLUSION

In summary, three cobalt dipyrrin-bisphenol complexes with different *meso*-aryl substituents have been synthesized, and their spectroscopic and electrochemical properties characterized in both noncoordinating and coordinating solvents. The various charge, spin, and axial ligation states have also been examined by means of DFT calculations. The experimental and

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computational studies, together, afford detailed insight into the question of ligand noninnocence in the DPPCo complexes.

The facile reduction potentials ($E_{1/2} \sim 0.0$ V vs SCE) of the complexes in noncoordinating (CH2Cl2) and weakly coordinating (PhCN and DMSO) solvents are suggestive of a $(DPP^{\bullet 2^{-}})Co^{II}$ formulation for the neutral complexes, a conclusion that is consistent with the DFT calculations. This contrasts with that seen in pyridine, where the complexes are reduced at significantly more negative potentials ($E_{1/2} \sim -1.0$ V), thus indicating a 6c low-spin Co(III) center that is quite resistant to reduction. The fact that the one-electron-reduced state exhibits similar optical spectra in all four solvents appears to indicate a common 4c or 5c (DPP³⁻)Co^{II} state throughout, again consistent with the DFT calculations. Our spectral studies do not allow a definitive assignment of the cationic states. DFT calculations, however, indicate a (DPP⁻)Co^{II} state with a doubly oxidized DPP ligand for the 5c complexes and a $(DPP^{\bullet 2-})Co^{III}$ state with a low-spin Co(III) center for the 6c complexes. A ferromagnetically coupled, S = 1 (DPP^{•2-})Co^{II} description for the 5c monopyridine complex also provides an explanation for the observed slow binding of a second pyridine ligand, leading to the 6c low-spin cobalt(III) bis(pyridine) complex.

The $(DPP^{\bullet 2^{-}})Co^{II}$, $(DPP^{3^{-}})Co^{II}$, and $(DPP^{-})Co^{II}$ formulations of the neutral, anionic, and cationic states of the 5c complexes exactly parallel the $(Cor^{\bullet 2^{-}})Co^{II}$, $(Cor^{3^{-}})Co^{II}$, and $(Cor^{-})Co^{II}$ formulations proposed for the analogous charged states of 5c CorCo monopyridine adducts. The ground-state $(DPP^{\bullet 2^{-}})Co^{II}$ description is analogous to that proposed for CorCo, CorCo(PPh₃), and CorCo(CO), as well as to that for the MnCl, FeCl, FeNO, Fe₂(μ -O), Cu, and Pt corrole derivatives.¹¹ These extensive parallels between DPP and corrole potentially presage a bright future for transition-metal DPP complexes in areas such as catalytic transformations and small molecule sensing, where metallocorroles are already playing a significant role.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03006.

¹H NMR and MS spectra for 1-3, UV-visible spectral changes with curve fitting for titrations, TGA for $1Py_2$, Mulliken spin populations and bond distances for selected states, EPR spectra for 3, X-ray data for 1, and optimized Cartesian coordinates (PDF)

Accession Codes

CCDC 1880078 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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