Inorganic Chemistry
Article
pubs.acs.org/IC

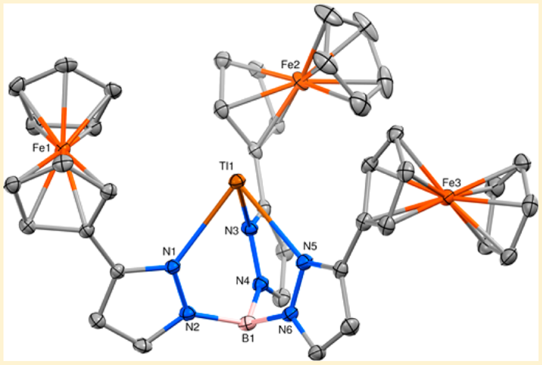
Ferrocenyl-Substituted Tris(pyrazolyl)borates—A New Ligand Type Combining Redox Activity with Resistance to Hydrogen Atom Abstraction

Eric R. Sirianni, Glenn P. A. Yap, and Klaus H. Theopold*

Department of Chemistry and Biochemistry, Brown Laboratory, University of Delaware, Newark, Delaware 19716, United States

Supporting Information

ABSTRACT: The low-temperature syntheses of ferrocenyl-substituted tris(pyrazolyl)borate ligands Tp$^{\mathrm{Fc*}}$ (hydrobis(3-ferrocenylpyrazolyl)-mono(5-ferrocenylpyrazolyl)borate), Tp$^{\mathrm{Fc,Me*}}$ (hydrobis(3-ferrocenyl-5-methylpyrazolyl)mono(5-ferrocenyl-3-methylpyrazolyl)borate), and Tp$^{\mathrm{Fc,iPr}}$ (hydrotris(3-ferrocenyl-5-isopropylpyrazolyl)borate) are reported. The Tl salts of Tp$^{\mathrm{Fc*}}$ and Tp$^{\mathrm{Fc,Me*}}$ can be thermally isomerized to the symmetric Tp$^{\mathrm{Fc}}$ (hydrotris(3-ferrocenylpyrazolyl)borate) and Tp$^{\mathrm{Fc,Me}}$ (hydrotris(3-ferrocenyl-5-methylpyrazolyl)borate) species, respectively. Conversely, upon heating, the thermal isomerization of Tp$^{\mathrm{Fc,iPr}}$ results in the generation of a mixture of regioisomers. These ligands display a reversible three-electron oxidation. The preparations of Tp$^{\mathrm{CF3,Fc}}$Tl (hydrotris(3-trifluoromethyl-5-ferrocenylpyrazolyl)borate) and PhTp$^{\mathrm{Fc}}$ (phenyltris(3-ferrocenylpyrazolyl)borate) are also reported.



INTRODUCTION

Tris(pyrazolyl)borate (Tp) ligands, aka "scorpionates", are ubiquitous in contemporary inorganic chemistry. Much of the appeal of these nitrogen tripods stems from their relative ease of synthesis and facile modification, both electronic and steric.[1] In this laboratory, we have long employed sterically hindered scorpionates, specifically Tp$^{\mathrm{tBu,Me}}$ and occasionally Tp$^{\mathrm{iPr,Me}}$, in attempts to activate dioxygen and to stabilize elusive terminal metal−oxo and −imido complexes of late transition metals (such as Co). Isolation and characterization of these highly reactive species have proven challenging and have repeatedly led to the isolation of products of C−H activation of the ligands.[2] Therefore, it was deemed desirable to synthesize novel Tp ligands that both retain the steric encumbrance of the aforementioned "tetrahedral enforcers" and feature stronger C−H bonds.[3] Employing ferrocenyl substituents on Tp appeared to be an attractive alternative to alkyl substituents, because of ferrocene's steric bulk and extremely strong C−H bonds (calculated at 117 kcal/mol).[4] An additional benefit of such a Tp ligand might be its potential redox activity, which might be used to influence reactivity at the metal coordinated by a putative Tp$^{\mathrm{Fc,R}}$ ligand.

To date, only "third generation" tris(pyrazolyl)borates containing ferrocene, i.e., those with ferrocene bonded to the boron, have been synthesized.[5] Trofimenko et al. reported the first example of a bidentate ferrocenyl-substituted bis(pyrazolyl)borate (Bp$^{\mathrm{Fc}}$) ligand in the early 1990s, but the corresponding tris(pyrazolyl)borate was never synthesized, due to "lability" of the ferrocenyl substituents.[6] Herein we describe a low-temperature synthesis of several redox active "second generation" tris(pyrazolyl)borate ligands, i.e., those in which ferrocene is bonded directly to the pyrazolyl rings.

EXPERIMENTAL SECTION

General Details. All reactions were run under a nitrogen atmosphere using standard glovebox and Schlenk techniques unless otherwise stated. Diethyl ether, pentane, tetrahydrofuran (THF), and toluene were dried by distillation from Na or K-benzophenone ketyl under a nitrogen atmosphere or by passing the solvent through activated alumina columns followed by a nitrogen purge to remove dissolved oxygen.[7] Organic chemicals were bought from Aldrich or Acros, and acetylferrocene was purchased from Strem. NMR spectra were obtained on a Bruker AVIII-400 or AV 600 spectrometer and were referenced to the residual protons of the solvent (CD_2Cl_2, 5.32 ppm; $CDCl_3$, 7.27 ppm; C_6D_6, 7.15 ppm). FT-IR spectra were recorded on Mattson Alpha Centauri or Nicolet Magna-IR 560 spectrometers with a resolution of 4 cm^{-1}. X-ray crystallographic studies were conducted at the University of Delaware X-ray Crystallography Laboratory. Elemental analyses were obtained from Robertson Microlit, Ledgewood, NJ (and by Intertek Pharmaceutical Services, Whitehouse, NJ, for **5**). 3-Ferrocenylpyrazole,[6] 3-ferrocenyl-5-methylpyrazole,[8] 3-ferrocenyl-5-trifluoromethylpyrazole,[9] and $Li(PhBH_3)\cdot 2THF$[10] were prepared by literature procedures. ***Note:*** *Thallium salts are poisonous; accordingly these compounds should be handled with the appropriate precautions and waste products must be disposed of properly.*

3-Ferrocenyl-5-isopropylpyrazole, Pz$^{\mathrm{Fc,iPr}}$H. Under an inert atmosphere, 15 g (0.066 mol) of acetylferrocene was dissolved in 100 mL of THF in a round-bottom flask equipped with a magnetic stir bar. A total of 2.63 g (0.066 mol) of KH was added in small increments, and the mixture was allowed to stir for 4 h. The resulting orange precipitate was collected on a frit and washed with THF until the washings were no longer colored. The orange solid was dried under vacuum yielding 16.6 g (0.062 mol, 95%) of $K[CH_2C(O)Fc]$. Under a

Received: July 1, 2014
Published: August 21, 2014

constant purge of N_2, a round-bottom flask equipped with a stir bar was charged with the 16.6 g (0.062 mol) of K[$CH_2C(O)Fc$] and 50 mL of ethylisobutyrate; this mixture was heated to 40 °C for 12 h. The resulting solid was filtered off quickly in air on a frit and washed with pentanes before being dissolved in methanol. A total of 4.27 g (0.062 mol) of hydrazine monohydrochloride was added, and the solution was refluxed for 6 h. The solution was added to 100 mL of water, and the mixture was extracted with methylene chloride. The methylene chloride fraction was stripped, and the resulting residue was dissolved in methanol. A total of 1.55 mL (0.031 mol) of hydrazine monohydrate was added, and the solution was refluxed for 1 h. The solution was poured into ice water and allowed to stir for 1 h. The solid was collected on a frit and washed with copious amounts of water. The solid was dried under vacuum overnight yielding 11.1 g (0.038 mol, 57% based on acetylferrocene) of the product. ^{1}H NMR (400 MHz, $CDCl_3$): 6.08 (s, 1 H), 4.57 (s, 2 H), 4.24 (s, 2 H), 4.06 (s, 5 H), 2.98 (m, 1 H), 1.3 (d, *J* = 6.59 Hz, 6 H) ppm. IR (KBR): 3093 (w), 2967 (s), 2927 (w), 1595 (s), 1577 (s), 1488 (s), 1362(s), 1129 (s), 1105 (s), 1061 (s), 1026 (s), 813 (w), 525 (s), 503 (s), 488 (s), 454 (s) cm^{-1}. Mp: 160−162 °C. Mass Spectrum (ESI) *m/z*, (%): 294, (100). Anal. Calcd for $C_{16}H_{18}N_2Fe$: C, 65.33; H, 6.17; N, 9.52. Found: C, 65.09; H, 6.25; N, 9.47.

Hydrobis(3-ferrocenylpyrazolyl)mono(5-ferrocenylpyrazolyl)-borato-thallium(I), Tp^{Fc*}Tl (1). A total of 7.05 g (0.028 mol) of 3-ferrocenylpyrazole, 0.20 g (0.009 mol) of $LiBH_4$, 25 mL of toluene, and 0.3 mL (1.7 mmol) of di(isopropoxy)methylborane were combined inside a thick walled glass ampule under N_2 atmosphere. The solution was kept at 110 °C for 3 days during which a precipitate formed. The mixture was filtered and the solid collected on a frit, washed with several portions of toluene, and dried in air. The solid was transferred to a round-bottom flask and dissolved in a minimum amount of THF to which an aqueous solution of 2.50 g (0.0095 mol) of thallium acetate was added, and the mixture was allowed to stir overnight. During the course of the reaction, an orange precipitate formed. The solid was collected on a frit, washed with several portions of water to remove the lithium acetate, and washed with hot methanol to remove excess pyrazole. The resulting product was allowed to dry at 100 °C for 3 h under vacuum yielding 4.51 g (4.65 mmol, 51%) of **1**. ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (s, 2 H), 7.45 (s, 1 H), 6.38 (s 1 H), 6.24 (s, 2 H), 4.58 (s, 4 H), 4.55 (s, 2 H), 4.30 (s, 2 H), 4.24 (s, 4 H), 4.09 (s, 5 H), 4.05 (s, 10 H) ppm. ^{11}B NMR: −3.23 ppm. IR (KBR): 3086 (w), 2483 (w, B−H), 1547 (s), 1489 (s), 1424 (m), 1240 (s), 1189 (w), 938 (s), 870 (s), 818 (w), 763 (m), 718 (m), 647 (s), 623 (s), 505 (w), 443 (s) cm^{-1}. Mp: 192−194 °C. Mass Spectrum (LIFDI) *m/z*, (%): 970.074, (100, M$^+$).

Hydrotris(3-ferrocenylpyrazolyl)borato-thallium(I), Tp^{Fc}Tl (6). Thermal Isomerization of Tp^{Fc*}Tl (1) to Tp^{Fc}Tl (6). A solid sample of Tp^{Fc*}Tl was placed inside a round-bottom flask and heated under vacuum at 220 °C for 1 h. The sample was allowed to cool to RT, quantitatively yielding the thallium salt **6** of the symmetric Tp^{Fc} ligand. ^{1}H NMR (400 MHz, $CDCl_3$): 7.62 (s, 3 H), 6.26 (s, 3 H), 4.57 (s, 6 H), 4.22 (s, 6 H), 4.03 (s, 15 H) ppm. ^{11}B NMR: −1.23 ppm. IR (KBR): 3090 (w), 2420 (w, B−H), 1549 (s), 1488 (s), 1424 (s), 1336 (s), 1204 (s), 1188 (s), 1045 (s) 1001 (s) 869 (s), 815 (s), 764 (m), 723 (s), 508 (w), 487 (s) cm^{-1}. Mp: 267−269 °C. Anal. Calcd for $C_{39}H_{34}N_6BFe_3Tl$: C, 48.32; H, 3.53; N, 8.67. Found: C, 47.71; H, 3.26; N, 8.47.

Hydrobis(3-ferrocenyl-5-methylpyrazolyl)mono(3-methyl-5-ferrocenylpyrazolyl)borato-thallium(I), Tp^{Fc,Me*}Tl (2). A total of 7.50 g (0.028 mol) of 3-ferrocenyl-5-methylpyrazole, 0.20 (0.009 mol) g of $LiBH_4$, 25 mL of toluene, and 0.3 mL (1.7 mmol) of di(isopropoxy)methylborane were combined inside a thick walled glass ampule under N_2 atmosphere. The solution was kept at 110 °C for 3 days, during which time a precipitate formed. The orange solid was collected on a frit and washed with several portions of hot toluene followed by pentane and dried. The solid was then added to a round-bottom flask containing 2.50 g (0.0095 mol) of thallium acetate and 150 mL of THF and allowed to stir overnight. The solution was filtered through a bed of Celite, and the solvent was removed under vacuum. A total of 150 mL of methanol was added to the orange tar and allowed to stir until an orange solid formed. The solid was collected on a frit, washed with several portions of methanol, and dried at 100 °C for 3 h under vacuum yielding 6.76 g (6.69 mmol, 73%) of **2**. ^{1}H NMR (400 MHz, CD_2Cl_2): 6.32 (s 1 H), 6.14 (s, 2 H), 4.58 (s, 4 H), 4.51 (s, 2 H), 4.34 (s, 2 H), 4.29 (s, 4 H), 4.17 (s, 5 H), 4.12 (s, 10 H), 2.39 (s, 3 H) 2.27 (s, 6 H) ppm. ^{11}B NMR: −7.31 ppm. IR (KBR): 3086 (w), 2918 (s), 2546 (w, B−H), 1646 (m), 1553 (s) 1424 (w), 1401 (s), 1362 (s), 1314 (s), 1225 (s), 1181 (w), 1027 (s), 1000 (s), 911 (s), 882 (s), 818 (s), 740 (s), 673 (s), 648 (s) 505 (s), 437 (m) cm^{-1}. Mp: 248−252 °C (blackening with melting). Mass Spectrum (LIFDI) *m/z*, (%): 1012.121, (100, M$^+$).

Hydrotris(3-ferrocenyl-5-methylpyrazolyl)borato-thallium-(I), Tp^{Fc,Me}Tl (7). Thermal Isomerization of Tp^{Fc,Me*}Tl (2) to Tp^{Fc,Me}Tl (7). A solid sample of Tp^{Fc,Me*}Tl (**2**) was placed inside a round-bottom flask and heated under vacuum to 250 °C for 1 h. The sample was allowed to cool to room temperature, quantitatively yielding the thallium salt 7 of the symmetric Tp^{Fc,Me} ligand. ^{1}H NMR (400 MHz, $CDCl_3$): 6.12 (s, 3 H), 4.59 (s, 6 H), 4.25 (s, 6 H), 4.11 (s, 15 H) 2.50 (s, 9 H) ppm. ^{11}B NMR: −7.84 ppm. IR (KBR): 3091 (m), 2917 (w), 2523 (w, B−H), 1559 (s), 1515 (s), 1425 (w), 1346 (s), 1318 (s), 1225 (s), 1179 (m), 1068 (m), 1000 (s), 973 (s), 882 (s), 644 (s), 507 (s) cm^{-1}. Mp: 285−287 °C. Anal. Calcd for $C_{42}H_{40}N_6BFe_3Tl$: C, 49.87; H, 3.99; N, 8.31. Found: C, 49.30; H, 3.46; N, 8.13.

Hydrotris(3-ferrocenyl-5-*iso*-propylpyrazolyl)borato-thallium(I), Tp^{Fc,iPr}Tl (3). A total of 10.0 g (0.034 mol) of 3-ferrocenyl-5-*iso*-propylpyrazole, 0.26 g (0.011 mol) of $LiBH_4$, and 0.38 mL (2.0 mmol) of di(isopropoxy)methylborane were combined in a thick walled glass ampule along with 60 mL of toluene. The reaction was allowed to stir overnight at room temperature and then heated at 100 °C for 3 days. The vessel was carefully vented and the toluene removed under vacuum and gentle heating. The residue was dissolved in a minimum amount of THF and transferred to a 250 mL round-bottom flask. To this solution, 3.0 g (0.011 mol) of solid TlOAc was added, and the mixture was allowed to stir overnight. The solution was filtered through a bed of Celite and the solvent removed under vacuum. The resulting residue was triturated with methanol until a precipitate formed. The orange solid was collected on a frit, washed with several portions of hot methanol until the washings were colorless, and dried under vacuum yielding 7.7 g (7.03 mmol, 64%) of **3**. ^{1}H NMR (400 MHz, C_6D_6): 6.29 (s, 3 H), 4.58 (s, 6 H), 4.01 (s, 6 H), 3.98 (s, 15 H), 3.64 (m, 3 H), 1.24 (d, *J* = 5.05 Hz, 18 H) ppm. ^{11}B NMR: −7.57 ppm. IR (KBr): 3435 (w), 3092 (s), 2962 (s), 2927 (s), 2868 (s), 2504 (w, B−H), 1652 (m), 1555 (s), 1460 (m), 1398 (s), 1294 (s), 1175 (s), 1105 (s), 1047 (m), 1000 (s), 975 (s), 817 (w), 785 (s), 503 (w) cm^{-1}. Mp: 178−180 °C. Anal. Calcd for $C_{48}H_{52}N_6BFe_3Tl$: C, 52.62; H, 4.78; N, 7.67. Found: C, 52.15; H, 4.62; N, 7.59.

Hydrotris(3-trifluoromethyl-5-ferrocenylpyrazolyl)borato-thallium(I), Tp^{CF3,Fc}Tl (4). A total of 8.00 g (0.025 mol) of 3-ferrocenyl-5-trifluoromethylpyrazole, 0.18 g (0.008 mol) of lithium borohydride, and 0.28 mL (1.5 mmol) of MeB(O^{i}Pr)$_2$ were combined in a thick-walled glass ampule along with 15 mL of toluene. The reaction was allowed to heat at 100 °C for 3 days. The resulting mixture was stripped of toluene and dissolved in a minimum amount of THF, and 2.20 g (0.008 mol) of TlOAc was added. The solution was then allowed to stir overnight. The solution was filtered through Celite and the THF stripped. The resulting residue was triturated with methanol and the solid collected on a frit, washed with hot methanol until the washings were colorless, and dried under vacuum yielding 4.96 g (4.23 mmol, 53%) of **4**. ^{1}H NMR (600 MHz, CD_2Cl_2): 6.64 (s, 3H), 4.02 (s, 12 H), 3.88 (s, 15 H) ppm. ^{19}F NMR: 59.17 (d, J_{F-Tl} = 821 Hz, 9 F) ppm. ^{11}B NMR: −6.39 ppm. IR (KBr): 3123 (s), 3093 (w), 2630 (w, B−H), 1646 (m), 1561 (s), 1508 (s), 1462 (s), 1369 (s), 1261 (s), 1123 (m), 1067 (w), 983 (s), 885 (s), 812 (m), 755 (s), 505 (s) cm^{-1}. Mp: 268−270 °C. Anal. Calcd for $C_{42}H_{31}N_6BF_9Fe_3Tl$: C, 42.99; H, 2.66; N, 7.16. Found: C, 42.81; H, 2.55; N, 7.06.

Phenyltris(3-ferrocenylpyrazolyl)borato-thallium(I), PhTp^{Fc}Tl (5). In a thick walled glass ampule equipped with a magnetic stir bar, a mixture of 2.1 g (8.67 mmol) of Li[$PhBH_3$]·2THF, 6.8 g (0.026 mol) of 3-ferrocenylpyrazole, and 0.28 mL (1.6 mmol) of

Table 1. Crystallographic Data and Refinement Details for Compounds 1−7

	1	2	3	4	5	6	7
formula	$C_{39}H_{34}BFe_3N_6Tl$	$C_{44}H_{46}BFe_3N_6OSTl$	$C_{96}H_{104}B_2Fe_6N_{12}Tl_2$	$C_{42}H_{31}BF_9Fe_3N_6Tl$	$C_{45}H_{38}BFe_3N_6Tl$	$C_{39}H_{34}BFe_3N_6Tl$	$C_{42}H_{40}BFe_3N_6Tl$
formula wt	969.45	1089.66	1095.69	1173.46	1045.54	969.45	1011.53
T (°C)	−78(2)	−78(2)	−78(2)	−78(2)	−78(2)	−78(2)	−78(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	7.4987(10)	11.5633(7)	21.384(3)	10.6673(16)	11.8746(14)	12.4131(8)	13.0542(7)
b (Å)	23.029(3)	13.6431(8)	21.384(3)	11.2558(17)	13.8172(17)	12.5355(8)	13.1951(7)
c (Å)	19.906(3)	14.3940(9)	16.938(4)	18.130(3)	23.992(3)	13.3993(8)	13.3690(7)
α (deg)	90	71.3780(10)	90	95.653(3)	90	107.9235(10)	108.3310(10)
β (deg)	94.727(3)	77.6110(10)	90	90.620(3)	102.011(2)	113.8710(9)	106.4350(10)
γ (deg)	90	71.2460(10)	120	110.879(2)	90	100.7072(10)	109.8410(10)
V (Å^3)	3425.8(8)	2021.8(2)	6708(3)	2021.6(5)	3850.3(8)	1694.79(18)	1850.07(17)
Z	4	2	3	2	4	2	2
D_{calc} (g cm^{-3})	1.88	1.79	1.627	1.928	1.804	1.9	1.816
μ (cm^{-1})	0.5974	0.5124	0.4587	0.5111	0.5323	0.6038	0.5535
$R(F_o)^a$	0.0414	0.0197	0.0484	0.0488	0.0338	0.0261	0.0289
$R_w(F_o^2)^b$	0.0763	0.052	0.0764	0.0935	0.0671	0.0534	0.0599

[a] $R(F_o) = \sum[(F_o) - (F_c)]/\sum(F_o)$. [b] $R_w(F_o^2) = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

Table 2. Selected Interatomic Distances and Angles for Compounds 1−7

	1		2		3		4	
distance (Å)	Tl−N(1)	2.573(4)	Tl−N(1)	2.4963(17)	Tl−N(1)	2.573(4)	Tl−N(1)	2.587(5)
	Tl−N(3)	2.654(4)	Tl−N(3)	2.5514(17)	Tl−Tl^b	3.5367(10)	Tl−N(3)	2.588(4)
	Tl−N(6)	2.643(4)	Tl−N(6)	2.5222(18)			Tl−N(5)	2.635(5)
bond angle (deg)	N(1)−Tl−N(3)	78.06(13)	N(1)−Tl−N(3)	76.66(5)	N(1)−Tl−N(1)^b	76.23(13)	N(1)−Tl−N(3)	71.00(14)
	N(1)−Tl−N(6)	75.36(13)	N(1)−Tl−N(6)	72.55(6)			N(1)−Tl−N(5)	70.49(14)
	N(3)−Tl−N(6)	75.53(13)	N(3)−Tl−N(6)	76.49(6)			N(3)−Tl−N(5)	77.13(14)

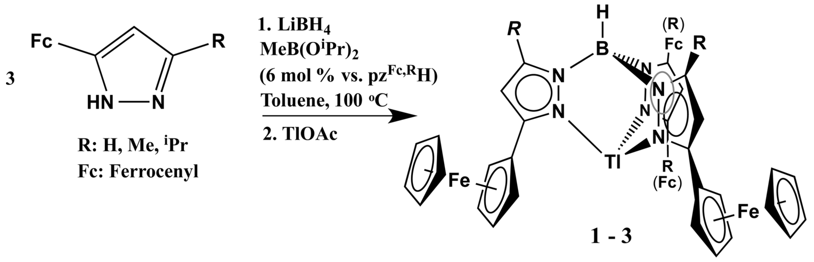
	5		6		7	
distance (Å)	Tl−N(1)	2.571(3)	Tl(1)−N(1)	2.562(3)	Tl−N(1)	2.582(3)
	Tl−N(3)	2.593(3)	Tl(1)−N(3)	2.594(3)	Tl−N(3)	2.529(3)
	Tl−CNT^a	3.205(3)	Tl(1)−N(5)	2.549(3)	Tl−N(5)	2.553(3)
bond angle (deg)	N(1)−Tl−N(3)	73.12(9)	N(1)−Tl(1)−N(3)	75.34(8)	N(1)−Tl−N(3)	75.44(9)
	N(1)−Tl−CNT^a	86.47(9)	N(1)−Tl(1)−N(5)	76.93(8)	N(1)−Tl−N(5)	75.51(9)
	N(3)−Tl−CNT^a	85.32(9)	N(3)−Tl(1)−N(5)	75.96(8)	N(3)−Tl−N(5)	78.03(9)

[a] CNT refers to the centroid of the phenyl group of **5**. [b] Generated from sixfold rotoinversion symmetry.

$MeB(O^iPr)_2$ in toluene (30 mL) was stirred at 100 °C for 3 days. The orange precipitate was filtered, washed with hot toluene (3 × 15 mL), and dried in vacuo. A mixture of the crude $PhTp^{Fc}Li$ and 1.1 g (4.0 mmol) TlOAc in 50/50 mixture of THF/DMF (100 mL) was stirred at room temperature for 1 day. The solution was filtered through Celite and the solvent removed from the filtrate under vacuum. The resulting residue was triturated with methanol and the solid collected on a frit, washed with several portions of methanol until the washings were colorless, and dried under vacuum, yielding 7.06 g (6.76 mmol, 78%) of the **5**. ^{1}H NMR (400 MHz, $CDCl_3$): 7.47 (s, 3 H), 7.40 (s, 3H), 7.16 (m, 2 H), 6.40 (s, 3 H), 4.66 (s, 6 H), 4.32 (s, 6 H), 4.13 (s, 15 H) ppm. ^{11}B NMR: 1.11 ppm. IR (KBr): 3090 (s), 2923 (s), 2852 (w), 1652 (w), 1551 (s), 1489 (s), 1314 (w), 1193 (s), 1175 (s), 1001, (s), 964 (w), 870 (s), 817 (s), 706 (w), 506 (s), 486 (s) cm^{-1}. Mp: 217−219 °C. Anal. Calcd for $C_{45}H_{38}N_6BFe_3Tl$: C, 51.69; H, 3.66; N, 8.04. Found: C, 51.00; H, 3.27; N, 7.79.

X-ray Structural Analysis for Compounds 1−7. Crystallographic data and refinement details are presented in Table 1. Selected bond distances and angles are listed in Table 2. Crystals were mounted using viscous oil onto plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were obtained from 36 data frames, 0.3° ω, from three different sections of the Ewald sphere. No symmetry higher than triclinic was observed for **2**, **4**, **6**, and **7**. The systematic absences in the diffraction data, unit cell parameters, and equivalent reflections are consistent with $R3$ and $R\bar{3}$ for **3** and, uniquely, for $P2_1/c$ for **1** and **5**. For the triclinic and trigonal cases, solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The data sets were treated with absorption corrections based on redundant multiscan data (Apex2, Bruker-AXS Inc., Madison, WI, 2007). The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2. The dimeric structure of **3** is centered at sixfold rotoinversion. A dimethyl sulfoxide solvent molecule was located in the asymmetric unit of **2**. A trifluoro methyl group in **4** was located disordered in two positions with 54/46 refined site occupancies, treated with geometrical restraints, and constrained to have equal atomic displacement between chemically equivalent disordered contributions. Slight yet significant disorder in cyclopentadienide (Cp) ligands that could not be resolved was observed, one Cp each, in **1** and **5**. The disordered groups were treated with rigid-bond U restraints. All non-hydrogen atoms were refined with anisotropic displacement parameters. Borohydride H atoms on **1**, **3**, and **7** were located from the difference map and constrained to U_{iso} equal to 1.2 B atom U_{eq}. All other hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2, or 1.5 for methyl, U_{eq} of the attached atom. Scattering factors are contained in the SHELX-2013 program library.[11] Structural information has been deposited with the Cambridge Structural Crystallographic Centre under depositary numbers CCDC 994933−994939.

Scheme 1. Synthesis of $Tp^{Fc,R}$ Ligands as Thallium Salts



RESULTS AND DISCUSSION

Our initial attempts to synthesize ferrocenyl-substituted hydrotris(pyrazolyl)borates fell afoul of the previously noted thermal decomposition of the free pyrazoles. Thus, the high temperatures required to effect the threefold substitution at boron resulted in the formation of 1,1′-bis(pyrazolyl)ferrocene and free ferrocene. This disproportionation of the metallocene dictated a less severe preparative procedure. Coincidentally, Chen and Jordan had recently reported a Lewis acid catalyzed low-temperature tris(pyrazolyl)borate synthesis.[12] Appropriate modification of this procedure–involving slightly increased catalyst loadings and reaction temperatures–did eventually produce the desired Tp ligands in acceptable yields (see Scheme 1).

The ^{1}H NMR spectra of thallium salts **1** (R = H) and **2** (R = Me) thus obtained revealed two sets of pyrazolyl proton resonances, in a 2:1 ratio, indicating the formation of unsymmetric ligands as the only products. X-ray crystallography subsequently confirmed that both $Tp^{Fc*}Tl$ (**1**) and $Tp^{Fc,Me*}Tl$ (**2**) were singly "N-confused" regioisomers (i.e., one of the pyrazole groups exhibited the Fc-substituent in the 5-position—adjacent to boron; the superscripted asterisk "*" denotes this type of isomerism).[1b] The molecular structure of **1** is shown in Figure 1, and selected interatomic distances and angles are listed in Table 2 (The analogous structure of **2** is depicted in the Supporting Information, Figure 1S).

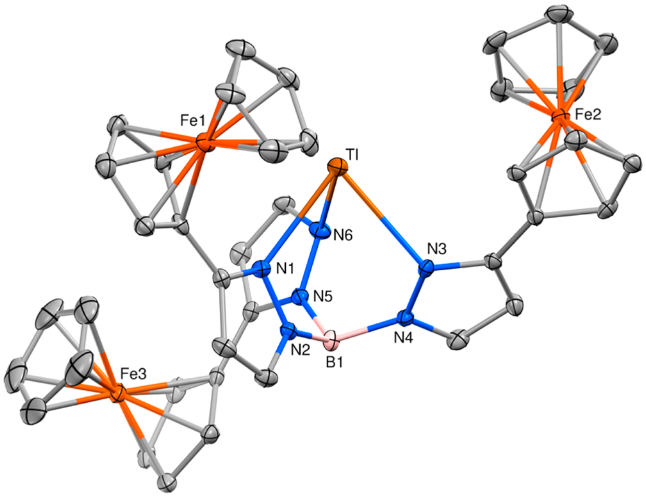


Figure 1. Molecular structure of $Tp^{Fc*}Tl$ (**1**) at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Notably, $Tp^{Fc,iPr}Tl$ (**3**) did not suffer the same N-confusion problem. Its ^{1}H NMR spectrum exhibited only one set of resonances, consistent with a threefold symmetric ligand. This expectation was born out by its crystal structure (shown in Figure 2); however, **3** offered another surprise. In contrast to all other compounds reported here and contrary to the vast majority of extant TpTl derivatives, the structure of **3** in the solid state features a dimer with a short Tl–Tl distance of 3.5367(1) Å! To our knowledge, the only other Tp derivatives exhibiting comparable interactions in the solid state are dimeric $[Tp^{Tol}Tl]_2$ (Tl–Tl: 3.86 Å) and tetrameric $[Tp^{cPr}Tl]_4$ (Tl–Tl: 3.64 Å).[13] Although the valence electron configuration of Tl(I)—consisting of the proverbial $6s^2$ "inert pair"—would not intuitively suggest a propensity for Tl–Tl bonding, there exist a significant number of compounds in which Tl(I)–Tl(I) distances shorter than the sum of two van der Waals radii (i.e., 1.96 Å) have been observed.[14] These interactions, averaging ~3.5 Å, are generally too weak to persist in solution. In trying to discern why only **3**, of all the compounds reported herein, exhibits such an interaction, we note that its density in the solid state is significantly lower (see Table 1). Accordingly, we suggest that packing forces associated with inherently more efficient filling of space dominate the weak Tl–Tl interactions for all but **3**, the monomer of which apparently does not pack well.

From a utilitarian viewpoint the formation of the N-confused ligands in **1** and **2** is less than ideal. However, we considered the possibility that the low-temperature synthesis results in the formation of kinetic products, which might be converted into the more useful C_3-symmetric products upon heating. Such a phenomenon has previously been observed in the synthesis of $Tp^{Ms}Tl$ (Tp^{Ms} = hydrotris(3-mesitylpyrazolyl)borate).[15] The attempted preparation of this ligand in a high-boiling solvent resulted in the isolation of the N-confused kinetic product, $Tp^{Ms*}Tl$ (Tp^{Ms*} = hydrotris(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)borate), along with the minor thermodynamic product, $Tp^{Ms}Tl$. However, $Tp^{Ms*}Tl$ could be rearranged into the symmetric isomer upon heating. These results inspired an exploration of the thermal isomerization of **1** and **2**. Satisfyingly, heating solid samples of the $Tp^{Fc*}Tl$ (**1**) or $Tp^{Fc,Me*}Tl$ (**2**) under vacuum to 220–250 °C resulted in their quantitative transformation into the symmetric isomers **6** and **7** (see Scheme 2). Heating of the symmetric $Tp^{Fc,iPr}Tl$, in contrast, resulted in the formation of a mixture of several regioisomers, as indicated by ^{1}H NMR spectroscopy. Attempts to separate this mixture proved impractical. Only the symmetric compound **3** could be recovered by fractional crystallization.

The ^{1}H NMR spectra of **6** and **7** featured only one set of pyrazole resonances,respectively, and X-ray crystallographic structure determinations confirmed the formation of the symmetric ligands (see Figure 3 for $Tp^{Fc,Me}Tl$ (**7**) and Supporting Information Figure 2S for $Tp^{Fc}Tl$ (**6**)). Selected interatomic distances and angles are listed in Table 2.

The symmetric compounds exhibited slightly different physical properties, with some discernible trends. Thus, the

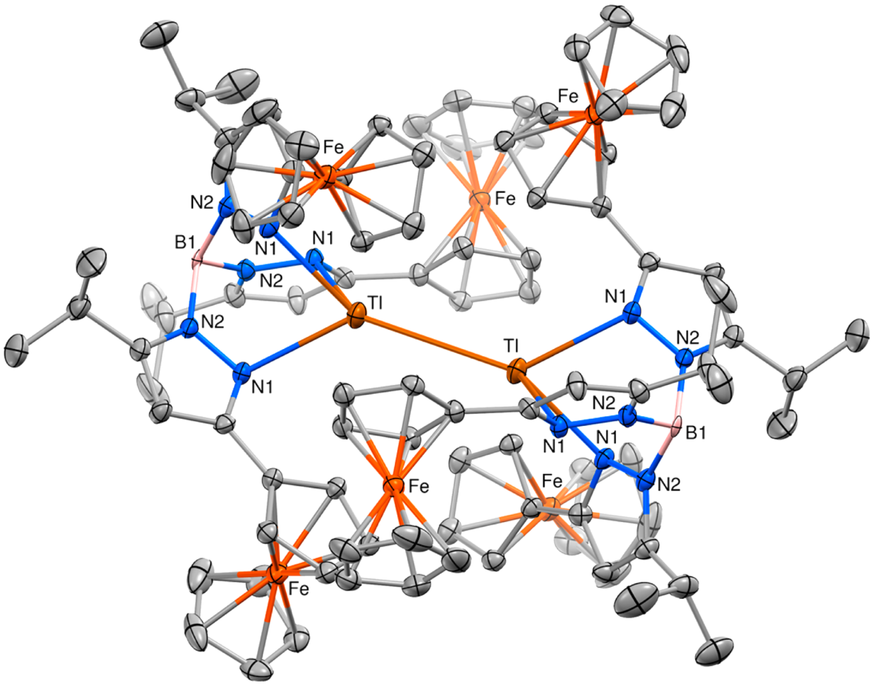


Figure 2. Molecular structure of $[\mathrm{Tp}^{\mathrm{Fc},i\mathrm{Pr}}\mathrm{Tl}]_2$ (**3**) in the solid state. Thermal ellipsoids are drawn at the 30% probability level, and all hydrogen atoms have been omitted for clarity.

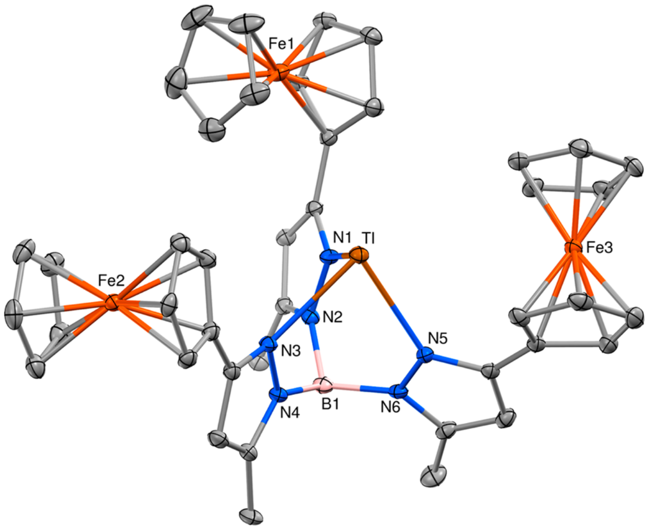


Figure 3. Molecular structure of $\mathrm{Tp}^{\mathrm{Fc,Me}}\mathrm{Tl}$ (**7**). Thermal ellipsoids are drawn at the 30% probability level, and all hydrogen atoms have been omitted for clarity.

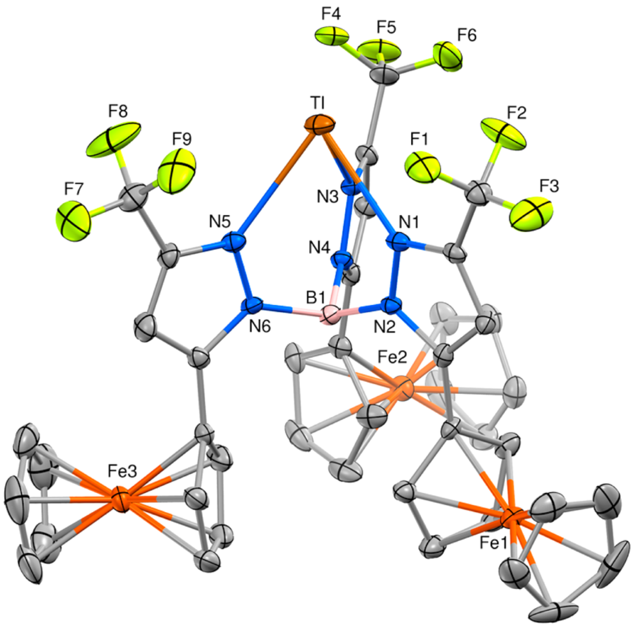
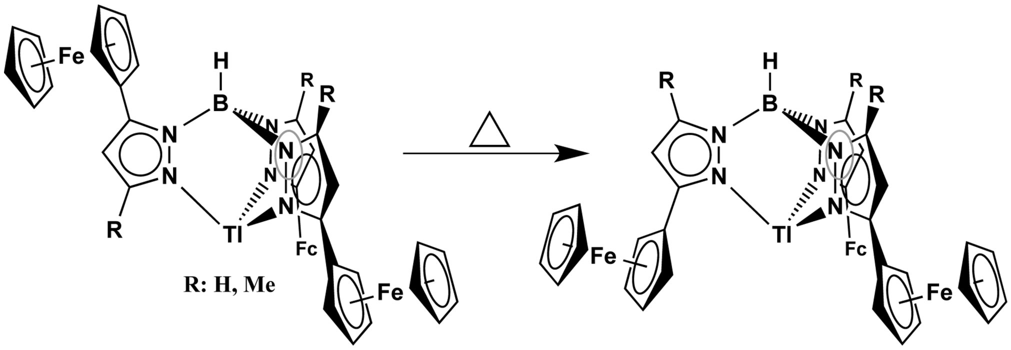


Figure 4. Molecular structure of $\mathrm{Tp}^{\mathrm{CF3,Fc}}\mathrm{Tl}$ (**4**). Thermal ellipsoids are drawn at the 30% probability level, and all hydrogen atoms have been omitted for clarity.

melting points of symmetric **6** (267 °C) and **7** (285 °C) are significantly elevated over those of regioisomers **1** (192 °C) and **2** (248 °C). IR spectra revealed a redshift in the B−H stretching frequency from 2483 to 2420 cm^{-1} for **1**/**6** and from 2546 to 2523 cm^{-1} for **2**/**7**, respectively. Likewise, the $^{11}\mathrm{B}$ NMR resonance of **1** shifts downfield from −3.23 ppm for the N-confused ligand to −1.23 ppm for the symmetric ligand of **6**. These observations are all consistent with the trends in the $\mathrm{Tp}^{\mathrm{Ms*}}\mathrm{Tl}/\mathrm{Tp}^{\mathrm{Ms}}\mathrm{Tl}$ system.[15] This harmony is only broken by the fact that $\mathrm{Tp}^{\mathrm{Fc,Me}}\mathrm{Tl}$ (**7**) displays its $^{11}\mathrm{B}$ NMR resonance at −7.84 ppm, i.e., slightly upfield compared to its regioisomer at −7.31 ppm.

Having thus procured a series of ferrocenyl-substituted tris(pyrazolyl)borates, we sought to round out this portfolio of such ligands by (i) introducing electron-withdrawing substituents in place of the donating alkyl groups and (ii) adding a representative with substitution on boron. On the first count, and ever mindful of our aim to create ligands that resist C−H activation by reactive ligands (e.g., oxo or imido groups), we chose the introduction of perfluoromethyl groups. Accordingly, utilization of three equivalents of 3-ferrocenyl-5-trifluoromethyl-pyrazole under the same reaction conditions as before produced a new thallium trispyrazolyl(borate) **4** in adequate yield (53%). Its $^{1}\mathrm{H}$ NMR spectrum showed only one set of pyrazolyl resonances, heralding the formation of a symmetric ligand. However, while the

Scheme 2. Thermal Isomerization of $\mathrm{Tp^{Fc,R*}Tl}$ to $\mathrm{Tp^{Fc,R}Tl}$ (R = H, Me)



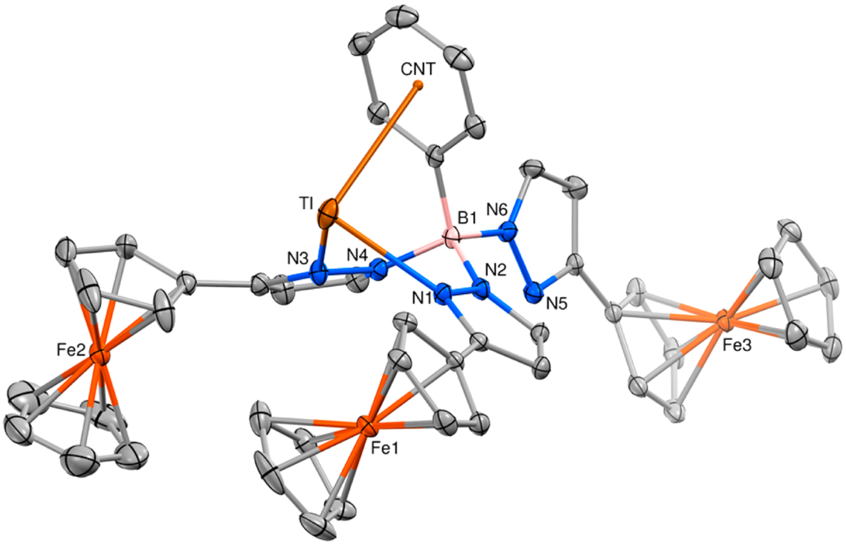


Figure 5. Molecular structure of $\mathrm{PhTp^{Fc}Tl}$ (**5**). Thermal ellipsoids are drawn at the 30% probability level, and all hydrogen atoms have been omitted for clarity.

X-ray crystal structure of **4** (see Figure 4) indeed showed the symmetric structure of the ligand that was apparent in the ^{1}H NMR spectrum, it also revealed that all of the ferrocenyl substituents are now in the 5-position and that the trifluoromethyl groups occupy the 3-positions of the pyrazole rings! Similar hydrotris(pyrazolyl)borates with bulky substituents, namely, hydrotris[3-trifluoromethyl-5-(2-thienyl)pyrazolyl]borate thallium(I) ($\mathrm{Tp^{CF3,Tn}Tl}$)[16] and hydrotris(3-trifluoromethyl-5-phenylpyrazolyl)-borate ($\mathrm{Tp^{CF3,Ph}Tl}$),[17] also display the trifluoromethyl groups in the 3-position of the pyrazolyl groups, suggesting a general preference for the more electron rich nitrogen of the pyrazole to bind to the boron atom. Lest this conclusion sound too authoritative, we note in passing that we have also prepared (in a different solvent) and structurally characterized $\mathrm{Bp^{Fc,CF3}Tl}$ (see Figure 3S in the Supporting Information), i.e., a bis(pyrazolyl)-borate of the very same pyrazole that exhibits the opposite regiochemistry (i.e., both ferrocenyl moieties in the 3-position and $\mathrm{CF_3}$-groups adjacent to boron). To date we have not ascertained whether this is a true intermediate in the preparation of **4**, but this observation emphasizes the fact that regioisomerism in Bp and Tp ligands can be a subtle effect governed by kinetics as well as thermodynamic preferences.

Finally, we have also extended the scope of our synthesis to ligands with tetra-substituted boron. For example, heating three equivalents of 3-ferrocenylpyrazole with $\mathrm{Li[PhBH_3]}$ and $\mathrm{MeB(O^iPr)_2}$ (6 mol % vs pyrazole) in toluene for 3 days resulted in the precipitation of the corresponding phenyltris-(3-ferrocenylpyrazolyl)borate ($\mathrm{PhTp^{Fc}}$) ligand as the lithium salt. After work up with TlOAc, $\mathrm{PhTp^{Fc}Tl}$ (**5**) was isolated in 78% yield as an orange solid. The solution ^{1}H NMR spectrum of this compound also suggested a symmetric disposition of the pyrazolyl moieties. However, the solid state structure of **5** (see Figure 5) revealed yet another structural motif, namely, a thallium atom that is coordinated by only two of the available pyrazolyl groups while engaging in an interaction with the π-system of the phenyl substituent on boron. This type of coordination is not uncommon for phenyltris(pyrazolyl)borate ligands with bulky substituted pyrazoles.[18] In solution, **5** may either adapt a different structure, i.e., with all three pyrazolyl moieties coordinated to thallium, or, more likely, the degenerate exchange of the coordinated and noncoordinated pyrazolyl groups is fast on the NMR time scale.

The ferrocenyl groups of the new ligands **1**−**7** are of course redox active, and stepwise removal of between one and three electrons per ligand can be envisioned, which might affect the reactivity of any metal ions coordinated by these ligands. The results of cyclic voltammetry experiments on a representative set of compounds are shown in Figure 6. These ligands each display a single reversible redox process at a potential of approximately +0.62 V versus decamethylferrocene ($\mathrm{Cp^*_2Fe}$, E^0 = −0.59 V vs $\mathrm{Fc/Fc^+}$).[19] Integrations of the half wave currents against the reference compound were consistent with

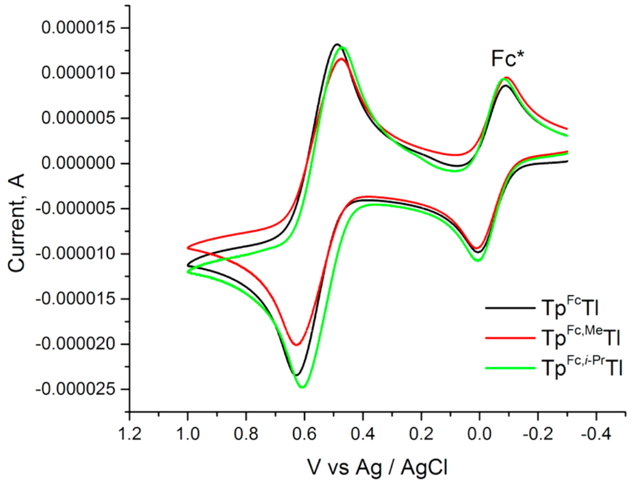


Figure 6. Cyclic voltammetric responses of **6**, **7**, and **3** in CH$_2$Cl$_2$ solution containing 0.1 M [NBu$_4$][PF$_6$] and Cp*$_2$Fe as a reference, recorded at a platinum electrode using a scan rate of 100 mV/s.

the concerted removal of three electrons per ligand molecule. Apparently there exists little to no electronic communication between the three ferrocenyl substituents, resulting in their simultaneous oxidation at a redox potential that differs only very slightly from that of ferrocene itself.

■ CONCLUSION

The obstacles associated with the synthesis of ferrocenyl-substituted hydrotris(pyrazolyl)borate ligands have been overcome via implementation of a low-temperature preparative procedure. Two of these compounds, i.e., Tp$^{\mathrm{Fc}*}$Tl and Tp$^{\mathrm{Fc,Me}*}$Tl, were initially isolated as N-confused regioisomers, but they can be easily rearranged to the desired symmetric ligand via heating in the solid state. These compounds represent a new class of redox-active Tp ligands, which display a single reversible three-electron oxidation. We anticipate that ligands of the type Tp$^{\mathrm{Fc,R}}$ may find use in situations where substantial steric protection of the metal must be combined with resistance of the 3-substituents to C−H activation. The redox activity of the ligands may be an additional benefit. We are currently exploring these possibilities in the coordination chemistry of first row transition metals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Molecular structures—determined by X-ray diffraction—of Tp$^{\mathrm{Fc,Me}*}$Tl (**2**), Tp$^{\mathrm{Fc}}$Tl (**6**), and Bp$^{\mathrm{Fc,CF3}}$Tl and crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Klaus H. Theopold. E-mail: theopold@udel.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has been supported by a grant from the U.S. Department of Energy (DE-FG02-92ER14273, to K.H.T., and by an instrumentation grant from the U.S. National Science Foundation (CRIF CHE-1048367). We thank Mr. John DiMeglio for assistance with the electrochemical experiments.

■ DEDICATION

Dedicated to the memory of Swiatoslaw "Jerry" Trofimenko, sage of all things scorpionate.

■ REFERENCES

(1) (a) Trofimenko, S. *Scorpionates*; Imperial College Press: London, 1999. (b) Pettinari, C. *Scorpionates II: Chelating Borate Ligands*; Imperial College Press: London, 2008.

(2) (a) Egan, J. W.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445−2446. (b) Reinaud, O. M.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, *116*, 6979−6980. (c) Thyagarajan, S.; Incarvito, C.; Rheingold, A.; Theopold, K. *Chem. Commun.* **2001**, 2198−2199. (d) Thyagarajan, S.; Shay, D. T.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2003**, *125*, 4440−4441. (e) Shay, D.; Yap, G.; Zakharov, L.; Rheingold, A.; Theopold, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1508−1510.

(3) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

(4) Elihn, K.; Larsson, K. *Thin Solid Films* **2004**, *458*, 325−329.

(5) (a) Guo, S. L.; Peters, F.; de Biani, F. F.; Bats, J. W.; Herdtweck, E.; Zanello, P.; Wagner, M. *Inorg. Chem.* **2001**, *40*, 4928−4936. (b) Herdtweck, E.; Peters, F.; Scherer, W.; Wagner, M. *Polyhedron* **1998**, *17*, 1149−1157. (c) de Biani, F. F.; Jakle, F.; Spiegler, M.; Wagner, M.; Zanello, P. *Inorg. Chem.* **1997**, *36*, 2103−2111. (d) Jakle, F.; Polborn, K.; Wagner, M. *Chem. Ber.* **1996**, *129*, 603−606.

(6) Niedenzu, K.; Serwatowski, J.; Trofimenko, S. *Inorg. Chem.* **1991**, *30*, 524−527.

(7) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

(8) Chabert, N.; Jacquet, L.; Marzin, C.; Tarrago, G. *New J. Chem.* **1995**, *19*, 443−452.

(9) Zhang, Q.; Song, W. L.; Hossain, A. M. S.; Liu, Z. D.; Hu, G. J.; Tian, Y. P.; Wu, J. Y.; Jin, B. K.; Zhou, H. P.; Yang, J. X.; Zhang, S. Y. *Dalton Trans.* **2011**, *40*, 3510−3516.

(10) Tsoureas, N.; Bevis, T.; Butts, C. P.; Hamilton, A.; Owen, G. R. *Organometallics* **2009**, *28*, 5222−5232.

(11) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.

(12) Chen, C. L.; Jordan, R. F. *Organometallics* **2010**, *29*, 3679−3682.

(13) (a) Ferguson, G.; Jennings, M. C.; Lalor, F. J.; Shanahan, C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 2079−2082. (b) Rheingold, A. L.; Liable-Sands, L. M.; Trofimenko, S. *Chem. Commun.* **1997**, 1691−1692.

(14) (a) Akhbari, K.; Morsali, A. *Coord. Chem. Rev.* **2010**, *254*, 1977−2006. (b) Ghosh, P.; Rheingold, A. L.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 5464−5467.

(15) Rheingold, A. L.; White, C. B.; Trofimenko, S. *Inorg. Chem.* **1993**, *32*, 3471−3477.

(16) Han, R. Y.; Ghosh, P.; Desrosiers, P. J.; Trofimenko, S.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1997**, 3713−3717.

(17) Dias, H. V. R.; Goh, T. K. H. H. *Polyhedron* **2004**, *23*, 273−282.

(18) (a) Janiak, C.; Braun, L.; Girgsdies, F. *J. Chem. Soc., Dalton Trans.* **1999**, 3133−3136. (b) Kisko, J. L.; Hascall, T.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 10561−10562. (c) Kisko, J. L.; Hascall, T.; Kimblin, C.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1999**, 1929−1935.

(19) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: Hoboken, NJ, 2001.