

## Synthesis, Structures, and Properties of a Series of Four-, Five-, and Six-Coordinate Cobalt(III) Triazacorrole Complexes: The First Examples of Transition Metal Corrolazines

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The syntheses of the first transition metal corrolazine complexes, in which the meso carbon atoms of a corrole framework have been replaced by N atoms, are reported. Metalation of the corrolazine [(TBP)<sub>8</sub>CzH<sub>3</sub>] (TBP = 4-*tert*-butylphenyl) (**1**) with Co(acac)<sub>2</sub> gives [(TBP)<sub>8</sub>CzCo<sup>III</sup>] (**2**) in good yield. Addition of PPh<sub>3</sub> to **2** in pyridine results in the formation of [(TBP)<sub>8</sub>CzCo<sup>III</sup>(PPh<sub>3</sub>)] (**3**), which was characterized by X-ray crystallography. Likewise, addition of an excess of pyridine to **2** in CH<sub>2</sub>Cl<sub>2</sub> followed by slow diffusion of MeOH gives [(TBP)<sub>8</sub>CzCo<sup>III</sup>(py)<sub>2</sub>] (**4**) as a crystalline solid, which was also characterized by X-ray crystallography. The crystal structures of **3** and **4** reveal that the corrolazine cavity is significantly smaller (~0.1 Å) than their regular corrole analogues. Characterization of **2–4** by UV–vis spectroscopy reveals some interesting features in the absorption spectra of these compounds, including a dramatic red-shift of the Soret band. In addition, binding of pyridine to **2** was evaluated quantitatively by UV–vis titration, revealing a formation constant of  $\beta_2 = 9.0 \times 10^7 \text{ M}^{-2}$ , which is larger than any of the regular Co<sup>III</sup> corrole analogues.

Transition metal corrole complexes have been under intense investigation recently. Corroles are tetrapyrrolic macrocycles that have the same C<sub>α</sub>–C<sub>α</sub> linkage as the cobalt-containing nonaromatic corrin ring of vitamin B-12, yet they maintain the 18 πe<sup>-</sup> aromatic core found in porphyrins and phthalocyanines.<sup>1–3</sup> Considerable efforts have been expended on the syntheses and characterization of cobalt corroles in particular because of their biological relevance, and because

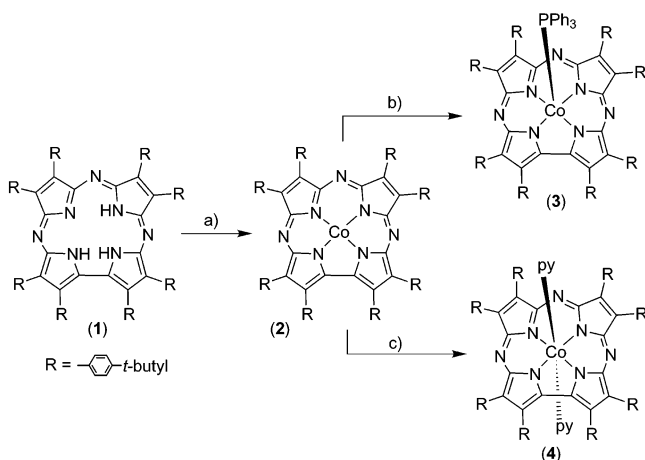
of their relative ease of synthesis<sup>4–7</sup> compared to other metallocorroles. We recently reported the synthesis of the first triazacorrole (“corrolazine”, Cz) compound, [(TBP)<sub>8</sub>CzP<sup>V</sup>(OH)(OH)] (TBP = 4-*tert*-butylphenyl), in which the meso carbon atoms of a conventional corrole ring have been replaced with nitrogen atoms. This phosphorus-containing corrolazine was converted to the free base [(TBP)<sub>8</sub>CzH<sub>3</sub>] (**1**) by a novel reductive demetalation strategy.<sup>8</sup> Although it was predicted that metal-free **1** would allow entry into a new family of transition metal corrole-like complexes, to date no such complexes have been reported in the literature. Herein, we describe the synthesis and spectroscopic characterization of [(TBP)<sub>8</sub>CzCo<sup>III</sup>] (**2**), [(TBP)<sub>8</sub>CzCo<sup>III</sup>(PPh<sub>3</sub>)] (**3**), and [(TBP)<sub>8</sub>CzCo<sup>III</sup>(py)<sub>2</sub>] (**4**), starting from the versatile precursor **1**. Compounds **2–4** are the first examples of transition metal corrolazine complexes.

The neutral, four-coordinate Co<sup>III</sup> complex [(TBP)<sub>8</sub>CzCo<sup>III</sup>] was prepared by heating **1** with an excess of Co<sup>II</sup>(acac)<sub>2</sub> in pyridine (Scheme 1). Removal of the pyridine under vacuum and purification by column chromatography (silica gel, hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1/1 (v/v)) led to the isolation of the product in 86% yield. Many of the other conventional cobalt(III) corroles (i.e., corroles with carbon atoms at the meso positions) have been isolated and fully characterized only in the presence of strong axial ligands (e.g., PPh<sub>3</sub>, pyridine), affording the five- or six-coordinate complexes.<sup>4–7</sup> In addition, a recent study of (tpfc)Co<sup>III</sup> (tpfc = 5,10,15-tris-(pentafluorophenyl)corrole) showed that in the absence of axial ligands this complex was not stable and spontaneously oxidized to give a dimerized product with a direct C<sub>β</sub>–C<sub>β</sub>

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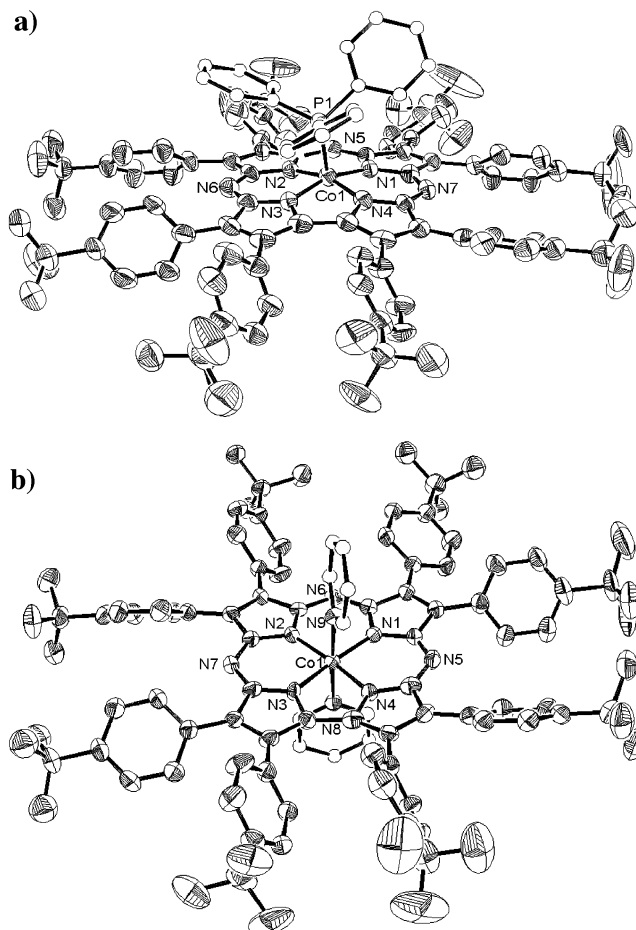
Scheme 1 <sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) Co(acac)<sub>2</sub>, pyridine, 115 °C, 1 h; (b) 5 equiv of PPh<sub>3</sub>, pyridine, 115 °C, 1 h; (c) 2% pyridine in CH<sub>2</sub>Cl<sub>2</sub>.

bond.<sup>6</sup> The stability of **2** may be due to a combination of the oxidatively resistant meso nitrogen atoms and phenyl substituents that block all eight of the  $\beta$  positions in the Cz ring.

The <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub> exhibits sharp peaks that are shifted over a wide range (+27 to –23 ppm). The well-resolved pattern is easily interpreted according to the *C*<sub>2v</sub> symmetry of **2**, with 4 peaks appearing between 1.6 and 5.1 ppm for the *tert*-butyl protons and 8 resonances between 26.4 and –21.9 ppm for the unique sets of phenyl ring protons. The large chemical shifts indicate that the cobalt(III) ion is paramagnetic. Recent DFT calculations have shown that the ground spin state for square planar Co<sup>III</sup>–corrole should be *S* = 1.<sup>9</sup> The magnitude and alternating sign of the isotropic shifts for the phenyl ring protons suggest that they are dominated by contact contributions arising from significant  $\pi$ -delocalization of the unpaired spin density on the metal.<sup>10,11</sup> This delocalization brings to light the possible “noninnocent” nature of the corrolazine ring in **2**, which is of some interest because of the recent debate concerning the noninnocence of conventional corrole rings in various high-valent complexes.<sup>12–14</sup> However, the <sup>1</sup>H NMR spectrum of **2** does not by itself point to complete charge transfer; that is, it does not prove that a (Cz<sup>2-</sup>)Co<sup>II</sup> description is more appropriate than a (Cz<sup>3-</sup>)Co<sup>III</sup> assignment. Further spectroscopic analysis is needed to provide a definitive description.

A solution of 5 equiv of PPh<sub>3</sub> and **2** in pyridine was refluxed for 1 h, and then, the pyridine was removed under vacuum to give [(TBP)<sub>8</sub>CzCo<sup>III</sup>(PPh<sub>3</sub>)] (**3**) as a crude green-brown solid (Scheme 1). Purification by chromatography (silica gel, hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1/1 (v/v)) gave **3** in 83% yield,



**Figure 1.** (a) ORTEP diagram of [(TBP)<sub>8</sub>CzCo<sup>III</sup>(PPh<sub>3</sub>)] (**3**). Selected bond lengths [Å]: Co1–N1 1.838(3), Co1–N2 1.852(3), Co1–N3 1.826(3), Co1–N4 1.834(3), Co1–P1 2.175(1). (b) ORTEP diagram of [(TBP)<sub>8</sub>CzCo<sup>III</sup>–(py)<sub>2</sub>] (**4**). Selected bond lengths [Å]: Co1–N1 1.838(3), Co1–N2 1.850(4), Co1–N3 1.830(3), Co1–N4 1.834(3), Co1–N8 1.970(4), Co1–N9 2.000(4). Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms have been omitted for clarity.

and <sup>1</sup>H NMR spectroscopy revealed a diamagnetic spectrum, indicating that the Co<sup>III</sup> ion has been converted from a high-spin to a low-spin configuration. The molecular structure of **3** is shown in Figure 1a.<sup>15</sup> Despite the steric crowding that might be expected from the 8 peripheral phenyl substituents, the 23-atom corrole core exhibits substantial planarity, with the maximum displacement from the average plane being –0.19(1) Å for C(11) ( $\alpha$ -C atom adjacent to N(3)) and +0.22(1) Å for N(4), and the mean displacement from the plane being 0.10(1) Å. The cavity size of **3**, as measured by the distances between trans pyrrole nitrogen atoms (N<sub>p</sub>–N<sub>p</sub> = 3.638 and 3.612 Å), is significantly smaller than the cavity size of conventional Co<sup>III</sup>–PPh<sub>3</sub> corroles (*d*(N<sub>p</sub>–N<sub>p</sub>(av)) = 3.72 Å).<sup>7,16–18</sup> There is also a larger displacement of the Co<sup>III</sup> ion out of the plane of the corrolazine, compare Co–Cz–(plane) = 0.44(1) Å versus Co–corrole(plane) = 0.29–0.39

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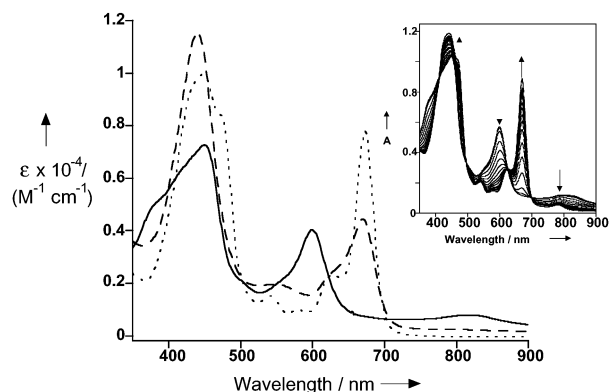
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**Figure 2.** UV-vis spectra of **2** (—) and **3** (---) in  $\text{CH}_2\text{Cl}_2$  and **4** (···) in  $\text{CH}_2\text{Cl}_2$ /pyridine. Inset: changes in the UV-vis spectrum upon titration of pyridine (0;  $6.2 \times 10^{-6}$ – $1.5 \times 10^{-3}$  M) into a solution of **2** ( $1.43 \times 10^{-4}$  M) in  $\text{CH}_2\text{Cl}_2$ .

$\text{\AA}$ .<sup>7,16,17</sup> The average Co–N<sub>p</sub> distance for **3** (1.838(9)  $\text{\AA}$ ) is also somewhat smaller than that found in the conventional analogues (1.87–1.92  $\text{\AA}$ ).<sup>7,16–18</sup>

Addition of an excess of pyridine to **2** in  $\text{CH}_2\text{Cl}_2$  ( $\text{CH}_2\text{Cl}_2$ /pyridine, 49/1, (v/v)), followed by the slow diffusion of MeOH, gave [(TBP)<sub>8</sub>CzCo<sup>III</sup>(py)<sub>2</sub>] (**4**) (Scheme 1) as a crystalline solid. The crystal structure of **4** is shown in Figure 1b.<sup>15</sup> As found in **3**, the cavity size (N<sub>p</sub>–N<sub>p</sub> = 3.663, 3.678  $\text{\AA}$ ) and the mean Co–N<sub>p</sub> distance (1.838(9)  $\text{\AA}$ ) of **4** are smaller than those of recently reported analogues, for example, (Me<sub>4</sub>Ph<sub>4</sub>Cor)Co(py)<sub>2</sub> ((Co–N<sub>p</sub>)<sub>av</sub> = 1.894(5)  $\text{\AA}$ , N<sub>p</sub>–N<sub>p</sub> = 3.772, 3.790  $\text{\AA}$ )<sup>5</sup> and [(tpfc)Co(py)<sub>2</sub>] (Co–N<sub>p</sub> = 1.873–1.900  $\text{\AA}$ , N<sub>p</sub>–N<sub>p</sub> = 3.766, 3.774  $\text{\AA}$ ).<sup>6</sup> As opposed to **3**, the cobalt ion in **4** is seated directly in the plane of the ring (0.084  $\text{\AA}$  out-of-plane displacement) in order to accommodate the second axial ligand. Curiously, the  $\sim 90^\circ$  dihedral angle between the planes of the two axial pyridines is quite different from the dihedral angle of  $\sim 0^\circ$  for [(tpfc)Co(py)<sub>2</sub>],<sup>6</sup> yet it matches that for (Me<sub>4</sub>Ph<sub>4</sub>Cor)Co(py)<sub>2</sub>.<sup>5</sup>

A comparison of the UV-vis spectra of **2**–**4** (Figure 2) is enlightening. Although all three complexes exhibit spectra that are similar to that of tetraazaporphyrins, with intense Soret and Q-bands, the Soret bands for **2**–**4** (450, 441, and 445 nm, respectively) as well as for the phosphorus (447 nm) and metal-free (460 nm) Czs reported previously<sup>8</sup> are dramatically red-shifted compared to those of tetraazaporphyrins ( $\lambda_{\text{max}}(\text{Soret}) < 400$  nm).<sup>19,20</sup> The Soret transition in a tetraazaporphyrin can be ascribed to a porphyrin-like four-orbital electronic transition  $a_{2u}(\pi, \text{second HOMO}) \rightarrow e_g(\pi^*, \text{LUMO})$  (in  $D_{4h}$  symmetry) in which the second HOMO has large orbital coefficients on the meso positions. We suggest that the Cz red-shift is caused by a destabilization of this second HOMO upon removal of an electronegative meso N atom during ring contraction.<sup>20</sup> Additionally, there is a large red-shift in the Q-band (600 to 670 nm) upon binding of PPh<sub>3</sub> or pyridine to **2**. We used this change in the UV-vis

spectrum upon addition of pyridine to obtain the formation constant for **4** via a spectrophotometric titration.

The inset of Figure 2 shows that upon successive addition of pyridine in  $\text{CH}_2\text{Cl}_2$ , the initial spectrum of **2** is converted to a spectrum that matches that of **4**. Clean isobestic behavior is present throughout the titration, indicating that the monopyridine intermediate, which would be a third absorbing species, is not observed and the overall equilibrium is best described by the direct formation of **4** from **2**. Quantitative evaluation of the formation constant ( $\beta_2$ ) for this reaction was obtained by a Hill plot,<sup>21</sup> which exhibits a slope of  $\sim 2$  throughout the pyridine concentration range, confirming the presumed 2:1 binding stoichiometry. The value of  $\beta_2 = 9.0 \times 10^7 \text{ M}^{-2}$  was determined from this analysis and indicates very strong overall binding of the two axial pyridines, although the individual 1:1 binding events (represented by the binding constants  $K_1$  and  $K_2$ ) cannot be distinguished. It is clear, however, that  $K_2$  must be significantly larger than  $K_1$  to account for the lack of any observable monopyridine intermediate. Iron(III) porphyrates<sup>21</sup> show similar behavior in the binding of pyridine with  $K_2 \gg K_1$ , and only  $\beta_2$  can be extrapolated. In contrast, a series of Co<sup>III</sup> corroles with both alkyl and aryl  $\beta$ -carbon substituents exhibits successive 1:1 binding of pyridine with  $K_1 = 6.0 \times 10^3$ – $3.0 \times 10^5 \text{ M}^{-1}$  and  $K_2 = 38$ – $240 \text{ M}^{-1}$ , giving formation constants ( $\beta_2 = K_1K_2$ ) of  $6 \times 10^5$ – $5 \times 10^7 \text{ M}^{-2}$ .<sup>5</sup> The formation constant found for **4** is larger than those found for any of the latter Co<sup>III</sup> corrole complexes.

The smaller cavity size found for corrolazine **4** is expected to result in stronger  $\sigma$  donation from the pyrrole N atoms and, hence, a decreased Lewis acidity at the metal center compared to that of conventional corroles. This hypothesis is clearly disproven by the  $\beta_2$  value for **4**, which implies that the Co<sup>III</sup> ion in **4** is a better Lewis acid than in most other corroles. A simple explanation comes from a comparison of the electronegativity of N versus C at the meso positions; the more electronegative meso N atoms of a corrolazine ring result in a Co<sup>III</sup> ion that is significantly more Lewis acidic.<sup>22</sup> These findings suggest that further novel reactivity involving cobalt and other transition metal corrolazines can be expected.

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**Supporting Information Available:** Synthetic details for **2**–**4** and X-ray crystallographic data for **3** and **4** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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