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Sandwich Compounds of Cyanotrispyrazolylborates: Complexation-Induced Ligand Isomerization

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Reaction of the new cyanoscorpionate ligand, hydrotris(4-cyano-3-phenyl)pyrazolylborate ($\mathrm{Tp}^{\mathrm{Ph,4CN}}$) with Co(II), Mn(II), and Fe(II) unexpectedly results in the isolation only of crystals containing sandwich complexes in which the ligands have been isomerized to produce the heterocyanoscorpionate hydrobis(4-cyano-3-phenylpyrazolyl)(4-cyano-5-phenylpyrazolyl)borate ($\mathrm{Tp}^{\mathrm{Ph,4CN*}}$). The three complexes have been characterized crystallographically and are isostructural, with each ligand acting in a tridentate manner toward the metal. The isomerization of the ligand appears to be more facile than that of the analogous non-cyano ligand, $\mathrm{Tp}^{\mathrm{Ph}}$, with which crystals of the unisomerized sandwich compound have been isolated for Mn(II) and Fe(II).

Introduction

Since their development in the mid-1960's by Trofimenko,[1] scorpionate ligands have become an important part of the inorganic chemist's arsenal.[2] As face-capping tridentate anionic ligands, they have been used as supporting ligands in complexes serving purposes ranging from organometallic catalysts[3] to biomimetic model complexes.[4] The popularity of these ligands stems, in large part, from their flexibility. The pyrazole ring has three carbon atoms which can be functionalized relatively easily, allowing for the addition of substituents which greatly affect the steric and/or electronic properties of the ligand. This feature has led to a large number of second-generation scorpionates, the vast majority of which feature alkyl or aryl groups in the 3- and/or 5-positions of the rings. These second-generation ligands have allowed for the isolation of numerous complex types not accessible with the unsubstituted Tp ligand and have been shown to influence the electronic properties of the coordinated metal ion by virtue of interligand steric interactions.[5]

Far less well studied are scorpionates bearing moderate-to-strong electron-withdrawing or electron-donating pyrazole substituents. Trofimenko and others have reported a number of scorpionates with halogen substituents in the 4-position.[6] Dias and others have published many reports using scorpionates with trifluoromethyl groups in the 3- and 5-positions of the pyrazole ring.[7,8] This latter class of ligands has

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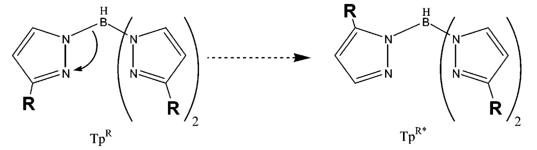

Figure 1. Borotropic shift resulting in isomerization of the ligand from Tp^R to Tp^{R*}.

demonstrated the expected reduction of electron density at the metal and has been used to stabilize complexes and chemistry which are otherwise difficult to realize.[8] We have been investigating scorpionate ligands with cyano substituents in the 4-position of the pyrazole ring.[9] Aside from the strong electron-withdrawing properties of the cyano groups, these ligands also present the possibility for the formation of coordination polymers through simultaneous coordination of metals at both the pyrazole and cyano N atoms.[10] Both we and Trofimenko[11] have reported the synthesis and characterization of metal complexes of 4-cyano-substituted bispyrazolylborates, our ligands bearing substituents in the 3-position and Trofimenko's ligands being otherwise unsubstituted.

Among the earliest types of coordination compounds isolated with the parent Tp ligand were the "sandwich" compounds with the formula Tp_2M.[1,6a] Formation of this class of compound is highly favored for the unsubstituted Tp ligand with metal ions that prefer octahedral coordination. Addition of bulky substituents at the 3-position of the pyrazole rings introduces steric interactions between the ligands of the sandwich compounds and increasingly favors monosubstituted compounds of the form $TpMX_n$. Thus, Tp^{Ph} was used to isolate 5-coordinate complexes such as Tp^{Ph}-Co(SCN)(thf)[12] but could also be incorporated into the sandwich compounds $Tp^{Ph}{}_2M$.[5c,13] The bulkier Tp^{t-Bu} ligand, on the other hand, produced the 4-coordinate $Tp^{t-Bu}Co(SCN)$,[12] and no sandwich compounds of this ligand have been reported. An interesting feature of scorpionate ligands was discovered in attempting the synthesis of sandwich compounds with $Tp^{i-Pr,4Br}$. Formation of such a compound was realized only with the coordination-induced isomerization of the ligand to $Tp^{i-Pr,4Br*}$, in which one pyrazole experiences a "borotropic" shift placing the bulky substituent in the 5-position (Figure 1).[14] Subsequently, other examples of this isomerization have been reported, including with Tp^{Ph} and related ligands.[15] We report herein the syntheses, X-ray crystal structures, and characterization of sandwich compounds of the $Tp^{Ph,4CN}$ ligand, all of which display the borotropic shift isomerization.

Experimental Section

General. Unless otherwise stated, all solvents and reagents were used as received from Aldrich, Acros, Fisher Scientific, and TCI-America (Cyanoacetic acid, *tert*-butyl ester) without further purification. IR spectra were recorded on a Nicolet Avatar 360 FTIR. Electrospray mass spectra were obtained on a Finnigan LCQ DECA spectrometer. NMR spectra were obtained using either a Varian Mercury 300 MHz or Varian Inova 400 MHz NMR spectrometer. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, AZ. When dry solvents are specified, they were prepared by distillation from sodium/benzophenone. $Fe(CF_3SO_3)_2{\cdot}2CH_3CN$[16] and 4-cyano-3-phenylpyrazole[9] were prepared as previously reported.

X-ray Crystallography. Co, Fe, and Mn Complexes. Data were collected using Bruker CCD diffractometers equipped with a Bruker KRYO-FLEX low-temperature apparatus. Suitable crystals were identified under a polarizing microscope and affixed with oil in a Hampton Research Cryoloop and transferred to the coldstream of the diffractometer. Data collection was performed using the Bruker APEX2 (Fe complex) or Bruker SMART (Mn and Co complexes) software, data reduction was performed using Bruker SAINT software, and structure solution (direct methods) and refinement (full-matrix least-squares) were performed using SHELXS-97[17] and SHELXL-97[17] within the Bruker SHELXTL suite. Final refinement was performed using the WinGX suite,[18] and thermal ellipsoid plots were prepared using Raster3D.[19] Data were corrected for Lorentz and polarization effects and for absorption (multiscan) using the Bruker SADABS program. Hydrogen atoms were placed at calculated idealized positions and were not refined. All non-hydrogen atoms were refined using anisotropic thermal parameters. Pertinent details are given in Table 1.

Tl Complex. Data were collected on a Nonius CAD4 diffractometer equipped with an Oxford Cryosystems Cryostream 700 low-temperature apparatus. Suitable crystals were identified under a polarizing microscope, affixed with oil to a glass fiber, and transferred to the coldstream of the diffractometer. Data reduction, structure solution, and refinement were performed using the WinGX suite.[18] Thermal ellipsoid plots were prepared using ORTEP3.[20] Data were corrected for Lorentz and polarization effects and for absorption (ψ-scans). Hydrogen atoms were placed at calculated idealized positions and were not refined. All non-hydrogen atoms were refined using anisotropic thermal parameters. Pertinent details are given in Table 1.

Potassium Hydrotris(4-cyano-3-phenylpyrazolyl)borate, $KTp^{Ph,4CN}$. To 0.700 g (4.14 mmol) of 4-cyano-3-phenylpyrazole was added 0.056 g (1.04 mmol) of KBH_4. The two solids were ground together with a mortar and pestle and placed into a round-bottom flask equipped with a water-cooled condenser. The flask was placed in an oil bath, which was heated slowly to 230 °C. As the pyrazole

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Table 1. X-ray Data Collection and Structure Solution Parameters

compound	$(Tp^{Ph,4CN})*_2Co$	$(Tp^{Ph,4CN})*_2Mn$	$(Tp^{Ph,4CN})*_2Fe$	$TlTp^{Ph,4CN}$
molecular formula	$C_{60}H_{38}N_{18}B_2Co$	$C_{60}H_{38}N_{18}B_2Mn$	$C_{60}H_{38}N_{18}B_2Fe$	$C_{30}H_{19}N_9BTl$
fw	1091.6	1087.6	1088.6	720.74
diffractometer	Bruker PROTEUM R/ Pt_{135}		Bruker SMART APEX II	Nonius CAD4
radiation/λ, Å	Cu Kα/1.5418	Cu Kα/1.5418	Cu Kα/1.5418	Mo Kα/0.7107
temp (K)	100	100	100	150
color, habit	pink, needle	pale yellow, needle	light yellow, needle	yellow, prism
cryst syst	monoclinic	monoclinic	monoclinic	trigonal
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P3$
cryst size (mm^3)	0.23 × 0.04 × 0.04	0.23 × 0.06 × 0.06	0.13 × 0.07 × 0.03	.25 × 0.18 × 0.10
a (Å)	10.557(4)	10.552(5)	10.552(3)	15.077(6)
b (Å)	19.558(7)	19.682(9)	19.622(8)	15.077(6)
c (Å)	27.953(10)	28.311(10)	28.089(10)	8.0562(16)
α (deg)	90	90	90	90.00(2)
β (deg)	99.8(3)	99.4(3)	99.5(3)	90.00(2)
γ (deg)	90	90	90	119.90(3)
V (Å^3)	5687.2(4)	5801.3(5)	5742.1(4)	1587.5(9)
Z	4	4	4	2
calcd density (g cm^{-3})	1.27	1.25	1.26	1.54
octants collected	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
max. h, k, l	12, 21, 32	11, 21, 31	11, 21, 31	18, 16, 9
θ range (deg)	1.4−31.8	1.4−31.4	1.4−29.6	1.6−26
μ, mm^{-1}	2.814	2.290	2.551	5.12
reflns/unique (R_{int})	35 966/8891(0.046)	50 224/8630(0.060)	28 292/8150(0.151)	6445/2083(0.099)
obs [$>2\sigma$]/params	6181/738	6778/738	3451/739	1457/125
R_{obs}, R_{all}	0.070, 0.106	0.105, 0.126	0.091, 0.215	0.035, 0.091
GOF	1.035	1.137	1.022	1.102
max/min trans	0.895, 0.564	0.896, 0.564	0.926, 0.733	.6285, .3609
max/min peak, e•Å^{-3}	0.773, −0.324	1.138, −0.859	0.529, −0.326	1.714, −1.047

melted and reacted with KBH_4, bubbles of hydrogen gas were released. The reaction was continued for 2 h. After cooling, the solid product was washed with CH_3CN and boiling toluene to give $KTp^{Ph,4CN}$ as a pale yellow solid (0.479 g, 0.86 mmol, 82.7%). IR (cm^{-1}, KBr pellet): 695(s), 773(s), 2230(ν_{CN}, s), 2456(ν_{BH}, m). ^1H NMR (DMSO-d_6, δ downfield of TMS): 7.45 (m, 3H), 7.90 (m, 2H), 8.30 (s, 1H). ESI-MS (THF, negative detection): (m/z) = 168.1 $[pz^{Ph,4CN}]^-$, 516.3 $[Tp^{Ph,4CN}]^-$, 1055.0 $[Na(Tp^{Ph,4CN})_2]^-$.

Thallium Hydrotris(4-cyano-3-phenylpyrazolyl)borate [$TITp^{Ph,4CN}$]. To a solution of $KTp^{Ph,4CN}$ (1.74 g, 3.1 mmol) in 20 mL of methanol was added a solution of $TINO_3$ (0.83 g, 3.1 mmol) in 20 mL of 50/50 methanol/water. The mixture was stirred for 1 h. Concentration of the solution on a rotary evaporator resulted in a yellow precipitate of **$TITp^{Ph,4CN}$**, which was collected and washed with water to give 1.84 g (2.56 mmol, 82.6%) of light yellow powder. IR (KBr, cm^{-1}: 2448(υ_{BH}, m), 2226(υ_{CN}, s). ESI-MS (CH_3OH, positive detection): m/z = 744.1 $[TITp^{t\text{-}Bu,4CN}]Na^+$. Elemental anal. Found (calcd for $C_{30}H_{19}N_9BT1{\cdot}4H_2O$): C, 45.62 (45.45); H, 3.35 (3.43); N, 14.29 (15.90). X-ray-quality crystals were grown by layering a solution of $KTp^{Ph,4CN}$ in methanol on top of a solution of $TINO_3$ in water/methanol. After allowing the solutions to diffuse together for a week, the top was removed and the solvent allowed to slowly evaporate, producing light yellow crystals.

Bis(hydrobis(4-cyano-3-phenylpyrazolyl)(4-cyano-5-phenylpyrazolyl)borato)manganese(II) [$(Tp^{Ph,4CN*})_2Mn$]. Under nitrogen, $KTp^{Ph,4CN}$ (0.483 g, 0.86 mmol) was added to a solution of $Mn(CF_3SO_3)_2{\cdot}2CH_3CN$ (0.187 g, 0.43 mmol) in 10 mL of dry THF. The colorless solution turned light yellow immediately. The mixture was stirred for an hour, after which the solvent was removed under reduced pressure to give a colorless solid. Dissolution in 50 mL of CH_2Cl_2, followed by filtration to remove any precipitates and removal of solvent under vacuum, gave as a pale yellow solid (0.351 g, 0.32 mmol, 75.6%). IR (cm^{-1}, KBr pellet): 694(s), 775(s), 2234(ν_{CN}, s), 2458(ν_{BH}, w). Elemental Analysis, Found (Calcd) for $C_{60}H_{38}N_{18}B_2Mn{\cdot}2CH_2Cl_2{\cdot}H_2O$: C, 59.35 (58.38); H, 4.50 (3.48); N, 18.79 (19.77). X-ray quality crystals were grown by layering a solution of $KTp^{Ph,4CN}$ in methanol on top of a solution of $Mn(CF_3SO_3)_2{\cdot}2CH_3CN$ in methanol/ CH_2Cl_2. After allowing the solutions to diffuse together for a week, the top was removed and the solvent allowed to slowly evaporate, producing pale yellow crystals. IR (cm^{-1}, KBr pellet): 696(s), 774(s), 2234(ν_{CN}, s), 2520(ν_{BH}, w). X-ray data collection and structure solution parameters are listed in Table 1.

Bis(hydrobis(4-cyano-3-phenylpyrazolyl)(4-cyano-5-phenylpyrazolyl)borato)iron(II) [$(Tp^{Ph,4CN*})_2Fe$]. To a solution of $Fe(CF_3SO_3)_2{\cdot}2CH_3CN$ (0.583 g, 1.33 mmol) in 20 mL of dry methanol was added $KTp^{Ph,4CN}$ (1.483 g, 2.67 mmol) under nitrogen. The light yellow solution turned green immediately. The mixture was stirred for an hour and the solvent was removed under reduced pressure to give a green solid, which was dissolved in 20 mL of CH_2Cl_2. The solution was filtered to remove any precipitate, and the solvent was removed under reduced pressure. The final product was a light green solid (1.194 g, 1.09 mmol, 82.3%). IR (cm^{-1}, KBr pellet): 694(s), 774(s), 2231(ν_{CN}, s), 2479(ν_{BH}, w). Elemental Analysis, Found (Calcd) for $C_{60}H_{38}N_{18}B_2Fe$: C, 65.76 (66.20); H, 4.67 (3.52); N, 22.59 (23.16). X-ray quality crystals were grown by layering a solution of $KTp^{Ph,4CN}$ in methanol on top of a solution of $Fe(CF_3SO_3)_2{\cdot}2CH_3CN$ in methanol/CH_2Cl_2. After allowing the solutions to diffuse together for a week, the top was removed and the solvent allowed to slowly evaporate, producing light yellow crystals. IR (cm^{-1}, KBr pellet): 696(s), 774(s), 2235(ν_{CN}, s), 2517(ν_{BH}, w). X-ray data collection and structure solution parameters are listed in Table 1.

Bis(hydrobis(4-cyano-3-phenylpyrazolyl)(4-cyano-5-phenylpyrazolyl)borato)cobalt(II) [$(Tp^{Ph,4CN*})_2Co$] To a solution of $Co(ClO_4)_2{\cdot}6H_2O$ (0.185 g, 0.50 mmol) in 50 mL of 50:50 CH_3OH/ CH_2Cl_2 was added $KTp^{Ph,4CN}$ (0.561 g, 1.01 mmol). The pink solution turned purple immediately. The mixture was stirred for an hour until all the ligand had dissolved. The solvent was removed under reduced pressure to give a deep purple solid, which was dissolved in 50 mL of CH_2Cl_2. The solution was filtered to remove any precipitate, and the solvent was removed under reduced pressure. The final product was a purple solid (0.342 g, 0.31 mmol, 62.3%). IR (cm^{-1}, KBr pellet): 696(s), 775(s), 2233(ν_{CN}, s), 2482-

(ν_{BH}, w). Elemental Analysis, Found (Calcd) for $C_{60}H_{38}N_{18}B_2Co\cdot CH_3OH$: C, 65.63 (66.02); H, 3.51 (3.43); N, 22.92 (23.10). X-ray quality crystals were grown by layering a solution of $\text{KTp}^{\text{Ph,4CN}}$ in methanol on top of a solution of $Co(ClO_4)_2\cdot 6H_2O$ in CH_3OH/CH_2Cl_2. After allowing the solutions to diffuse together for a week, the top was removed and the solvent allowed to slowly evaporate, producing light purple crystals. IR (cm^{-1}, KBr pellet): 693(s), 775(s), 2236(ν_{CN}, s), 2521(ν_{BH}, w). X-ray data collection and structure solution parameters are listed in Table 1.

Results and Discussion

The first example of the borotropic shift in scorpionate complexes was reported with $\text{Tp}^{i-\text{Pr,4Br}}$.[14] The ligand was isolated in the normally favored conformation, with all three substituents directed away from the B−H vector. However, the only sandwich metal complexes which could be isolated involved ligands which had been isomerized such that the substituent on one pyrazole was in the 5-position. This phenomenon was rationalized by the fact that two of the $\text{Tp}^{i-\text{Pr,4Br}}$ ligands coordinated to a metal ion would have led to 12 methyl groups crowded around the equator of the coordination sphere. Isomerization of the ligand results in two of the isopropyl groups being directed away from the center and allows the other four isopropyl groups to move away from each other, thus decreasing the steric congestion.

Trofimenko and co-workers reported a number of years ago the preparation of Tp^{Ph}, identified as a ligand of intermediate steric bulk which could not support a sandwich compound but was able to participate in a 5-coordinate compound with two co-ligands.[12] It was subsequently demonstrated that, in the absence of a strongly coordinating anion, the sandwich compounds $\text{Tp}^{\text{Ph}}{}_2\text{M}$ of Fe^{II} and Mn^{II} are accessible and that these compounds had ligands displaying the "normal" conformation with all substituents in the 3-position.[5c] The Fe complex, however, has anomalously long Fe−N bonds and exhibits a very positive potential for oxidation to Fe^{III}. Treatment of this complex with *m*-chloroperoxybenzoic acid results in the isolation of $\text{Tp}^{\text{Ph*}}{}_2\text{Fe}$, containing the ligand in the isomerized form.[21] The Tp^{Ph} ligand is thus able to form the normal sandwich complex, unlike the $\text{Tp}^{i-\text{Pr,4Br}}$ ligand, but can be driven toward isomerization. By contrast, with the small Al^{3+} ion, the only isolable sandwich compound was $[\text{Tp}^{\text{Ph*}}{}_2\text{Al}]^+$.[22] The chemistry of Co^{II} with Tp^{Ph} and related ligands is somewhat more complex. No normal sandwich complex of Co has been reported with the Tp^{Ph} ligand, but Kläui and co-workers isolated a dark red, five-coordinate complex of Tp^{Ph}, in which one of the Tp ligands acts in the usual tridentate manner while the other Tp ligand coordinates to the Co through only two of the pyrazole N atoms.[23] The third pyrazole is rotated away from the metal, and the octahedral coordination around the metal is completed by an agostic interaction with the B−H bond of the bidentate Tp^{Ph} ligand. We isolated a similar complex containing one Tp^{Ph} ligand and one Bp^{Ph} ligand.[24] Pierpont and co-workers were able to isolate a normal sandwich complex of the related ligand $\text{Tp}^{\text{Cum,Me}}$.[25] On the other hand, Ruman, et al. synthesized the Na salts of both $\text{Tp}^{\text{Ph,Me}}$ and $\text{Tp}^{\text{Ph,Me*}}$ and were able to isolate the sandwich compounds of both.[26]

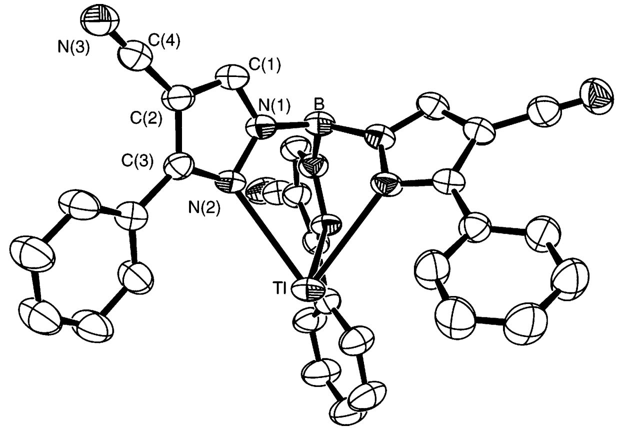

Figure 2. ORTEP drawing of $\text{TlTp}^{\text{Ph,4CN}}$ showing the 50% thermal ellipsoids.

On the basis of the chemistry of Tp^{Ph} with Fe and Mn, we expected to form similar sandwich complexes of the $\text{Tp}^{\text{Ph,4CN}}$ ligand, the only difference between the two ligands being the addition of the CN substituent at the 4-position. We have recently communicated the syntheses and crystal structures of Co and Cu complexes of the $\text{Bp}^{\text{Ph,4CN}}$ ligand,[9] which showed essentially the same structures as the analogous complexes of the non-cyano ligand Bp^{Ph}, indicating that the addition of the 4-cyano substituent has little effect, from an electronic standpoint, on the coordination geometry.

Potassium and Thallium Salts of the Ligand. The synthesis of the potassium salt of the ligand is unspectacular—it can be prepared easily from potassium borohydride and 4-cyano-3-phenylpyrazole using the pyrazole melt method that Trofimenko developed for the unsubstituted Tp. Reaction with $TlNO_3$ allowed isolation of the Tl salt, which was shown by crystallographic analysis to have all three pyrazoles in the 3-phenyl conformation. Infrared spectra of the ligand also show only one B−H stretching frequency, indicating the formation of only one isomer. An ORTEP drawing of $\text{TlTp}^{\text{Ph,4CN}}$ is given in Figure 2, with data collection and refinement parameters in Table 1. $\text{TlTp}^{\text{Ph,4CN}}$ crystallizes in the trigonal space group $P\bar{3}$, with both the Tl and B atoms situated on a crystallographic 3-fold axis.[15] The Tl ion is coordinated by the three available pyrazole N atoms of the Tp ligand. The Tl−N bonds (2.804(5) Å) are ca. 0.2 Å longer than those in TlTp^{Ph}.[27] In addition, there are short contacts

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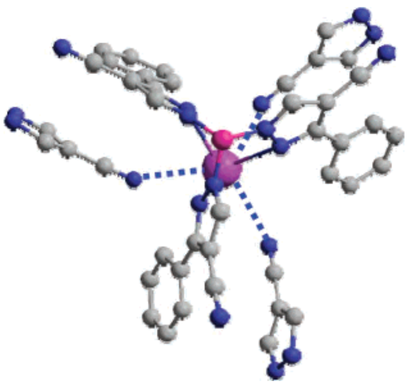

Figure 3. RASTER3D Drawing showing pyrazole interactions with $TlTp^{Ph,4CN*}$.

($Tl\cdots N$ 3.211 Å) between the Tl atom and N atoms from the CN substituents of three adjacent Tp ligands (Figure 3). There is also a short contact between the Tl atom and the B−H group of the Tp ligand directly beneath it ($Tl\cdots B$ 3.071 Å).

Iron, Cobalt, and Manganese Complexes. In a procedure similar to that resulting in the isolation of $Tp^{Ph}{}_2Mn$ and $Tp^{Ph}{}_2Fe$, triflate salts of Fe^{II} and Mn^{II} were reacted with $KTp^{Ph,4CN}$. The resulting light yellow Mn complex and light green Fe complex have IR spectra displaying B−H stretches at ca. 2480 cm^{-1} and CN stretches at ca. 2230 cm^{-1} and lacking resonances for the triflate anion, consistent with the formation of a complex with two anionic $Tp^{Ph,4CN}$ ligands balancing the divalent metal charge. Reaction of $KTp^{Ph,4CN}$ with $Co(ClO_4)_2$ produced a purple powder which displayed similar B−H and CN stretches, but none for perchlorate. We have been unable to isolate crystals of these materials directly. However, by layering a solution of $KTp^{Ph,4CN}$ in methanol on top of a solution of the metal salt in methanol/CH_2Cl_2, we were able to isolate crystalline materials in which the B−H stretch was shifted to the 2520 cm^{-1} region. This shift in B−H stretch is analogous to that seen in the Fe(II) complexes of Tp^{Ph} and Tp^{Ph*} ($\nu_{BH} = 2469$ and 2503 cm^{-1}, respectively). X-ray crystallography showed all of these complexes to contain the isomerized ligand $Tp^{Ph,4CN*}$. The three complexes are isostructural, crystallizing on a general position in the monoclinic space group $P2_1/n$. Thermal ellipsoid drawings of the three molecules are shown in Figure 4, with X-ray data collection and solution parameters in Table 1.

In each complex, there are two metal−N bond lengths (Table 2), a long one (M−N1a,b,d,e) associated with the two 3-substituted pyrazoles which are sterically prevented from closely approaching the metal and a short one (M−N1c,f) associated with the 5-substituted pyrazole. The breakdown in the trigonal symmetry of the complex is also seen in the coordination sphere bond angles. The angles involving the two 3-substituted pyrazoles on a ligand (N1a−M−N1b and N1d−M−N1e) are ∼80°, while the angles involving one 3-substituted pyrazole and one 5-substituted pyrazole are closer to 90°. The isomerization results in a phenyl ring from the opposite ligand being positioned between the 3-substituted and 5-substituted pyrazoles, while none is positioned between the two 3-substituted pyrazoles. This geometry also allows for some π-stacking between the 5-substituted pyrazole of one ligand and two phenyl groups from the other ligand, with the phenyl rings making angles of 15° and 16° with the pyrazole ring and centroid−centroid distances of 3.55 Å. One further consequence of the isomerization is relief of the constraint evident in the $Tp^{Ph}{}_2M$ complexes preventing the phenyl rings from rotating fully out of the plane of the pyrazole ring to which they are attached. This rotation is desirable in order to minimize interaction between the ortho H atom of the phenyl ring and the pyrazole ring. In the $Tp^{Ph}{}_2M$ complexes with M=Fe, Mn, or Cd, the dihedral angles between the phenyl and pyrazole rings range from 9° to 31°, while in the complexes of $Tp^{Ph,4CN*}$, these angles range from 42° to 53°.

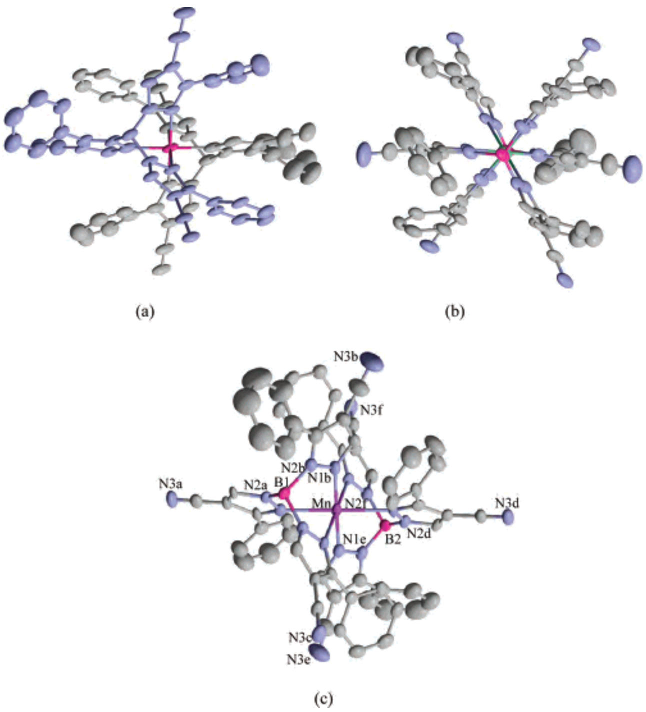

Figure 4. Raster3D Drawings of $(Tp^{Ph,4CN*})_2M$ showing 50% thermal ellipsoids. H atoms are omitted for clarity. (a) M = Co; the two ligands are depicted in blue and gray, respectively. (b) M = Fe; view down the B−Fe−B axis; atom representations: C, gray; N, blue; B, pink. (c) M = Mn, showing selected atom numbers, atom colors as in (b).

Table 2. Metal−Nitrogen Bond Lengths (Å) in Tp^R and Tp^{R*} Complexes

compound	short M−N bond	long M−N bond	ref
Tp_2Co	2.128		28
$(\eta^3\text{-}Tp^{Ph})(\eta^2\text{-}Tp^{Ph})Co$	2.103, 2.138	2.199	23
$Tp^{Ph}Bp^{Ph}Co$	2.125	2.177	24
$Tp^{Ph,Me}{}_2Co$		2.17, 2.20, 2.27	26
$Tp^{Ph,Me*}{}_2Co$	2.11, 2.15	2.17, 2.21, 2.24, 2.26	26
$Tp^{Ph,4CN*}{}_2Co$	2.042	2.226	this work
Tp_2Mn	2.25		29
$Tp^{Ph}{}_2Mn$		2.316	5c
$Tp^{Ph,4CN*}{}_2Mn$	2.160	2.309	this work
Tp_2Fe	1.975		5b
$Tp^{Ph}{}_2Fe$		2.248	5c
$Tp^{Ph*}{}_2Fe$	2.080	2.257	21
$Tp^{Ph,4CN*}{}_2Fe$	2.043	2.256	this work

Table 2 shows a comparison of M−N bond distances in Tp^{R} and Tp^{R*} complexes. The bond lengths in $Tp^{Ph,4CN*}{}_2Fe$ are very similar to those in $Tp^{Ph*}{}_2Fe$, with the short Fe−N bond slightly longer than the Fe−N bonds in Tp_2Fe and the long Fe−N bond very similar in length to that in the unisomerized $Tp^{Ph}{}_2Fe$. In the Mn and Co complexes, the short M−N bond is somewhat shorter even than M−N bonds in the complexes of unsubstituted Tp. The long Mn−N bonds in the Mn complex again are very similar in length to the M−N bonds in $Tp^{Ph}{}_2Mn$, while the long Co−N bond in $Tp^{Ph,4CN*}{}_2Co$ is similar in length to the long Co−N bonds in the bidentate/tridentate and sandwich Co compounds.

As mentioned above, the steric interactions that render the $Tp^{i-Pr,4Br}$ ligand unable to support a sandwich compound without isomerization of the ligand are not as strong in the phenyl systems. The Tp^{Ph} ligand can produce a sandwich compound without isomerization, albeit with lengthened M−N bonds. In the Fe case, only upon treatment with *m*-chloroperoxybenzoic acid is isomerization initiated. This isomerization proceeds through a transient, unisolated intermediate[21] which may involve coordination either of *m*-chloroperoxyacetate or of an oxo group transferred from MCPBA allowing the dissociation of one pyrazole N and enabling the 1,2-borotropic shift and reassociation of the pyrazole in a less strained conformation. With the $Tp^{Ph,4CN}$ ligand, it would appear that the unisomerized sandwich compound is also the kinetic product, although it has not been crystallographically characterized. Conversion to the isomerized product appears to be more facile in this case, requiring only a slower reaction in a protic solvent. In fact, when the initial product from the reaction between $Co(ClO_4)$ and $Tp^{Ph,4CN}$ is redissolved in methanol and allowed to sit for a week, the IR spectrum begins to show a shoulder growing in at 2520 cm^{-1}, indicating formation of the isomerized product.

Given the close correlation of the metrical parameters between $Tp^{Ph*}{}_2Fe$ and $Tp^{Ph,4CN*}{}_2Fe$, the more facile rearrangement cannot be explained on the basis of steric requirements of the ligand. An electronic argument would appear to be appropriate here, as it would be reasonable to expect that the electron-withdrawing cyano substituents, like the bis(trifluoromethyl) substituents studied by Dias, reduce the σ-donor ability of the pyrazole N atoms, making $Tp^{Ph,4CN}$ a weaker ligand and allowing for more facile dissociation of one pyrazole from the metal. This enables the ligand to undergo the borotropic shift to produce the thermodynamically more stable, less sterically congested product.

Conclusions

The class of cyanoscorpionate ligands, introduced with reports of bispyrazolylborates, has been extended to include trispyrazolylborates. The new ligand, $Tp^{Ph,4CN}$, forms octahedral sandwich compounds with the divalent first-row transition metal ions Fe^{II}, Mn^{II}, and Co^{II}. In forming such complexes, there is facile conversion to the isomerized ligand, $Tp^{Ph,4CN*}$.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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