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Tl(I), Fe(II), and Co(II) Complexes Supported by a Monoanionic *N,N,N′*-Heteroscorpionate Ligand Bis(3,5-di-tertbutylpyrazol-1-yl)-1-CH$_2$NAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$)

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The lithium salt (L)Li(THF) (L$^-$ = bis(3,5-di-tertbutylpyrazol-1-yl)-1-CH$_2$NAr, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) can be readily prepared from lithium bis(3,5-di-tertbutylpyrazol-1-yl)methide and the *N*-methyleneaniline H$_2$C═NAr. This *N,N,N′*-heteroscorpionate lithium reagent can be transmetalated with Tl(OTf), FeCl$_2$(THF)$_{1.5}$, and CoCl$_2$ to yield the (L)Tl, (L)FeCl, and (L)CoCl complexes, respectively. Single crystal structural data for compounds (L)Li(THF), (L)Tl, (L)FeCl, and (L)CoCl reveal in each case the hapticity of the sterically demanding, monoanionic L$^-$ ligand to be κ^3-N$_3$.

Introduction

Tris(pyrazolyl)borate ligands constitute an invaluable class of ligands for the stabilization of elements ranging from early- and late-transition metals, to main group, as well as the lanthanides and actinides.[1] One of several traits which makes these ligands attractive is their ability to coordinate in a κ^3 mode via the nitrogen lone pairs of the three pyrazolyl fragments. In addition, these ligands are tripodal yet monanionic, thus, they allow a greater degree of substitution chemistry at a sterically protected metal center.

To this extent, we have drawn our attention to a new class of tris(pyrazolyl)borate hybrids having instead the putative tris(3,5-ditertbutylpyrazol-1-yl)methane framework,[2] where one pyrazole pendant arm has been replaced with a hard monoanionic group, such as a methyleneanilide. Replacing the borate group avoids 1,2-borotropic rearrangements as well as bond cleavage reactions inflicted by the B−N linkages. In addition, these systems also allow one to introduce a hard donor as well as a monoanionic charge without sacrificing both the fac mode of coordination and steric protection.

Otero,[3] Carrano,[4] and Burzlaff[5] have reported an attractive class of heteroscorpionate ligands containing the bis(pyrazol-1-yl)methane skeleton. These systems can be readily prepared via replacement of one methylene hydrogen for a carboxylate, dithiocarboxylate, alkoxide, aryloxide, or 1,1-diphenylmethylcyclopentadienyl group. Likewise, Parkin and others[6] have also synthesized several heteroscoropionate hybrids with the

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bis(3,5-R_2pyrazol-1yl) methane (R = ^{t}Bu or CH_3) framework. Inspired by their work, we report the *N*,*N*,*N′*-heteroscorpionate analogue bis(3,5-di-tertbutylpyrazol-1-yl)-1-CH_2NAr, where Ar = 2,6-$^iPr_2C_6H_3$. This scorpionate-anilide hybrid can support Tl(I) as well as divalent Fe(II) and Co(II) scaffolds via κ^3 coordination of the ligand. For the latter two transition metals, the ligand enforces a tetrahedral geometry, which is a common trait among the parent tris(pyrazolyl)-borate system.[1]

Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere.[7] Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and were further dried by passage through one column of activated alumina and one of Q-5.[8] Diethyl ether and CH_2Cl_2 were dried by passage through two columns of activated alumina.[8] THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF was transferred under vacuum into bombs before being transferred into a drybox. C_6D_6 was purchased from Cambridge Isotope Laboratory (CIL), degassed, and dried over 4 Å molecular sieves and CaH_2, respectively. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Di-tertbutylpyrazole,[9] bis(3,5-di-tertbutylpyrazol-1-yl)methane,[5b] lithium bis(3,5-di-tertbutylpyrazol-1-yl)methide (generated and used in situ),[5b] methyleneaniline $H_2C{=}NAr$ (Ar = 2,6-$^iPr_2C_6H_3$),[10] and $FeCl_2(THF)_{1.5}$ [11] were prepared according to the literature. All other chemicals were used as received. Infrared spectra (KBr plates, Nujol) were measured using a Nicolet 510P FTIR spectrometer. CHN analysis was performed by Desert Analytics, Tucson, AZ. ^1H and ^{13}C spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^1H and ^{13}C NMR spectra are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 and 128.0 ppm). ^{205}Tl NMR spectral data were collected on a Varian Inova 500 instrument. Chemical shifts were externally referenced to 0.1 M aqueous $Tl(NO_3)$ at 0.0 ppm.[12] Cyclic voltammetry was performed in predried solutions of THF (0.3−0.5 M of predried and recrystallized TBAH, Aldrich). A platinum disk (2.0 mm diameter, Bioanalytical Systems), a platinum wire, and silver wire were employed as the working, auxiliary, and reference electrodes, respectively. A one-compartment cell was used in the CV measurement. The electrochemical response was collected with the assistance of an E2 Epsilon (BAS) autolab potentiostat/galvanostat with BAS software. The IR drop correction was applied when significant resistance was noted. All potentials were reported against the ferrocenium/ferrocene couple (0 V) measured as an internal standard, and the spectra were recorded under an N_2 atmosphere. In a typical CV experiment, 15−20 mg of crystalline **3** or **4** were dissolved in ∼5 mL of a TBAH solution in THF at 26 °C. X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2(g) at low temperatures.

Synthesis of 1. In a 500 mL round-bottom flask bis(3,5-di-*tert*-butylpyrazole-1-yl)-methane (3.5 g, 9.4 mmol) was dissolved in THF (200 mL), and the solution cooled to −78 °C. An analogously cold *n*BuLi solution (1.6 M solution, 6.17 mL, 9.87 mmol) was added to the cold solution via cannula. The solution was stirred for 1.5 h at this temperature and then allowed to warm to −51 °C. *N*-methyleneaniline $H_2C{=}NAr$ [1.78 gm, 9.4 mmol] was added by cannula transfer, and the mixture was allowed to stir for 30 min at −51 °C. The reaction mixture was then warmed slowly to room temperature (using an ice bath) and stirred for an additional hour. The volatiles were evaporated completely to yield a solid which was washed with cold hexane to give pure product (L)Li(THF) (**1**) (L^- = bis(3,5-di-tertbutylpyrazol-1-yl)-1-CH_2NAr, Ar = 2,6-$^iPr_2C_6H_3$) (4.61 gm, 7.2 mmol, 76.6% yield). ^1H NMR (24 °C, 300.1 MHz, C_6D_6): δ 7.22 (d, Ar, 2H), 7.05 (t, C*H*CH_2NAr, 1H), 6.92 (t, Ar, 1H), 5.88 (s, Ar, 2H), 4.32 (d, CHCH_2NAr, 2H), 3.48 (septet overlapped with THF resonance, C*H*Me_2, 6H), 1.30−1.17 (br, CHMe_2, CMe_3 and THF resonance, 34H), 1.09 (s, CMe_3, 18H). ^{13}C NMR (23 °C, 75.46 MHz, C_6D_6): δ 160.5, 160.0, 152.7, 142.9, 123.4, 115.5, 101.5, 74.9 (*C*HCH_2NAr, J_{C-H} = 142 Hz), 69.0 (THF), 63.4 (CH*C*H_2NAr, J_{C-H} = 129 Hz), 32.7 (*C*Me_3), 32.3 (*C*Me_3), 31.84 (CMe_3), 30.9 (CMe_3), 28.3 (*C*HMe_2), 25.6 (THF), 25.2 (CHMe_2). Anal. Calcd for $C_{40}H_{66}N_5LiO$: C, 75.08; H, 10.40; N, 10.94. Found: C, 74.74; H, 10.46; N, 11.25.

Synthesis of the Free Base HL. In a Schlenk flask the lithium salt **1** (2.0 g, 3.1 mmol) was dissolved in THF, and degassed water (56.26 mg, 3.1 mmol) was added dropwise. The mixture was stirred for 1 h, and the THF was evaporated under reduced pressure to afford **HL** as a white solid (1.68 g, 2.98 mmol, 96% yield). ^1H NMR (24 °C, 300.1 MHz, C_6D_6): δ 7.52 (t, C*H*CH_2NHAr,1H), 7.16 (m, Ar, 3H), 6.09 (s, Ar, 2H), 4.22 (br, CHCH_2N*H*Ar, 1H), 4.12 (dd, CHCH_2NHAr, 2H), 3.46 (septet, C*H*Me_2, 2H), 1.45 (s, CMe_3, 18 H), 1.34 (d, CHMe_2, 12H), 1.17(s, CMe_3, 18H). ^{13}C NMR (24 °C, 75.46 MHz, C_6D_6): δ 159.9, 154.7, 143.5, 142.9, 124.7, 124.5, 103.7, 78.89 (*C*HCH_2NHAr), 55.14 (CH*C*H_2NHAr), 33.03 (*C*Me_3) 32.89 (*C*Me_3), 31.29 (CMe_3), 30.86 (CMe_3), 28.52 (*C*HMe_2), 25.12 (CHMe_2). MS-CI, $[M + H]^+$: calcd 562.89, found 562.48.

Deprotonation of HL to Afford 1. HL was dissolved (300 mg, 0.53 mmol) in toluene (∼10 mL) and cooled to −35 °C. *n*BuLi (1.6 M solution, 0.33 mL, 0.53 mmol) was diluted in hexane (∼5 mL) and added dropwise to the H(L) solution after it was cooled to −35 °C. The mixture was stirred for 1 h, and the white precipitate was collected by drying the solution in vacuo. That white residue was washed with cold hexane to yield LLi (most likely $[LLi]_x$) (314 mg, 0.49 mmol, 92% yield). Exposure of the white solid to THF and evaporation of the solvent lead to clean formation of **1** as shown by ^1H NMR in C_6D_6 (vide supra).

Synthesis of 2. Complex **1** (181 mg, 0.283 mmol) was dissolved in THF (∼5 mL) and cooled to −35 °C in a vial. In an another vial Tl(OTF) (100 mg, 0.283 mmol) in THF (∼5 mL) was cooled

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to −35 °C. Complex **1** was added dropwise to the Tl(OTF) solution and stirred for 1 h. THF was removed in vacuo, and the residue was extracted with benzene. The solution was filtered, and the filtrate was dried in vacuo and extracted in diethyl ether. The Et_2O solution was concentrated and cooled to −35 °C to yield colorless crystals of (L)Tl (**2**) (172 mg, 0.225 mmol, 79.4% yield). The solution and the white crystals of **2** begin to rapidly decompose to a dark precipitate. Workup of the reaction mixture must be rapid, and the solids must be stored cold and in the absence of light to prevent decomposition. ^1H NMR (24 °C, 300.1 MHz, C_6D_6): δ 7.38 (d, Ar, 2H), 7.12 (t, Ar, 1H), 6.96 (br, C*H*CH_2NAr, 1H), 6.08 (s, Ar, 2H), 5.70 (br, CHCH_2NAr, 2H), 3.78 (septet, C*H*Me_2, 2H), 1.41−1.38 (br, CHMe_2 and CMe_3, 30H), 1.14 (s, CMe_3, 18H). ^{13}C NMR (24 °C, 75.46 MHz, C_6D_6): δ 160.6, 153.2, 146.6, 127.8, 123.5, 121.1, 102.7, 78.0 (*C*HCH_2NAr), 61.6 (CHCH_2NAr), 32.6 (*C*Me_3), 32.3 (CMe_3), 31.1 (CMe_3), 27.1 (*C*HMe_2), 25.2 (CHMe_2). One carbon resonance was not located. ^{205}Tl NMR (24 °C, 289.35, C_6D_6): 3300 ($\Delta\nu_{1/2} = 4492$ Hz). MS-CI, $[M + H]^+$: calcd 766.39, found 766.39. Multiple attempts to obtain satisfactory elemental analysis failed given the sensitivity of the complex.

Synthesis of 3. Complex **1** (272 mg, 0.426 mmol) was dissolved in toluene (∼5 mL), and $FeCl_2(THF)_{1.5}$ (100 mg, 0.426 mmol) in toluene (∼5 mL) was added dropwise after both solutions were cooled to −35 °C. The reaction mixture was stirred for 12 h, and the yellow solution was filtered. The filtrate was evaporated in vacuo. The residue was extracted with toluene and filtered. The solution was slowly concentrated, and yellow crystals of (L)FeCl (**3**) were obtained by cooling the solution to −35 °C (186 mg, 0.302 mmol, 70.8% yield). ^1H NMR (24 °C, 300.1 MHz, C_6D_6): δ 14.1 ($\Delta\nu_{1/2} = 119$ Hz), 12.3 ($\Delta\nu_{1/2} = 36$ Hz), 11.16 (br), 6.99 ($\Delta\nu_{1/2} = 61$ Hz), 6.42 ($\Delta\nu_{1/2} = 69$ Hz), 2.37 ($\Delta\nu_{1/2} = 273$ Hz), −21.9 (br), −22.2 ($\Delta\nu_{1/2} = 35$ Hz), −29.1 ($\Delta\nu_{1/2} = 32$ Hz). IR (KBr plates, Nujol): 1542 (s), 1477 (m), 1432 (s), 1361 (s), 1315 (s), 1253 (s), 1227 (m), 1204 (m), 1121 (m), 908 (m) cm^{-1}. μ_{eff}: 4.92 μ_B (C_6D_6, 25 °C, Evan's method). Anal. Calcd for $C_{36}H_{58}N_5FeCl$: C, 66.30; H, 8.96; N, 10.74. Found: C, 66.18; H, 8.78; H, 10.61.

Synthesis of 4. Complex **1** (300 mg, 0.469 mmol) was dissolved in THF (∼10 mL) and added dropwise to a cold (−35 °C) suspension of $CoCl_2$ (60.6 mg, 0.468 mmol) in THF (∼5 mL). After the mixture was stirred for 12 h, THF was evaporated in vacuo, and the dark green residue was extracted with toluene. The toluene solution was then filtered, and the filtrate was concentrated and cooled to give green crystals of (L)CoCl (**4**) (194 mg, 0.313 mmol, 66.7% yield). ^1H NMR (24 °C, 300.1 MHz, C_6D_6): δ 72.6 ($\Delta\nu_{1/2} = 58$ Hz), 58.6 ($\Delta\nu_{1/2} = 22$ Hz), 13.1 ($\Delta\nu_{1/2} = 53$ Hz), −4.69 ($\Delta\nu_{1/2} = 11$ Hz), −19.8 ($\Delta\nu_{1/2} = 15$ Hz). IR (KBr plates, Nujol): 3071(m), 3040(m), 1959(m), 1814(m), 1526(m), 1474 (s), 1030 (s) cm^{-1}. μ_{eff}: 3.83 μ_B (C_6D_6, 25 °C, Evan's method). Anal. Calcd for $C_{36}H_{58}N_5CoCl$: C, 66.03; H, 8.93; N, 10.70. Found: C, 65.69; H, 8.84; N, 10.58.

X-ray Crystallography. Inert atmosphere techniques were used to place the crystal onto the tip of a glass capillary (0.06−0.20 mm diameter) mounted on a SMART6000 (Bruker) at 121−126(2) K. A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20−30 frames. The data collection was carried out using graphite-monochromated Mo Kα radiation with a frame time of 5−30 s ad a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at −43° in 2θ. Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration (SAINT).[14] The structure was solved using SHELXS-97 and refined with SHELXL-97.[15] A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were refined with isotropic displacement parameters (unless otherwise specified).

Complex 1. Transparent colorless crystals of various morphologies were grown at −35 °C from a saturated THF solution. Intensity statistics and systematic absences suggested the centrosymmetric space group $P\bar{1}$, and subsequent solution and refinement confirmed this choice. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

Complex 2. Colorless elongated prisms were grown at −35 °C from a saturated toluene solution. Intensity statistics and systematic absences suggested the centrosymmetric space group $C2/c$, and subsequent solution and refinement confirmed this choice. An analytical absorption correction was applied (SADABS).[16] All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

Complex 3. Pale yellow single needles were grown at −35 °C from a saturated CH_2Cl_2 solution layered with pentane. Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice.

Complex 4. Dark wedge-shaped crystals were grown at −35 °C from a saturated toluene solution. Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/c$, and subsequent solution and refinement confirmed this choice. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

Results and Discussion

Treatment of lithium bis(3,5-di-tertbutylpyrazol-1-yl)methide,[5b] prepared in situ from ^nBuLi and bis(3,5-di-tertbutylpyrazol-1-yl)methane[5b] at −78 °C, with the *N*-methyleneaniline $H_2C{=}NAr$ (Ar = 2,6-$^iPr_2C_6H_3$),[10] elicited a rapid color change from colorless to yellow. Workup of the reaction mixture gives (L)Li(THF) (**1**) (L^- = bis(3,5-di-tertbutylpyrazol-1-yl)-1-CH_2NAr) as an off-white crystalline material in a 77% yield (Scheme 1). ^1H and ^{13}C NMR solution spectra of **1** are consistent with this complex retaining C_s symmetry in solution, which is manifested by only two inequivalent tertbutyl groups as well as only one isopropyl methine environment. The methylene protons connecting the bis(3,5-di-tertbutylpyrazol-1-yl)methane unit to the anilide are broad suggesting that a dynamic process is occurring in this system. Unfortunately, variable-temperature ^1H NMR studies (−50 °C) of **1** did not resolve the resonance.

To ascertain the coordination mode of the novel L^- surrogate, we obtained single-crystal X-ray diffraction data

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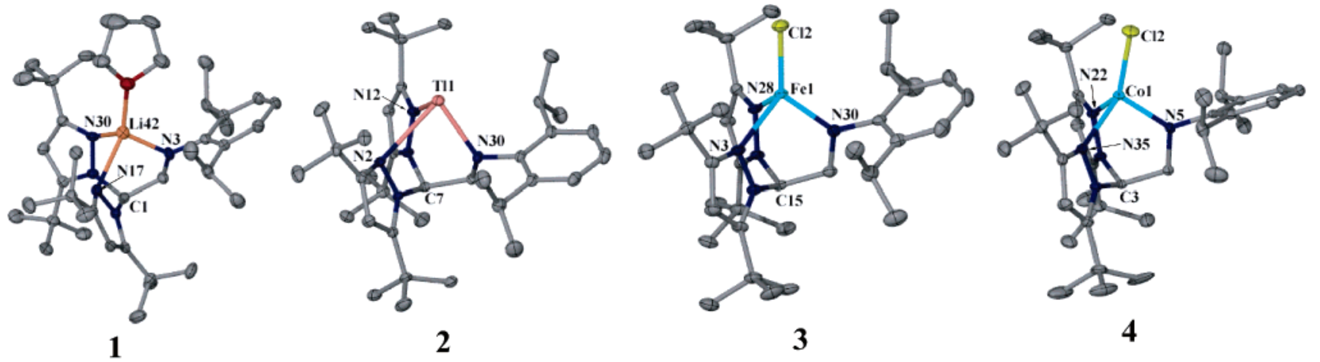
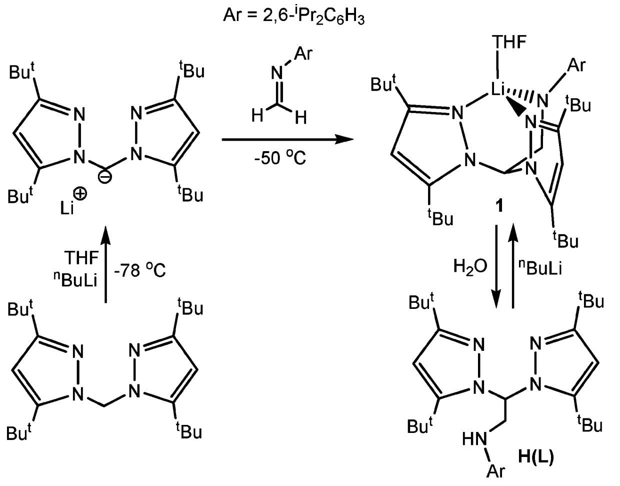


Figure 1. Molecular structures of complexes **1**−**4** depicting thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules have been excluded for the purpose of clarity. Crystallographic data for each structure is displayed in Table 1, and selected metrical parameters are shown in Table 2.

Scheme 1. Synthesis of Compound **1** and the Free Base **HL**



Ar represents the 2,6-^{i}Pr$_2$C$_6$H$_3$ aryl group.

of **1**. As shown in Figure 1, the geometry at lithium is tetrahedral, where one THF molecule occupies the apical site and the L$^-$ displays a κ^3 coordination mode. The anilido distance is significantly shorter (1.929(3) Å) than the two nitrogen donors from two pyrazolyl arms (2.109(3) and 2.270(3) Å). Crystallographic data for **1** are displayed in Table 1, and selected metrical parameters are shown in Table 2.[17] Over extended periods of time complex **1** decomposes slowly to the free aniline H(L). As a result, solids of **1** are best stored in the protonated form. To generate H(L) cleanly, THF solutions of **1** are treated with H_2O to afford the free ligand as a white solid which can be stored indefinitely. Anhydrous THF solutions of H(L) react smoothly with ^{n}BuLi at −35 °C to produce the salt **1** (Scheme 1), which can be utilized for subsequent transmetalation reactions.

To probe the coordination ability of **1**, we carried out transmetalation reactions of this ligand with Tl(I), Fe(II), and Co(II) precursors. Accordingly, when a cold THF solution of **1** is added dropwise to a cold THF solution containing Tl(OTf),[18] an orange color is immediately observed. The reaction mixture must be filtered rapidly to avoid the gradual decomposition of the thallium complex. Hence, extraction of the product with C_6H_6, followed by filtration and cooling, gives the Tl(I) complex (L)Tl (**2**) as a pale yellow solid in a 72% isolated yield (Scheme 2). Solids must be stored cold and in the absence of light to avoid the formation of thallium metal. The ^{1}H NMR spectrum of **2** corroborates well with the lithium derivative **1**, but the methylene hydrogens are much broader suggesting a slower dynamic process occurring on the NMR time scale. Most notably, the ^{205}Tl NMR spectrum of **2** reveals a broad resonance at 3355 ppm ($\Delta\nu_{1/2} \approx 4493$ Hz) and unambiguously confirms formation of a thallium(I) complex bearing this ligand.[19]

Thallium(I) is a soft metal, and as a result, Tl−amide linkages are exceedingly reactive and often decompose thermally or photolytically to give Tl metal.[20] Despite bearing a hard amide donor group, complex **2** is remarkably stable allowing for spectroscopic and structural elucidation. Accordingly, the single-crystal structure analysis of **2** depicts a highly distorted κ^3 tripodal ligand where the anilide N−Tl distance (2.274(4) Å) deviates significantly from that of the two pyrazolyl N−Tl bonds (2.670(5) and 2.702(4) Å, Figure 1). To accommodate the large Tl(I) ion, the two nitrogen atoms from the pyrazolyl arms (N2 and N12) are skewed in a propellerlike fashion, while the Tl(I) atom is displaced ∼1.80 Å above the imaginary N_3 plane thus conforming the complex to a pseudo-trigonal pyramid geometry. Complex**2** represents a structurally characterized heteroscorpionate analogue of Tl(I) tris(pyrazolyl)borate systems.[21] Crystallographic data for the structure of **2** are displayed in Table 1, and selected metrical parameters are shown in Table 2.

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Table 1. Crystallographic Data for Complexes **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{40}H_{66}LiN_5O$	$C_{36}H_{58}N_5Tl$	$C_{36}H_{58}ClFeN_5$	$C_{36}H_{58}ClCoN_5$
fw	639.92	765.24	652.17	655.25
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2(1)/n$	$P2(1)/c$
a (Å)	9.9605(12)	24.613(2)	11.507(5)	15.0257(18)
b (Å)	11.5019(14)	20.2102(16)	17.699(10)	12.0207(14)
c (Å)	18.077(2)	17.7282(14)	19.360(12)	21.061(3)
α (deg)	102.866(3)			
β (deg)	91.019(4)	125.337(2)	106.927(19)	98.543(3)
γ (deg)	98.275(4)			
V (Å^3)	1995.3(4)	7194.0(10)	3772(4)	3761.8(8)
Z	2	8	4	4
D_{calcd} (g cm^{-3})	1.065	1.413	1.148	1.157
cryst size (mm)	0.25 × 0.20 × 0.20	0.35 × 0.15 × 0.15	0.20 × 0.10 × 0.06	0.30 × 0.20 × 0.20
solvent habit, color	X, colorless	X, colorless	CH_2Cl_2/Et_2O, yellow	X, dark
h, k, l	$-12 \leq h \leq 12$	$-34 \leq h \leq 34$	$-12 \leq h \leq 14$	$-21 \leq h \leq 20$
	$-14 \leq k \leq 14$	$-28 \leq k \leq 28$	$-11 \leq k \leq 22$	$-16 \leq k \leq 14$
	$-23 \leq l \leq 23$	$-24 \leq l \leq 24$	$-25 \leq l \leq 25$	$-29 \leq l \leq 29$
F(000)	704	3120	1408	1412
Θ range	1.94−27.55	2.33−30.05	2.08−27.47	2.22−30.03
linear abs coeff (mm^{-1})	0.064	4.520	0.500	0.557
total reflns collected	25559	97311	13975	34515
independent reflns	9180	10531	8375	10967
unique reflns	4336	8925	2515	6883
R_{int}	0.0947	0.0454	0.1295	0.0669
data/params	9180/710	10500/611	8375/404	10125/620
R_1, R_2 (for $I > 2\sigma(I)$)	0.0460, 0.0765	0.0183, 0.0402	0.0570, 0.0982	0.0362, 0.0687
GOF	0.751	1.020	0.655	0.852
peak/hole (e/Å^{-3})	0.252/−0.205	2.748/−2.130	0.487/−0.284	0.401/−0.529

Table 2. Selected Interatomic Distances (Å) and Angles (deg)

1							
Li42−N3	1.929(3)	Li42−N30	2.109(3)	Li42−N17	2.270(3)	Li42−O43	2.038(3)
N3−C2	1.428(2)	C2−C1	1.541(2)	C1−N16	1.468(2)	C1−N29	1.459(2)
N16−N17	1.367(9)	N29−N30	1.378(8)				
O43−Li42−N3	116.8(6)	O43−Li42−N30	122.8(6)	N3−Li42−N17	94.3(4)	N17−Li42−N30	85.0(2)
O43−Li42−N17	133.2(5)	N3−Li42−N30	95.0(4)				
2							
Tl1−N30	2.274(4)	Tl1−N12	2.670(5)	Tl1−N2	2.702(4)	N6−N2	1.368(8)
N30−C29	1.438(2)	C29−C7	1.544(2)	C7−N6	1.476(2)	C7−N8	1.463(2)
N8−N12	1.370(9)						
N30−Tl1−N12	78.65(5)	N30−Tl1−N2	76.75(5)	N2−Tl1−N12	64.66(4)		
3							
Fe1−Cl2	2.288(8)	Fe1−N30	1.925(4)	Fe1−N3	2.115(4)	Fe1−N28	2.203(4)
N30−C29	1.438(5)	C29−C15	1.532(5)	C15−N9	1.453(5)	C15−N16	1.479(5)
N16−N28	1.380(4)	N9−N3	1.380(5)				
Cl2−Fe1−N30	124.7(3)	Cl2−Fe1−N3	123.4(2)	Cl2−Fe1−N28	126.8(1)	N30−Fe1−N3	93.6(6)
N30−Fe1−N28	95.7(5)	N3−Fe1−N28	81.0(4)				
4							
Co1−Cl2	2.2195(5)	Co1−N5	1.887(3)	Co1−N22	2.059(3)	Co1−N35	2.100(3)
N5−C4	1.441(8)	C4−C3	1.526(2)	C3−N18	1.470(9)	C3−N31	1.469(9)
N31−N35	1.376(6)	N18−N22	1.378(6)				
Cl2−Co1−N5	113.59(4)	Cl2−Co1−N22	132.81(4)	Cl2−Co1−N35	130.31(4)	N5−Co1−N22	92.86(5)
N5−Co1−N35	94.27(5)	N35−Co1−N22	82.20(5)				

When **1** is added to $FeCl_2(THF)_{1.5}$[11] in a cold toluene slurry, yellow (L)FeCl **(1)** is isolated in an ∼71% yield (Scheme 2) upon workup of the reaction mixture. ^{1}H NMR spectra display broad resonances ranging from 14 to −29 ppm, consistent with a paramagnetic material. As expected for a monomeric high-spin Fe(II) system, the solution magnetic susceptibility measurement of complex **3** is in agreement with four unpaired electrons ($\mu_{eff} = 4.92\ \mu_B$). Cyclic voltammetry of a solution of **3** (THF/TBAH) showed one reversible oxidation wave and an irreversible reduction wave at −0.269 V and −3.31 V (Figure 2), respectively (referenced vs $FeCp_2/FeCp_2^+$). The remarkably negative reduction potential in **3** suggests that this species is highly electron rich and that chemical access of Fe(III) is far more likely than for Fe(I). Not surprisingly, attempts to chemically reduce **3** with powerful one-electron reductants such as KC_8 [22] have so far been unsuccessful.

The identity of complex **3** has been scrutinized not only by a combination of physical methods including Evans and elemental analysis but also by single-crystal X-ray diffraction

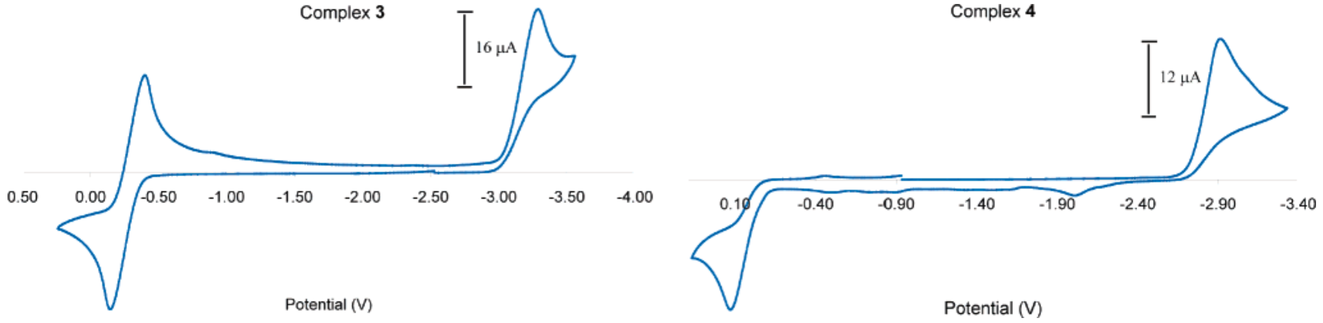
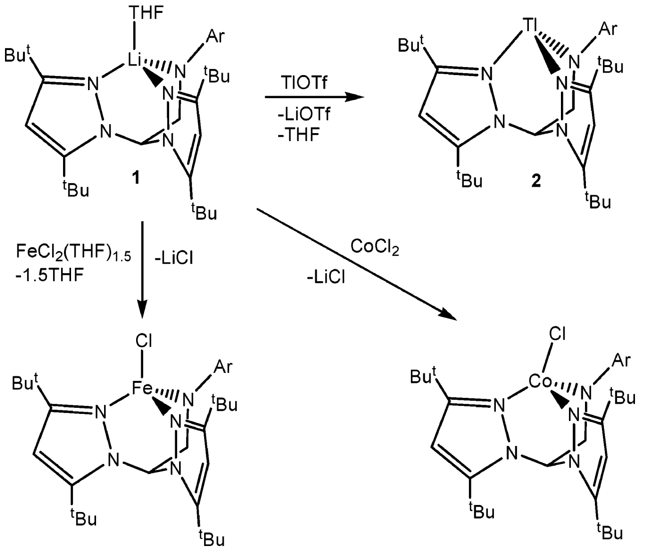


Figure 2. Cyclic voltamograms of complexes **3** and **4** in 0.3 M TBAPF$_6$ in THF using a scan rate of 250 mV/s and referenced to the FeCp$_2$$^{0/+}$ couple (0.0 V).

Scheme 2. Synthesis of Compounds **2**−**4** from **1**



Ar represents the 2,6-^{i}Pr$_2$C$_6$H$_3$ aryl group.

studies (Figure 1). The molecular structure of complex **3** is depicted in Figure 1, and the gross structural features of the FeN$_3$ core resemble the tetrahedral homoscorpionate ferrous analogues (Tp)FeCl (Tp = HB(3,5-R$_2$py; R = CH$_3$, ^{i}Pr; py = pyrazol-1-yl).[23] As observed previously with **1** and **2**, the anilido N−metal distance is significantly shorter (1.925(4) Å) than the pyrazolyl N−metal distances (2.203(4) and 2.115(4) Å). Given the steric encumbrance of the ligand, we speculate that the aryl group on the amide nitrogen is oriented parallel to the ligand N$_3$ plane, thus placing the isopropyl groups away from both the chloride and sterically imposing tertbutyl groups.

CoCl$_2$ can be also transmetalated smoothly with **1** in THF at −35 °C to produce dark green crystals of (L)CoCl (**4**) in a 67% yield. ^{1}H NMR solution spectra reveal several broad resonances ranging from 73 to −20 ppm, and solution magnetic measurements are consistent with a tetrahedral high-spin d^7 species ($\mu_{\mathrm{eff}} = 3.83\ \mu_B$). A cyclic voltammogram of a solution of **4** (THF/TBAH) showed one irreversible oxidation wave and one reduction wave at 0.388 V and −2.915 V, respectively (Figure 2). Chemically, it was found that reductants such as Na/Hg or Mg (powder) do not react with **4** in THF suggesting that this species is far more electron rich than the tris(pyrazolyl)borate Co(II) derivatives.[24] Single-crystal X-ray diffraction analysis of **4** exposes a mononuclear Co(II) center, but unlike **3** the geometry at the cobalt ion is that of a distorted tetrahedron. This is reflected by the imaginary C(3)−Co−Cl(2) angle, which is slightly deviated from linearity (168.7°) from that of the ferrous analogue **3** (C(15)−Fe−Cl(2), 177.8°). The distortion observed in the crystal structure of complex **4** is significant when compared to the close relative (Tp′)CoCl reported by Parkin and co-workers (Tp′ = tris(3-tertbutylpyrazol-1-yl)hydroborate).[23b] Close inspection of the Cl−Co−N (120.3(2), 122.2(1), and 122.2(2)) and N−Co−N (95.3(1), 94.8(2), and 95.3(1)) angles in (Tp′)CoCl reveals differences in the metrical parameters when compared with the structure of **4**. Hence we speculate that such distortion (toward the anilide nitrogen) originates from the amide component of the ligand in complex **4**. However, the exact reason for the axial distortion is currently unclear to us. Axial distortion observed in the crystal structure of **4** does break down the symmetry in the molecule but does not appear to change the multiplicity of the system (from triplet to singlet), thus implying that the splitting of the singly occupied molecular orbitals are not significant enough to promote electron pairing in **4**.[25]

Conclusion

Combining a hard amide donor with the bis(3,5-di-tertbutylpyrazol-1-yl)methane skeleton has produced a sterically encumbering scorpionate hybrid ligand. This monoanionic bis(3,5-di-tertbutylpyrazol-1-yl)-1-CH$_2$NAr ligand appears to be an excellent platform for tripodal frameworks of Li$^+$,

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Tl^+, and transition metals such as Fe^{2+} and Co^{2+}. Judging from the electrochemical reduction waves for both (L)FeCl and (L)CoCl, it is postulated that the "M(II)L" scaffold is highly electron rich, a factor which we attribute to the donating ability of the hard anilide pendant arm.

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Supporting Information Available: Complete experimental, spectroscopic, analytical, crystallographic details (in CIF files) for complexes **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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