Electronic Supplementary Information (ESI):

The final unadorned tris(azolyl)borate: Finishing what Trofimenko started in 1966

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Chemical Communications

Experimental Section

All reagents were purchased from commercial vendors and used without purification. Solution ^{1}H, $^{13}C\{^{1}H\}$, and ^{11}B NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz, Bruker Avance 400 MHz, or Varian VNMRS 500 MHz, narrow-bore broadband system. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts were referenced to the residual solvent. ^{11}B chemical shifts are reported relative to an external standard of neat BF_3•OEt_2. Solid $^{13}C\{^{1}H\}$ NMR were recorded on a Varian Inova 400 MHz spectrometer at room temperature. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The ESI/MS analyses were performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an electrospray ionization source from AB Sciex (Concord, Ontario, Canada). Sample solutions of ligand (**1**) for mass spectrometry were prepared in acetonitrile. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance. Solid state electronic absorption spectra were recorded on an Evolution 600 UV-VIS spectrometer with the Praying Mantis attachment. LiF was used as the reference material, and the polycrystalline samples were dried and ground before measurement. Thermogravametric analysis data were collected on a TA Instruments TGA Q50 under N_2. Powder X-ray diffraction (PXRD) data was collected using a Panalytical Empyrean θ-2θ diffractometer in reflectance Bragg-Brentano geometry. Cu-Kα radiation (λ = 1.5406 Å; 1,800 W, 45 kV, 40 mA) was focused using a planar Gobel Mirror riding the Kα line. Diffracted radiation was detected using a PIXcel^{3d} detector [(6° 2θ sampling width) equipped with a Ni monochrometer]. Carbon, hydrogen, and nitrogen analyses were obtained from Atlantic Microlab, Norcross, GA.

Synthesis of Na(HB($C_2H_2N_3$)$_3$) (L), (1). Sodium borohydride ($NaBH_4$) (0.138 g, 3.62 mmol) and 1,2,3-triazole (1.00 g, 14.5 mmol) were combined in a 50 mL round bottom flask with paracymene (15 mL) and stirred. The reaction was heated to 180 °C for one week during which time a white solid formed. The reaction mixture was cooled to room temperature and the white solid was collected on a 60 mL fine sintered-glass frit and was washed with toluene (3 x 10 mL) and hexanes (3 x 10 mL). The solid was moved to a 20 mL scintillation vial with tetrahydrofuran (10 mL) and stirred for 4 h. After allowing the solid to settle, the solvent was decanted. Additional THF (5 mL) was added and this mixture was then filtered using a medium sintered glass frit, leaving the pure white solid product that was dried under reduced pressure (0.782 g, 90.4% yield). Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation from water. ^{1}H NMR (DMSO-d_6, 499.74 MHz): δ 7.76 (s, 3H), 7.56 (s, 3H), 5.23 (br, 1H). ^{1}H NMR (D_2O, 499.74 MHz): δ 7.78 (s, 3H), 7.76 (s, 3H). ^{13}C NMR (DMSO-d_6, 125.67 MHz): δ 131.68, 127.27. ^{13}C NMR (D_2O, 125.67 MHz): δ 132.17, 127.74. ^{11}B NMR (DMSO-d_6, 128.42MHz): δ -1.36. IR (neat): 3137, 2457, 1664, 1477, 1421, 1278, 1227, 1194, 1123, 1096, 1061, 1024, 958, 867, 806, 740, 700 cm^{-1}. HR-ESI-MS (*m*/*z*): $[L]^-$ $C_6N_9H_7B$ 216.0924 (calcd.); 216.0916 (found). Anal. Calcd. for $C_6H_7BN_9Na$: C, 30.15; H, 2.95; N, 52.75. Found: C, 29.76; H, 2.96; N, 51.79.

Synthesis of $Fe(L)_2$, (2). Iron(II) sulfate pentahydrate (0.0303 g, 1.04 mmol) and **1** (0.0450 g, 2.08 mmol) were added to separate 20 mL scintillation vials and dissolved with 5 mL and 15 mL of water, respectively. The solution of **1** was then pipetted slowly into the iron sulfate solution and left at room temperature. After 3 d, red block crystals had formed (0.0399 g, 78.7% yield). CP/MAS ^{13}C NMR (100.53 MHz) δ 139.43, 135.70. IR (neat): 3117, 2916, 2517, 1472, 1436, 1376, 1288, 1262, 1204, 1189, 1134, 1098, 1058, 1034, 961, 794, 783, 740, 683, 647 cm^{-1}. UV-vis (solid state) λ_{max} 353, 510 nm. Anal. Calcd. for $C_{12}H_{14}B_2N_{18}Fe$: C, 29.54; H, 2.89; N, 51.68. Found: C, 29.23; H, 2.98; N, 50.60.

Synthesis of $Co(L)_2$, (3). Cobalt(II) nitrate hexahydrate (0.0303 g, 1.04 mmol) and **1** (0.0450 g, 2.08 mmol) were added to separate 20 mL scintillation vials and dissolved with 3 mL and 6 mL of water, respectively. The solution of **1** was then pipetted slowly into the metal solution and left at room temperature. After 3 d, yellow block crystals had formed (0.0337 g, 65.9% yield). IR (neat): 3174, 2500, 1473, 1438, 1284, 1249, 1190, 1133, 1060, 1032, 961, 812, 767, 736, 687 cm^{-1}. UV-vis (solid state) λ_{max} 297, 462, 512 nm. Anal. Calcd. for $C_{12}H_{14}B_2N_{18}Co$: C, 29.36; H, 2.87; N, 51.36. Found: C, 29.46; H, 2.78; N, 51.08.

Synthesis of $Ni(L)_2$, (4). Nickel(II) chloride hexahydrate (0.0247 g, 1.04 mmol) and **1** (0.0450 g, 2.08 mmol) were added to separate 20 mL scintillation vials and dissolved with 3 mL and 6 mL of water, respectively. The solution of **1** was then pipetted slowly into the metal solution and left at room temperature. After 3 d, pink block crystals had formed (0.0355 g, 69.5% yield). IR (neat): 3263, 3155, 3140, 2561, 2174, 1688, 1647, 1476, 1443, 1296, 1262, 1209, 1140, 1071, 1040, 967, 890, 771, 732 cm^{-1}. UV-vis (solid state) λ_{max} 350, 549, 792 nm. Anal. Calcd. for $C_{12}H_{14}B_2N_{18}Ni$: C, 29.37; H, 2.88; N, 51.38. Found: C, 29.53; H, 2.79; N, 51.13.

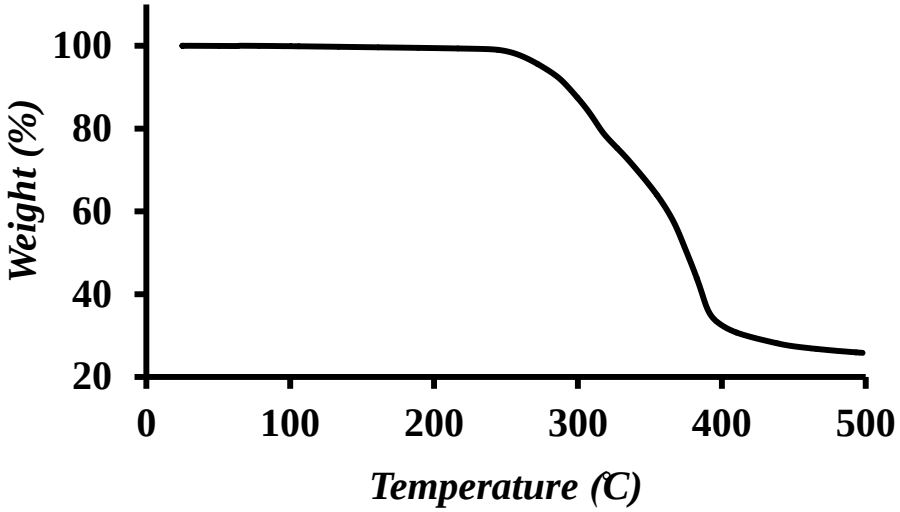
Synthesis of $Cd(L)_2$, (5). Cadmium(II) nitrate tetrahydrate (0.0321 g, 1.04 mmol) and **1** (0.0450 g, 2.08 mmol) were added to separate 20 mL scintillation vials and dissolved with 10 mL of water each. The solution of **1** was added to the metal solution by pipette. The vial was then heated to 85 °C overnight in an aluminum heating block. Colorless needle crystals were formed and collected using a Buchner funnel and filter paper (0.0522g, 95.3% yield). CP/MAS ^{13}C NMR (100.53 MHz) δ 133.40, 131.28, 126.94. IR (neat): 3364, 3134, 2476, 1650, 1482, 1422, 1286, 1279, 1227, 1214, 1204, 1121, 1105, 1094, 1069, 1021, 971, 878, 788, 760, 742, 728, 694 cm^{-1}. Anal. Calcd. for $C_{12}H_{14}B_2N_{18}Cd$: C, 26.48; H, 2.59; N, 46.31. Found: C, 25.74; H, 2.60; N, 44.84.

X-ray Structure Determinations. X-ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on glass fibers or nylon cyroloops. Each crystal was frozen under a stream of N_2 while data were collected on a Bruker APEX diffractometer. A matrix scan using at least 12 centered reflections was used to determine initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT 4.05. Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS, if necessary. Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structure. The structures

were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the SHELXTL 5.0 software package.

TGA data for 5.

Figure S1: TGA for **5**.



PXRD patterns for 5.

Figure S2: PXRD pattern for **5**: experimental (red) and simulated (black).

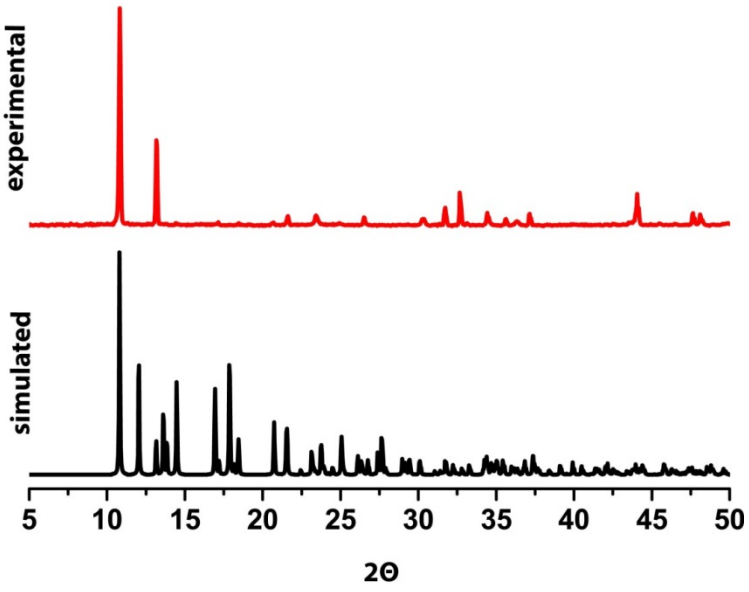


Figure S3: Labeled drawings to accompany Table 1.
A. Tris(1,2,3-triazolyl)borate complexes.
B. Tris(pyrazolyl)borate complexes.
C. Tris(1,2,4-triazolyl)borate complexes.

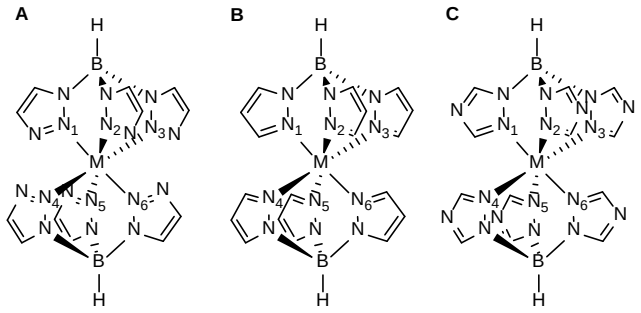


Table S1. Comparisons between metal complexes with (**1**) and analogous complexes with tripodal ligands.

	2	**Fe 2b[a]**	**2c[b]**	**3**	**Co 3b[c]**	**3c[b]**	**4**	**Ni 4b[d]**	**4c[e]**
Ligand	1,2,3-triazolyl	pyrazolyl	1,2,4-triazolyl	1,2,3-triazolyl	pyrazolyl	1,2,4-triazolyl	1,2,3-triazolyl	pyrazolyl	1,2,4-triazolyl
Space Group	$R\bar{3}$	$P\bar{1}$	Cmca	$R\bar{3}$	$P2_1/n$	Cmca	$R\bar{3}$	$P2_1/n$	Cmca
Bond Lengths[f]									
M-N(1)	1.957(1)	1.987(1)	1.994	2.102(1)	2.133(7)	2.128	2.067(9)	2.088(2)	2.079(3)
M-N(2)	1.957(1)	1.977(1)	1.994	2.102(1)	2.130(7)	2.121	2.067(9)	2.098(2)	2.095(2)
M-N(3)	1.957(1)	1.978(1)	1.992	2.102(1)	2.120(7)	2.128	2.067(9)	2.090(3)	2.089(2)
M-N(4)	1.957(1)	1.980(1)	1.992	2.102(1)	2.133(8)	2.128	2.067(9)	2.087(2)	2.082(3)
M-N(5)	1.957(1)	1.977(1)	1.994	2.102(1)	2.128(8)	2.121	2.067(9)	2.104(3)	2.095(2)
M-N(6)	1.957(1)	1.983(1)	1.994	2.102(1)	2.140(7)	2.128	2.067(9)	2.091(2)	2.089(2)
Bond Angles[g]									
Cis (intra)	88.52(4)	88.40(7)	87.91	86.19(5)	85.5(5)	85.27	87.13(4)	86.7(8)	86.19(7)
Cis (inter)	91.48(4)	91.60(8)	92.09	93.81(5)	94.5(3)	94.73	92.87(4)	93.2(8)	93.80(6)
Trans	180.00(5)	178.74(4)	180.0	180.00(5)	177.3(3)	180.0	180.00(6)	178.4(4)	179.58(4)

[a] Reference [1]
[b] Reference [2]
[c] Reference [3]
[d] Reference [4]
[e] Reference [5]
[f] All bond lengths are given in Å.
[g] All bond angles are given in degrees and are an average.

References.

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