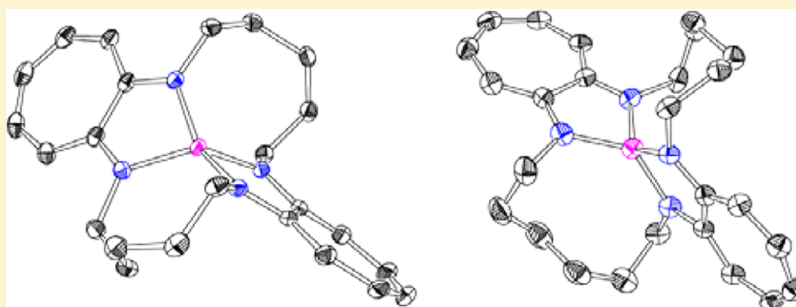


## Synthesis and Characterization of Mononuclear, Pseudotetrahedral Cobalt(III) Compounds

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**S** Supporting Information

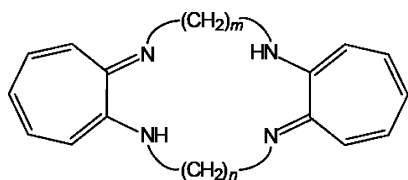


**ABSTRACT:** The preparation and characterization of two mononuclear cobalt(III) tropocoronand complexes,  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  and  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$ , are reported. The cobalt(III) centers exist in rare pseudotetrahedral conformations, with twist angles of  $65^\circ$  and  $74^\circ$  for the  $[\text{Co}(\text{TC-5,5})]^+$  and  $[\text{Co}(\text{TC-6,6})]^+$  species, respectively. Structural and electrochemical characteristics are compared with those of newly synthesized  $[\text{Ga}(\text{TC-5,5})](\text{GaCl}_4)$  and  $[\text{Ga}(\text{TC-6,6})](\text{GaCl}_4)$  analogues. The spin state of the pseudotetrahedral  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$  compound was determined to be  $S = 2$ , a change in spin state from the value of  $S = 1$  that occurs in the square-planar and distorted square-planar complexes,  $[\text{Co}(\text{TC-3,3})](\text{X})$  ( $\text{X} = \text{BPh}_4, \text{BAr}'_4$ ) and  $[\text{Co}(\text{TC-4,4})](\text{BPh}_4)$ , respectively.

### INTRODUCTION

The tetraazamacrocyclic architecture of the tropocoronand ligand provides a flexible scaffold that can accommodate varied coordination environments and stabilize unusual or otherwise unachievable geometries at transition-metal centers (Chart 1).<sup>1–4</sup>

**Chart 1. Tropocoronand Ligand Scaffold,  $\text{H}_2\text{TC-}m,n$ , Where  $m$  and  $n$  Represent the Number of Methylene Groups in Each Polymethylene Linker Chain**



In the absence of entatic tuning, cobalt(II) metal centers display a proclivity toward high-spin octahedral or tetrahedral configurations, and cobalt(III) centers prefer low-spin octahedral geometries.<sup>5</sup> Square-planar coordination environments are also readily observed for four-coordinate cobalt(III) complexes, but small molecules with cobalt(III) centers in tetrahedral environments are significantly scarce. The cobalt(III) center in  $[\text{CoW}_{12}\text{O}_{40}]^{5-}$  exists in a tetrahedral environment,<sup>5</sup> as does cobalt(III) in  $[\text{Co}(\text{nor})_4]^-$ ,<sup>6,7</sup> where nor is the norbornyl anion. A small number of mononuclear cobalt(III) imides have been

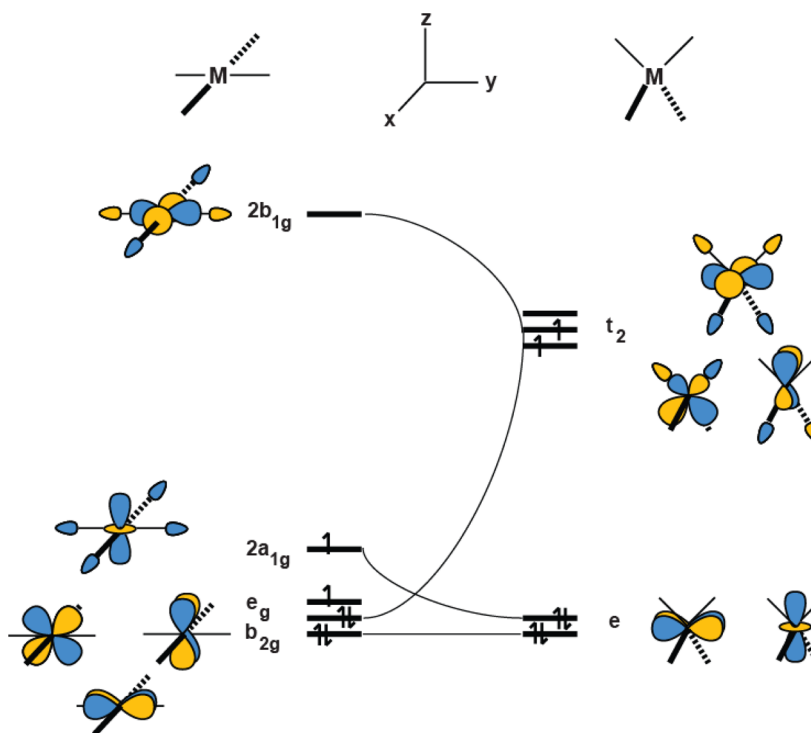
prepared and structurally characterized, and in these species, the multiple-bond character of the metal–imide interaction stabilizes the pseudotetrahedral geometry of cobalt(III).<sup>8–13</sup>

The reason for the rarity of cobalt(III) in tetrahedral environments becomes clear upon comparison of orbital splitting diagrams for a  $d^6$  metal center in square-planar versus tetrahedral geometries. The orbital filling diagram for a square-planar  $d^6$  center is shown in Figure 1 for an  $S = 1$  electronic configuration.<sup>14</sup> The allocation of electrons corresponds to minimization of electron repulsion interactions and is the observed electronic distribution in  $[\text{Co}(\text{TC-4,4})]^+$  complexes.<sup>15</sup> In contrast, the orbital distribution in a  $d^6$  tetrahedral orbital splitting diagram results in the partial occupancy of two destabilized  $t_2$  molecular orbitals, with no contribution to minimization of electron repulsion interactions. That is, the transition from square-planar to tetrahedral geometry results in partial filling of orbitals that are destabilized in the tetrahedral configuration relative to the square-planar one, without minimizing electron repulsion. The square-planar configuration also minimizes the electron–ligand repulsion from the  $d_{x^2-y^2}$  orbital.

Having the ability to control the environment at the metal center simply by changing the tropocoronand linker chain length places us in a unique situation to examine unusual

**Received:** April 22, 2014

**Published:** December 22, 2014



**Figure 1.** Orbital correlation diagram for the transition from square-planar to tetrahedral geometry, shown for the electron occupancy corresponding to a  $d^6$  metal center. Modified from Albright, Burdett, and Whangbo.<sup>14</sup>

coordination environments. The previously established series of four-coordinate cobalt(III) tropocoronand complexes comprises  $[\text{Co}(\text{TC-3,3})](\text{X})$  ( $\text{X} = \text{BPh}_4$ ,  $\text{BAr}'_4$ ) and  $[\text{Co}(\text{TC-4,4})](\text{BPh}_4)$ .<sup>15</sup> These species exist in square-planar or distorted square-planar geometries, with twist angles, defined as the angle between planes formed by the metal and the two sets of aminotroponeiminate nitrogen atoms, of  $8^\circ$  and  $41^\circ$  for the four-coordinate complexes.<sup>15</sup> In our pursuit to examine the size dependence of cobalt(II) and cobalt(III) tropocoronands on their ability to tune reactivity with nitric oxide,<sup>16,17</sup> we prepared and structurally characterized two pseudotetrahedral cobalt(III) complexes,  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  and  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$ . Their syntheses and properties are described here.

## EXPERIMENTAL METHODS

**General Considerations.** Handling of air- and moisture-sensitive materials was conducted in an MBraun glovebox under a nitrogen atmosphere. Reagents were used as purchased, without further purification. Methylene chloride and tetrahydrofuran (THF) solvents were purified by passage through activated alumina and stored over 4 Å molecular sieves under a nitrogen atmosphere prior to use. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, stored under an inert nitrogen atmosphere, and used without further purification. The syntheses of  $[\text{Co}(\text{TC-5,5})]$ ,<sup>3</sup>  $[\text{Co}(\text{TC-6,6})]$ ,<sup>3</sup>  $[\text{Zn}(\text{TC-5,5})]$ ,<sup>18</sup> and  $[\text{Zn}(\text{TC-6,6})]$ <sup>18</sup> are described elsewhere.  $\text{Fc}(\text{BPh}_4)$  was prepared according to previously published procedures.<sup>19,20</sup>

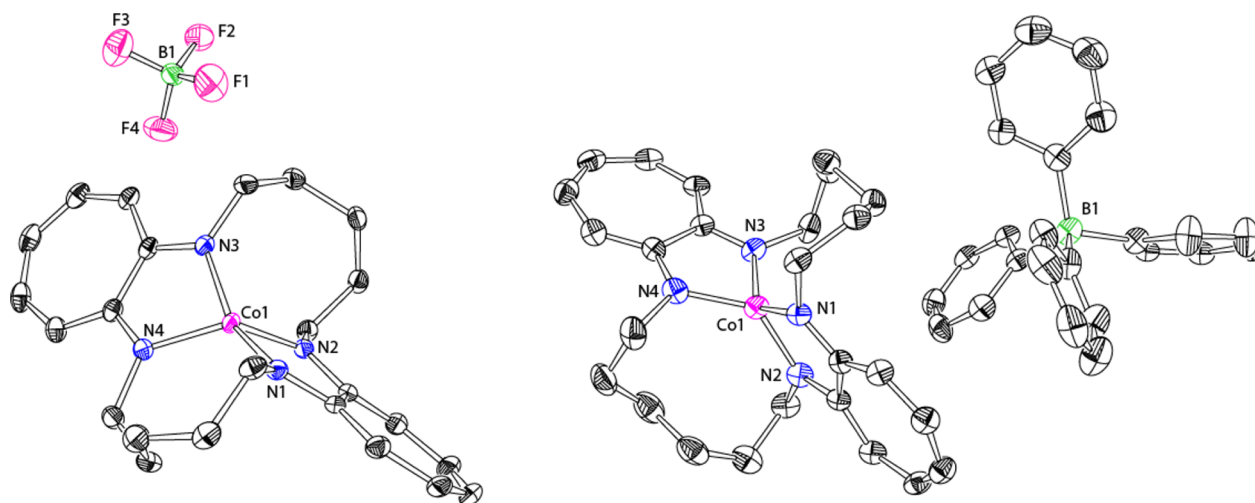
**Synthesis of  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$ .** To a solution of  $[\text{Co}(\text{TC-5,5})]$  (150 mg, 0.35 mmol) in methylene chloride was added  $\text{Fc}(\text{BF}_4)$  (94.4 mg, 0.346 mmol). The reaction was left to stir overnight. The solution was evaporated to dryness and the resultant solid was washed with diethyl ether ( $\text{Et}_2\text{O}$ ) to remove ferrocene. The solid was dried in vacuo. Recrystallization from dichloromethane (DCM)/ $\text{Et}_2\text{O}$  at  $-30^\circ\text{C}$  yielded X-ray-quality crystals (174 mg, 97% yield). UV–vis–NIR [ $\text{CDCl}_3$ ;  $\lambda$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 349 (13650), 412 (15670), 757 (11420), 1166 (9183). IR (KBr;  $\text{cm}^{-1}$ ):  $\nu_{\text{C=N}}$  1501,  $\nu_{\text{C=C}}$  1586.

Anal. Calcd for  $\text{C}_{24}\text{H}_{30}\text{BCoF}_4\text{N}_4 \cdot 0.32\text{CH}_2\text{Cl}_2$ : C, 53.35; H, 5.64; N, 10.23. Found: C, 53.33; H, 5.89; N, 10.21. Evidence for  $\text{CH}_2\text{Cl}_2$  appeared in the NMR spectrum taken in  $\text{CD}_2\text{Cl}_2$ .

**Synthesis of  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$ .** To a solution of  $[\text{Co}(\text{TC-6,6})]$  (200 mg, 0.4 mmol) in methylene chloride was added  $\text{Fc}(\text{BPh}_4)$  (218 mg, 0.434 mmol) in the dark. The reaction was allowed to stir overnight. The solution was evaporated to dryness, and the resultant solid was washed with  $\text{Et}_2\text{O}$  to remove ferrocene. The solid was dried in vacuo. Recrystallization from DCM/ $\text{Et}_2\text{O}$  at  $-30^\circ\text{C}$  yielded X-ray-quality crystals (330 mg, 97% yield). *Note:* We found methylene chloride solutions of  $\text{Fc}(\text{BPh}_4)$  to be unstable and attribute variations in product yield to this property. UV–vis–NIR [ $\text{CDCl}_3$ ;  $\lambda$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 271 (60900), 349 (21470), 424 (34560), 702 (2362), 981 (561), 1240 (475). IR (KBr;  $\text{cm}^{-1}$ ):  $\nu_{\text{C=N}}$  1504,  $\nu_{\text{C=C}}$  1595. Anal. Calcd for  $\text{C}_{50}\text{H}_{54}\text{BCoN}_4$ : C, 76.92; H, 6.97; N, 7.18. Found: C, 76.68; H, 6.71; N, 7.33.

**Synthesis of  $[\text{Ga}(\text{TC-5,5})](\text{GaCl}_4)$ .** To a solution of  $\text{H}_2\text{TC-5,5}$  (300 mg, 0.8 mmol) in THF was added NaHMDS (292 mg, 1.59 mmol), and the reaction was allowed to stir for 10 min.  $\text{GaCl}_3$  (448 mg, 1.59 mmol) was added to the solution as a solid, and the reaction was left to stir overnight. The solution was evaporated to dryness, suspended in  $\text{CH}_2\text{Cl}_2$ , and filtered through Celite. The resultant solid was washed with  $\text{Et}_2\text{O}$  and dried in vacuo. Recrystallization from  $\text{CH}_2\text{Cl}_2$ / $\text{Et}_2\text{O}$  at  $-30^\circ\text{C}$  yielded X-ray-quality crystals (370 mg, 70% yield).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.68 (m, 8H,  $\text{CH}_2$ ), 1.91 (m, 4H,  $\text{CH}_2$ ), 3.74 (m, 4H,  $\text{CH}_2$ ), 3.85 (m, 4H,  $\text{CH}_2$ ), 7.10 (t,  $J = 10$  Hz, 2H,  $\text{ArH}_\alpha$ ), 7.26 (d,  $J = 8$  Hz, 2H,  $\text{ArH}_\alpha$ ), 7.64 (t,  $J = 12$  Hz, 2H,  $\text{ArH}_\beta$ ). ESI-MS ( $[\text{M} - \text{GaCl}_4]^+$ ):  $m/z$  433.1 (calcd  $m/z$  433.12). UV–vis [ $\text{CDCl}_3$ ;  $\lambda$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 274 (sh, 63390), 280 (70810), 365 (40920), 416 (sh, 19480), 433 (27090). IR (KBr;  $\text{cm}^{-1}$ ):  $\nu_{\text{C=N}}$  1512,  $\nu_{\text{C=C}}$  1513. Anal. Calcd for  $\text{C}_{24}\text{H}_{30}\text{N}_4\text{Ga}_2\text{Cl}_4$ : C, 43.96; H, 4.61; N, 8.54. Found: C, 43.88; H, 4.44; N, 8.42.

**Synthesis of  $[\text{Ga}(\text{TC-6,6})](\text{GaCl}_4)$ .** To a solution of  $\text{H}_2\text{TC-6,6}$  (54 mg, 0.13 mmol) in THF was added NaHMDS (45 mg, 0.27 mmol), and the reaction was allowed to stir for 15 min.  $\text{GaCl}_3$  (70 mg, 0.27 mmol) was added to the solution as a solid, and the reaction was left to stir overnight. The solution was evaporated to dryness, suspended in  $\text{CH}_2\text{Cl}_2$ , and filtered through Celite. The



**Figure 2.** Thermal ellipsoid plots for  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  (left) and  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$  (right), shown at 50% probability. Hydrogen atoms have been omitted for clarity.

resultant solid was washed with  $\text{Et}_2\text{O}$  and dried in vacuo. Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  at  $-30^\circ\text{C}$  yielded X-ray-quality crystals (52 mg, 57% yield).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.13–1.26 (m, 8H,  $\text{CH}_2$ ), 1.44 (m, 4H,  $\text{CH}_2$ ), 2.19–2.26 (m, 4H,  $\text{CH}_2$ ), 3.64–3.71 (m, 4H,  $\text{CH}_2$ ), 3.97–4.02 (m, 4H,  $\text{CH}_2$ ), 7.12 (t,  $J = 8$  Hz, 2H,  $\text{ArH}_\gamma$ ), 7.35 (d,  $J = 8$  Hz, 2H,  $\text{ArH}_\alpha$ ), 7.60 (t,  $J = 6$  Hz, 2H,  $\text{ArH}_\beta$ ). ESI-MS ( $[\text{M} - \text{GaCl}_4]^+$ ):  $m/z$  471.1 (calcd  $m/z$  471.20). UV-vis [ $\text{CDCl}_3$ ;  $\lambda$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 272 (sh, 73750), 280 (83830), 363 (45720), 410 (sh, 22980), 422 (sh, 28930), 429 (37980). IR (KBr;  $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$  1514,  $\nu_{\text{C}=\text{C}}$  1595. Anal. Calcd for  $\text{C}_{26}\text{H}_{34}\text{N}_4\text{Ga}_2\text{Cl}_4$ : C, 45.67; H, 5.01; N, 8.19. Found: C, 45.98; H, 4.93; N, 7.86.

**Physical Measurements.**  $^1\text{H}$  NMR spectra were collected on a 400 MHz Bruker Avance spectrometer. Evan's method<sup>21,22</sup> measurements were made in  $\text{CD}_2\text{Cl}_2$  on a 500 MHz Varian INOVA spectrometer, and the temperature was measured by the residual peak separation of the  $^1\text{H}$  NMR of neat  $\text{CD}_3\text{OD}$ .<sup>23</sup> Optical spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer in 6SQ Starna cells. Solutions were prepared under a nitrogen atmosphere. Fourier transform infrared spectra were recorded on a Thermo Nicolet Avatar 360 spectrometer running the OMNIC software package. Electrospray ionization mass spectrometry (ESI-MS) analyses were performed on the Agilent 1100 series LC/MSD trap spectrometer. Cyclic voltammograms were recorded under nitrogen using the VersaSTAT3 potentiostat (Princeton Applied Research) and V3 Studio software. A glassy carbon working electrode, silver wire pseudoreference electrode, and platinum wire auxiliary electrode were used. Samples were prepared as 3–5 mM solutions in methylene chloride with 0.1 M ( $n\text{-Bu}_4\text{N}$ )( $\text{PF}_6$ ) as the supporting electrolyte. Reported spectra were recorded at 50 mV/s scan rates. The reversible  $\text{Fc}/\text{Fc}^+$  couple appeared at 0.57 V vs  $\text{Ag}/\text{Ag}^+$ .

**X-ray Crystallography.** Crystals were mounted in Paratone N oil and frozen at 100 K under a cold nitrogen stream controlled by a Cryopad low-temperature apparatus. Data were collected on a Bruker APEX CCD X-ray diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073$  Å) controlled by the APEX2 software package.<sup>24</sup> Empirical absorption correction was performed with SADABS.<sup>25</sup> The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares on  $F^2$  using the SHELXL-97 program incorporated into the SHELXTL software package.<sup>26</sup> Possible higher symmetries were evaluated by PLATON.<sup>27</sup> Non-hydrogen atoms were located and their positions refined anisotropically. Hydrogen atoms were assigned idealized positions and given thermal parameters 1.2 times the thermal parameters of the atoms to which they are attached. The structure of  $[\text{Ga}(\text{TC-6,6})](\text{GaCl}_4)$  contained voids filled with heavily disordered solvent molecules. The program SQUEEZE<sup>28</sup> was used to remove the contributions of the disordered solvent to the structure factors. The

electron density attributed to disordered solvent molecules created a channel along the  $6_3$  screw axis and corresponded to seven molecules of methylene chloride or  $\text{Et}_2\text{O}$ . The crystal of  $[\text{Ga}(\text{TC-6,6})](\text{GaCl}_4)$  was an inversion twin, and the percentage of the main twin component was refined to 58.2%. Thermal ellipsoid plots were generated by ORTEP-III.<sup>29</sup>

## RESULTS AND DISCUSSION

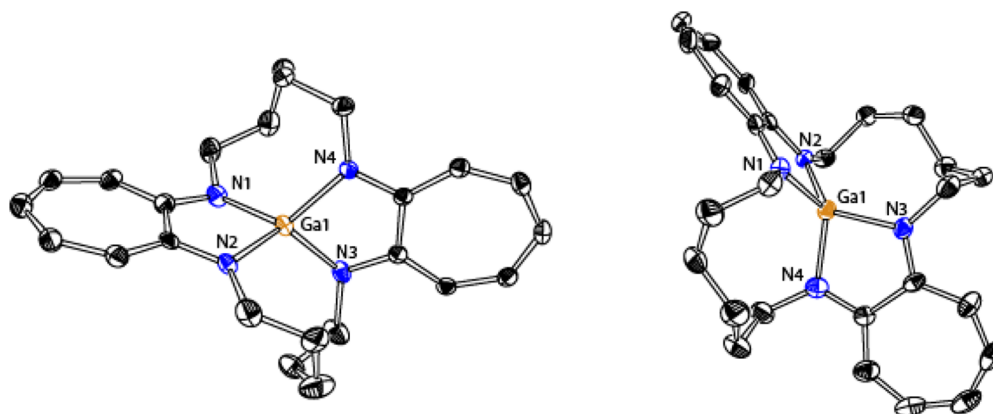
$[\text{Co}(\text{TC-5,5})]$  was successfully oxidized to  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  by reaction with ferrocenium tetrafluoroborate in DCM (Figure 2, left, and Tables S1 and S2 in the Supporting Information, SI). Structural characterization of  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  revealed the twist angle at cobalt to be  $65^\circ$ .<sup>2</sup> The average bond distance between the metal center and coordinating nitrogen atoms,  $\text{Co1}-\text{N}_{\text{ave}}$  is 1.85 Å, comparable to the 1.86 and 1.87 Å values in  $[\text{Co}(\text{TC-3,3})](\text{BPh}_4)$  and  $[\text{Co}(\text{TC-4,4})](\text{BAr}^{\text{F}}_4)$ , respectively.

We also oxidized  $[\text{Co}(\text{TC-6,6})]$  to  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$  with ferrocenium tetraphenylborate and structurally characterized the resulting cobalt(III) product (Figure 2, right, and Figure S2 and Tables S1 and S3 in the SI). The twist angle in  $[\text{Co}(\text{TC-6,6})]^+$  is  $74^\circ$ , the largest value observed for cobalt(III) tropocoronands to date.<sup>15</sup> The  $\text{Co1}-\text{N}_{\text{ave}}$  bond distance is 1.82 Å, somewhat shorter than that in previously reported cobalt(III) tropocoronand coordination compounds.<sup>15</sup> A comparison of bond lengths and twist angles for four-coordinate cobalt(II) and -(III) tropocoronand complexes is provided in Table 1.

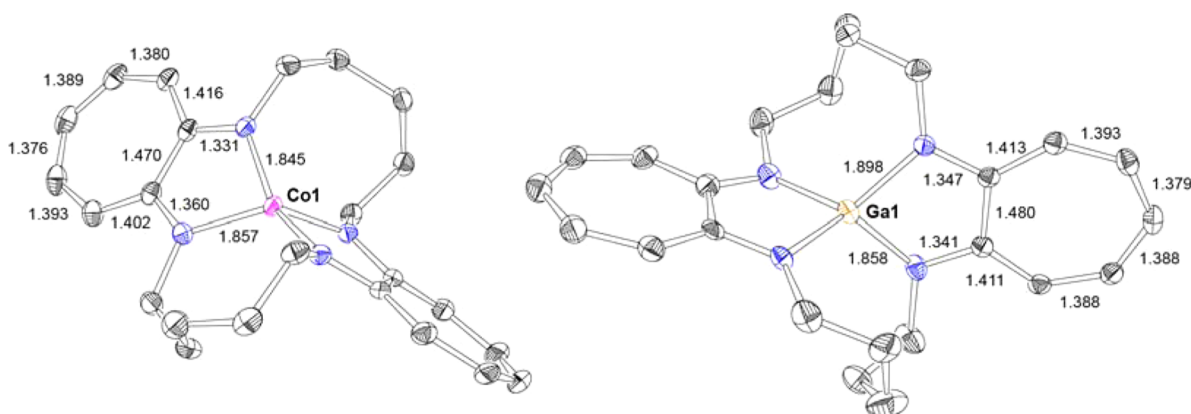
**Table 1.** Bond Lengths and Twist Angles in  $[\text{Co}(\text{TC-}m,n)]$  and  $[\text{Co}(\text{TC-}m,n)]^+$  Complexes Reported To Date

	$[\text{Co}(\text{TC-}m,n)]$				
	3,3 <sup>a</sup>	4,4 <sup>a</sup>	4,5 <sup>a</sup>	5,5 <sup>a</sup>	6,6 <sup>a</sup>
$\text{Co}-\text{N}_{\text{ave}}$ (Å)	1.86	1.88	1.96	1.97	1.97
twist angle (deg)	9	32	59	70	85
	$[\text{Co}(\text{TC-}m,n)]^+$				
	3,3 <sup>b</sup>	4,4 <sup>b</sup>	4,5 <sup>a</sup>	5,5 <sup>c</sup>	6,6 <sup>c</sup>
$\text{Co}-\text{N}_{\text{ave}}$ (Å)	1.86	1.87		1.85	1.82
twist angle (deg)	8	41		65	74

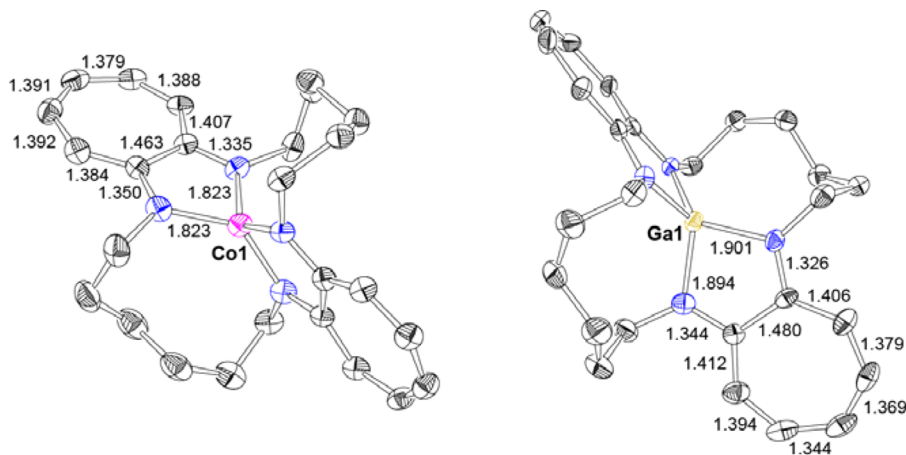
<sup>a</sup>Reference 3. <sup>b</sup>Reference 15. <sup>c</sup>This work.



**Figure 3.** Thermal ellipsoid plots for  $[\text{Ga}(\text{TC-5,5})](\text{GaCl}_4)$  and  $[\text{Ga}(\text{TC-6,6})](\text{GaCl}_4)$ , depicted at 50% probability. Hydrogen atoms and the gallium tetrachloride anions are omitted for clarity.



**Figure 4.** Comparison of structural parameters for  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  (left) and  $[\text{Ga}(\text{TC-5,5})](\text{GaCl}_4)$  (right). Distances (Å) shown are representative of bond distances within the tropocoronand ligand.



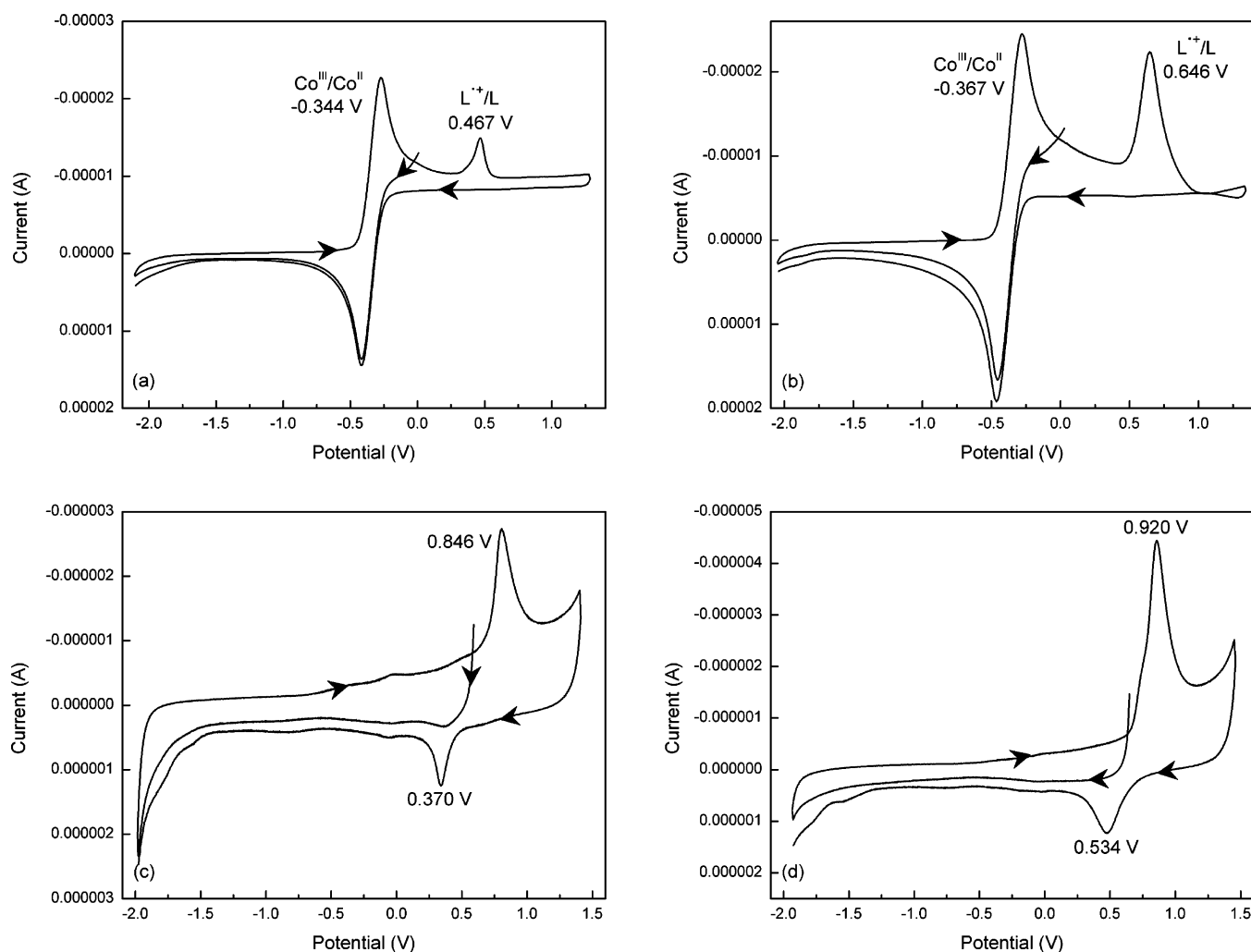
**Figure 5.** Comparison of structural parameters for  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$  (left) and  $[\text{Ga}(\text{TC-6,6})](\text{GaCl}_4)$  (right). Distances (Å) shown are representative of bond distances within the tropocoronand ligand.

Tetrahedral geometry is rare for cobalt(III) and, to our knowledge, has been observed in mononuclear small molecules only for  $[\text{Co}(\text{nor})_4]^-$  and a handful of cobalt(III) imido complexes to date.<sup>6–13</sup> The paucity of cobalt(III) in tetrahedral environments and the unusual geometries of the metal centers in  $[\text{Co}(\text{TC-5,5})]^+$  and  $[\text{Co}(\text{TC-6,6})]^+$  raised the possibility that oxidation of the parent cobalt(II) compounds occurred at the ligand rather than the metal center. We therefore prepared and characterized  $[\text{Ga}(\text{TC-5,5})](\text{GaCl}_4)$  and  $[\text{Ga}(\text{TC-6,6})](\text{GaCl}_4)$

and compared their structural and electrochemical properties with those of the analogous cobalt complexes (Figure 3 and Tables S1, S4, and S5 in the SI).

The  $[\text{Ga}(\text{TC-5,5})](\text{GaCl}_4)$  complex crystallizes in  $P2_1/c$  and exhibits crystallographic disorder over the entirety of the tropocoronand ligand (Figure S1 in the SI). The  $\text{N}_4$ -coordinated gallium(III) center has a twist angle of  $81^\circ$ , displaying distorted tetrahedral geometry. The average gallium–nitrogen distance,  $\text{Ga1}-\text{N}_{\text{ave}}$  is 1.88 Å.  $[\text{Ga}(\text{TC-6,6})](\text{GaCl}_4)$





**Figure 6.** Cyclic voltammograms of (a) [Co(TC-5,5)], (b) [Co(TC-6,6)], (c) [Ga(TC-5,5)](GaCl<sub>4</sub>), and (d) [Ga(TC-6,6)](GaCl<sub>4</sub>), referenced to Fc/Fc<sup>+</sup>.

6,6)](GaCl<sub>4</sub>) crystallizes in *P*6<sub>3</sub> and exhibits nearly perfect tetrahedral coordination at the gallium(III) center. The twist angle in [Ga(TC-6,6)]<sup>+</sup> is 89°, and Ga1–N<sub>ave</sub> is 1.89 Å.

Comparison of analogous bond distances between the [Co(TC-*n,n*)]<sup>+</sup> and [Ga(TC-*n,n*)]<sup>+</sup> complexes provided insight into the electron distribution in the former species (Figures 4 and 5). The metal–nitrogen bonds in both cobalt complexes are shorter than those in the analogous gallium(III) tropocoronands. The elongation of the Ga–N bond relative to the Co–N bond is probably a consequence of the greater covalent character of the cobalt tropocoronand compared to the gallium tropocoronand complex.<sup>30</sup>

In a review of the experimental and theoretical properties of transition-metal complexes bound to redox noninnocent ligands, Ray et al. note difficulties in using X-ray structural parameters to draw conclusions regarding ligand- versus metal-based oxidation in delocalized systems, where the electron of a ligand radical is shared between two different ligands.<sup>31</sup> The tropocoronand complexes provide such a delocalized system, for if a ligand radical were to form, the electron would be able to travel between the two aminotroponeiminate rings via the metal center. We are also aware of reports describing noninnocent ligands that undergo negligible structural rearrangement upon changes in redox state.<sup>31–38</sup> We therefore

turned to electrochemical methods for further evidence that oxidation of [Co(TC-5,5)] and [Co(TC-6,6)] results in cobalt(III) species.

Previously published cyclic voltammetry studies of [Co(TC-5,5)]<sup>15</sup> and [Co(TC-6,6)]<sup>15</sup> were repeated and compared to the results of analogous studies of [Ga(TC-5,5)](GaCl<sub>4</sub>) and [Ga(TC-6,6)](GaCl<sub>4</sub>) (Figure 6). We observed reversible couples at –0.344 V vs Fc/Fc<sup>+</sup> for [Co(TC-5,5)] and –0.367 V vs Fc/Fc<sup>+</sup> for [Co(TC-6,6)]. We assign these processes to metal-based redox reactions by comparison with electrochemical studies of [Zn(TC-5,5)] and [Zn(TC-6,6)].<sup>18</sup> The absence of similar reversible processes in the voltammograms of the zinc complexes is consistent with these redox events being metal-based. Additionally, we assign the irreversible features at 0.467 V in the [Co(TC-5,5)] voltammogram and at 0.646 V in the [Co(TC-6,6)] voltammogram to ligand-based oxidations. The cobalt(II)/cobalt(III) couples observed here appeared at ~100 mV more negative than those previously published.<sup>15</sup> The reason for this discrepancy is unknown, and the current values are considered to be correct. Cyclic voltammetry of [Ga(TC-5,5)](GaCl<sub>4</sub>) and [Ga(TC-6,6)](GaCl<sub>4</sub>) revealed ligand-based oxidations at 0.846 and 0.920 V vs Fc/Fc<sup>+</sup>, respectively. Metal-based redox processes were not observed. Ligand oxidation occurred at

more positive potentials in the gallium(III) complexes than in the analogous zinc(II) and cobalt(III) compounds.<sup>18</sup> The shift to more positive potentials in the gallium(III) tropocoronands relative to the zinc(II) analogues can be attributed to the higher oxidation state of the gallium center. Ligand oxidation in the gallium complexes may occur at more positive potentials than in the corresponding cobalt species because the cobalt center may be better able to stabilize the additional charge through covalent metal–ligand interactions than gallium.

We attempted to characterize  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  by X-band electron paramagnetic resonance (EPR) spectroscopy but were unable to observe any signal at 77 K. Helium temperature EPR spectroscopic studies of  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$  were equally unrevealing. The  $^1\text{H}$  NMR spectrum of  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  shows broad, low-intensity peaks in the diamagnetic region of the spectrum, which may correspond to a tropocoronand-containing species (Figure S3 in the SI). These features may be attributed to the ligand in  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$ . Peaks corresponding to protons of the tropocoronand ligand are absent in the  $^1\text{H}$  NMR spectrum of  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$ , but peaks for the tetraphenylborate counteranion are readily observed (Figure S4 in the SI).

Previous studies revealed that, as the total length of the linker chains ( $n + m$ ) of a  $(\text{TC-}m,n)^{2-}$  complex increases, both the geometry of the metal center and spin state change. The spin state of the distorted square-planar  $[\text{Ni}(\text{TC-4,5})]$  is  $S = 0$ , and that of the distorted tetrahedral  $[\text{Ni}(\text{TC-5,5})]$  is  $S = 1$ .<sup>39</sup> In the cobalt(II) system, a spin-state change is observed between  $[\text{Co}(\text{TC-4,4})]$  ( $S = 1/2$ ) and  $[\text{Co}(\text{TC-4,5})]$  ( $S = 3/2$ ).<sup>3</sup> We previously reported that  $[\text{Co}(\text{TC-3,3})](\text{BPh}_4)$  (twist angle =  $8^\circ$ ) and  $[\text{Co}(\text{TC-4,4})](\text{BPh}_4)$  (twist angle =  $41^\circ$ ) have spin state  $S = 1$  at room temperature and magnetic moments of  $\mu_{\text{eff}} = 3.1$  and  $3.6 \mu_{\text{B}}$ , respectively.<sup>15</sup> To determine whether a spin-state change occurs in the  $[\text{Co}(\text{TC-}m,n)]^+$  series, the magnetic susceptibility of  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$  was measured by Evan's method at room temperature. The magnetic moment was determined to be  $5.38 \mu_{\text{B}}$ , as expected for  $S = 2$ , confirming that a spin-state change does occur.

Calculations were performed with the use of ORCA<sup>40</sup> to supplement our understanding of the electronic structure of the  $[\text{Co}(\text{TC-}n,n)]^+$  series ( $n = 3\text{--}6$ ). In all cases, the optimized geometries [BP/SVP(TZVP on Co)] of the  $S = 2$  state had twist angles  $13\text{--}21^\circ$  larger than those of the  $S = 1$  state (Table S6 in the SI). This result supports the connection between the spin-state change and the square-planar to tetrahedral change in geometry. Subsequent energy computations at the B3LYP/def2-TZVP level predicted that the  $S = 1$  state is more stable than the  $S = 2$  state in all four species, with triplet–quintet gaps of 24.9, 18.9, 8.0, and 7.2 kcal/mol for  $n = 3\text{--}6$ , respectively (Figure S6 in the SI). Our experimental results show that a spin-state change to  $S = 2$  occurs for  $n = 5$  or 6. The computations suggest that the ground-state electronic structure for  $n = 5$  and 6 is  $S = 1$ , but there is a low energy barrier to accessing the  $S = 2$  state (7–8 kcal/mol). Even though this level of theory incorrectly predicts the ground state spin for  $n = 5$  and 6, the trend in the triplet–quintet energy gap across the series  $n = 3\text{--}6$  is correct. The triplet–quintet energy gap correlates almost linearly with the experimental twist angle ( $R^2 = 0.936$ ; Figure S6 in the SI). Electronic transitions predicted for the series support the spin-state change but are less conclusive (Figures S7–S10 in the SI). Additional computational details are provided in the SI. Molecular orbitals involved in the electronic transitions for all complexes

contained significant mixing between the cobalt and tropocoronand orbitals. Thus, assignments for the transitions in the electronic spectra could not be made without further work.

## SUMMARY AND CONCLUSIONS

Comparison of structural and electrochemical properties of the cobalt and gallium species  $[\text{Co}(\text{TC-5,5})]^+$ ,  $[\text{Co}(\text{TC-6,6})]^+$ ,  $[\text{Ga}(\text{TC-5,5})]^+$ , and  $[\text{Ga}(\text{TC-6,6})]^+$  confirmed the cobalt(III) character of the metal centers in  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  and  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$ . The synthesis of  $[\text{Co}(\text{TC-5,5})](\text{BF}_4)$  and  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$  augments the number of cobalt(III) species having the rare pseudotetrahedral geometry. Together with previous results from our laboratory, the present study reveals that a spin-state change from  $S = 1$  to  $S = 2$  occurs as the ligands tune the geometry of the complexes from pseudo-square-planar for  $[\text{Co}(\text{TC-}n,n)](\text{BPh}_4)$  ( $n = 3, 4$ ) to pseudotetrahedral for  $[\text{Co}(\text{TC-6,6})](\text{BPh}_4)$ .

## ASSOCIATED CONTENT

### Supporting Information

X-ray crystallographic data, computational methods, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant CHE0907905 to S.J.L. and by National Institute of Health Grant 1S10RR013886-01, awarded to the MIT Department of Chemistry Instrumentation Facility. The authors thank Dr. Peter Müller for assistance with X-ray crystallography and Dr. Daniel A. Lutterman, Dr. Danna Freedman, and Matthew J. Nava for valuable discussion.

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