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Synthesis and Characterization of Copper(II), Zinc(II), and Potassium Complexes of a Highly Fluorinated Bis(pyrazolyl)borate Ligand

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Highly fluorinated, dihydridobis(3,5-bis(trifluoromethyl)pyrazolyl)borate ligand, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ has been synthesized and characterized as its potassium salt. The copper(II) and zinc(II) complexes, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Cu$ and $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Zn$, have been prepared by metathesis of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]K$ with $Cu(OTf)_2$ and $Zn(OTf)_2$, respectively. All the new metal adducts have been characterized by X-ray diffraction. The potassium salt is polymeric and shows several K···F interactions. The Cu center of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Cu$ adopts a square planar geometry, whereas the Zn atom in $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Zn$ displays a tetrahedral coordination. Bis(pyrazolyl)borate ligands in the Zn adduct show a significantly distorted boat conformation. The nature and extent of this distortion is similar to that observed for the methylated analog, $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Zn$. This ligand allows a comparison of electronic effects of bis(pyrazolyl)borate ligands with similar steric properties. Crystallographic data for $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]K$: triclinic, space group $P\bar{1}$, with $a = 8.385(1)$ Å, $b = 10.097(2)$ Å, $c = 10.317(1)$ Å, $\alpha = 104.193(9)°$, $\beta = 104.366(6)°$, $\gamma = 91.733(9)°$, $V = 816.5(3)$ Å^3, and $Z = 2$. $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Cu$ is monoclinic, space group $C2/c$ with $a = 25.632(3)$ Å, $b = 9.197(1)$ Å, $c = 17.342(2)$ Å, $\beta = 129.292(5)°$, $V = 3164.0(6)$ Å^3, and $Z = 4$. $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Zn$ is triclinic, space group $P\bar{1}$, with $a = 9.104(1)$ Å, $b = 9.278(1)$ Å, $c = 18.700(2)$ Å, $\alpha = 83.560(6)°$, $\beta = 88.200(10)°$, $\gamma = 78.637(9)°$, $V = 1538.8(3)$ Å^3, and $Z = 2$. $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Zn$ is monoclinic, space group $C2/c$ with $a = 8.445(1)$ Å, $b = 14.514(2)$ Å, $c = 19.983(3)$ Å, $\beta = 90.831(8)°$, $V = 2449.1(6)$ Å^3, and $Z = 4$.

Introduction

Metal adducts of the fluorinated ligands often show very different physical and chemical properties relative to their non-fluorinated analogs.[1−4] Polyfluorinated ligands commonly improve the volatility, oxidation resistance, and fluorocarbon solubility of metal complexes. They have also been known to increase the activity of certain metal catalyzed reactions.[2,5,6] As a result, there is a considerable amount of interest in the synthesis and applications of fluorinated ligands.[1−4,7−25] One area of focus in our laboratory is the development of fluorinated poly(pyrazolyl)borates.[7,26] We have recently reported the synthesis of one such ligand, **1**, containing six, highly electron withdrawing trifluoromethyl substituents. This tris(pyrazolyl)borate ligand has allowed the isolation of several unique compounds in stable crystalline form. For example, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (**1**) has been used in the stabilization of a rare silver(I) carbonyl complex, $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$.[27] The corresponding compound with non-fluorinated tris(pyrazolyl)borate ligands is unknown. We have also utilized **1** to stabilize a monomeric In(I) complex.[28] The related In(I) compounds of non-fluorinated ligands are stable only when extremely bulky substituents are present on the ligand.[29−31] The interesting chemistry observed with **1** prompted us to extend our studies

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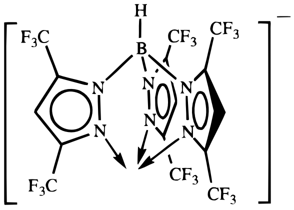
into the development of fluorinated *bis(pyrazolyl)borate* ligands, e.g. **2**.



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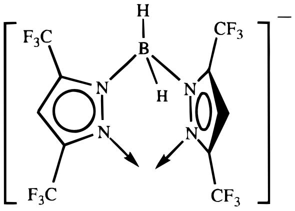

2

Bis(pyrazolyl)borate ligands have often been compared to β-diketonates.[32] Although, fluorinated β-diketones have been used widely in a variety of applications including NMR spectroscopy, chromatographic analysis of metals, and in the synthesis of volatile metal precursors for CVD studies,[21,33-40] the fluorinated bis(pyrazolyl)borates remain unexplored.[32] This report presents details of the synthesis and characterization of the potassium salt of a highly fluorinated bis(pyrazolyl)borate ligand, (dihydridobis(3,5-bis(trifluoromethyl)pyrazolyl)borato)-potassium and its utility in the synthesis of copper(II) and zinc(II) complexes, $[H_2B(3,5-(CF_3)_2Pz)_2]_2Cu$ and $[H_2B(3,5-(CF_3)_2Pz)_2]_2Zn$. These compounds have been characterized by X-ray crystallography. In order to study the effects of replacing methyls with trifluoromethyl groups on the pyrazole rings of bis(pyrazolyl)borate ligands, we have also investigated the crystal structure of the corresponding methylated species, $[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of purified nitrogen using a combination of glovebox (Vacuum Atmospheres single station drybox equipped with a −25 °C refrigerator) and standard Schlenk techniques. Solvents were purchased from commercial sources, distilled from conventional drying agents and degassed twice prior to use.[41] Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded at 25 °C on a Bruker MSL-300 spectrometer (^1H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.36 MHz) or Nicolet NT-200 spectrometer (^1H, 200.06 MHz; ^{13}C, 50.31 MHz), unless otherwise noted. Chemical shifts for ^1H NMR spectra are relative to internal Me_4Si or to residual protium in the deuterated solvents. The ^{13}C NMR spectra were run with ^1H decoupling and the chemical shifts are reported in ppm vs Me_4Si. ^{19}F NMR chemical shifts were referenced relative to an external $CFCl_3$ standard. IR spectra were recorded on a BioRad 40S spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed by Texas Analytical Laboratories, Inc., Houston, TX, or at the UTA using a PE-2400 CHN analyzer.

3,5-Bis(trifluoromethyl)pyrazole and $[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$ were prepared by literature methods.[42-44] KBH_4 (Aldrich), $Cu(OTf)_2$ (Aldrich) and $Zn(OTf)_2$ (Aldrich) were purchased and used as received.

Synthesis of $[H_2B(3,5-(CF_3)_2Pz)_2]K$ (3). 3,5-Bis(trifluoromethyl)-pyrazole (5.0 g, 24.5 mmol) in toluene (10 mL) was added at room temperature to KBH_4 (0.63 g, 11.7 mmol) in 20 mL of toluene. The reaction mixture was heated to ca. 115−120 °C while it was stirred for 20 h. A white precipitate was observed. The solvent was removed under reduced pressure and the product was extracted using ethyl ether and filtered to remove any insoluble material. The ether was then removed from the solution to obtain **3** as a white solid, 91% yield. The product was recrystallized from hot toluene; mp 189−190 °C. ^1H NMR (C_6D_6): δ 6.49 (s, CH). $^{13}C\{^1H\}$NMR (DMSO-d_6): δ 104.74 (br s, C-4), 120.48 (q, $^1J_{CF}$ = 269 Hz, CF_3), 121.78 (q, $^1J_{CF}$ = 268 Hz, CF_3), 136.31 (q, $^2J_{CF}$ = 38 Hz, CCF_3), 140.02 (q, $^2J_{CF}$ = 36 Hz, CCF_3); ^{19}F NMR (DMSO-d_6): δ −57.7, −59.7. IR (KBr), cm^{-1}: 3153, 2499, 2449, 2332, 1548, 1502, 1370, 1263, 1182, 1101, 1035, 980, 887, 825. Anal. Calcd for $C_{10}H_4BF_{12}KN_4$: C, 26.22; H, 0.88; N, 12.23. Found: C, 26.37; H, 0.66; N, 11.92.

Synthesis of $[H_2B(3,5-(CF_3)_2Pz)_2]_2Cu$ (4). Solid **3** (0.50 g, 1.09 mmol) and $Cu(OTf)_2$ (0.19 g, 0.52 mmol) were mixed in a Schlenk tube and Et_2O (40 mL) was added at 0 °C. The color of the solution became purple immediately. The mixture was allowed to warm up and was stirred overnight at room temperature. Volatiles were removed under vacuum, toluene (40 mL) was added, and the mixture was refluxed for 1 h. The mixture was filtered while hot, and the filtrate was allowed to cool slowly to obtain **4** as a purple solid. The solid was rinsed once with cold toluene and dried under vacuum: yield 36%, melts to a blue liquid at 234−235 °C (small amount of a white residue began to form on crystals around 210 °C). IR (KBr), cm^{-1}: 3167, 2572, 2470, 1554, 1497, 1396, 1266, 1188, 1153, 1107, 1051, 899, 838. Anal. Calcd for $C_{20}H_8B_2CuF_{24}N_8$: C, 26.65; H, 0.89; N, 12.43. Found: C, 26.54; H, 0.96; N, 12.34.

Synthesis of $[H_2B(3,5-(CF_3)_2Pz)_2]_2Zn$ (5). To a suspension of $Zn(OTf)_2$ (0.16 g, 0.44 mmol) in Et_2O was added solid **3** (0.40 g, 0.87 mmol) at room temperature. The resulting mixture was stirred for 24 h. Volatiles were removed under vacuum, toluene was added, and the mixture was refluxed for 1 h. The mixture was filtered while hot, and the filtrate was concentrated and cooled to 0 °C to obtain **5** as a colorless solid. Yield: 56%. mp: 155−157 °C. ^1H NMR (C_6D_6): 6.19 (s, CH). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 104.59 (br s, C-4), 120.44 (q, $^1J_{CF}$ = 269 Hz, CF_3), 121.74 (q, $^1J_{CF}$ = 268 Hz, CF_3), 136.26 (q, $^2J_{CF}$ = 38 Hz, CCF_3), 140.21 (q, $^2J_{CF}$ = 36 Hz, CCF_3). ^{19}F NMR (DMSO-d_6): δ −57.7, −59.7. IR (KBr), cm^{-1}: 3165, 2577, 2487, 2437, 1554, 1267, 1188, 1153, 1107, 1050, 840. Anal. Calcd for $C_{20}H_8B_2F_{24}N_8Zn$: C, 26.59; H, 0.89; N, 12.40; Found: C, 26.19; H, 0.77; N, 12.25.

X-ray Structure Determination of $[H_2B(3,5-(CF_3)_2Pz)_2]K$ (3). Crystal data and data collection and refinement parameters are summarized in Table 1. A colorless single crystal of **3** was mounted on a glass fiber using 5-min epoxy. Data were collected on a Siemens P4 diffractometer at T = 298 K with Mo Kα (λ = 0.710 73 Å, graphite monochromator) radiation using the $\theta-2\theta$ scan technique. Cell parameters were determined using 23 reflections. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using Siemens SHELXTL (PC version 4.2) software package.[45] A rotational disorder was observed for CF_3 fluorines of the C46 carbon. These fluorines were disordered over two sites each in a 0.75:0.25 ratio. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on B were located from the difference map and the positions and the isotropic thermal parameters were refined. The pyrazole ring hydrogens were included in calculated positions (C−H, 0.96 Å) and refined isotropically. Atomic positional parameters and selected bond lengths and angles of **3** are listed in Tables 2 and 3, respectively.

X-ray Structure Determination of $[H_2B(3,5-(CF_3)_2Pz)_2]_2Cu$ (4). Crystal data and data collection and refinement parameters are summarized in Table 1. A purple single crystal of **4** was mounted on a glass fiber using 5-min epoxy. Data were collected on a Siemens P4 diffractometer at T = 298 K with Mo Kα (λ = 0.710 73 Å, graphite

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Table 1. Crystal Data and Summary of Data Collection and Refinement

	$[H_2B(3,5-(CF_3)_2Pz)_2]K$	$[H_2B(3,5-(CF_3)_2Pz)_2]_2Cu$	$[H_2B(3,5-(CF_3)_2Pz)_2]_2Zn$	$[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$
formula	$C_{10}H_4BF_{12}KN_4$	$C_{20}H_8B_2CuF_{24}N_8$	$C_{20}H_8B_2F_{24}N_8Zn$	$C_{20}H_{32}B_2N_8Zn$
fw	458.1	901.5	903.3	471.5
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$
a, Å	8.385(1)	25.632(3)	9.104(1)	8.445(1)
b, Å	10.097(2)	9.197(1)	9.278(1)	14.514(2)
c, Å	10.317(1)	17.342(2)	18.700(2)	19.983(3)
α, deg	104.193(9)	90	83.560(6)	90
β, deg	104.366(6)	129.292(5)	88.200(10)	90.831(8)
γ, deg	91.733(9)	90	78.637(9)	90
vol, Å^3	816.5(3)	3164.0(6)	1538.8(3)	2449.1(6)
Z	2	4	2	4
D_{calc}, g/cm^3	1.863	1.892	1.950	1.279
μ(Mo Kα, 0.710 73 Å), mm^{-1}	0.458	0.862	0.975	1.026
T, K	298	298	298	298
2θ max, deg	45	45	50	45
R, R_w,[a] %	4.38, 5.23	4.83, 5.31	5.01, 5.42	5.24, 5.37

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

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for $[H_2B(3,5-(CF_3)_2Pz)_2]K$

	x	y	z	U(eq)
K	3727(1)	8061(1)	4768(1)	67(1)
N11	7336(4)	7248(3)	3382(3)	51(1)
N12	6040(4)	6587(3)	3577(3)	58(1)
N21	8038(4)	8824(3)	5824(3)	52(1)
N22	7043(4)	9668(3)	6394(3)	54(1)
C13	5740(5)	5399(4)	2608(4)	59(2)
C14	6808(5)	5290(4)	1780(4)	62(2)
C15	7805(4)	6485(4)	2300(4)	52(1)
C16	4445(7)	4383(5)	2592(6)	83(2)
F16A	3203(5)	4916(4)	2971(7)	181(3)
F16B	3859(6)	3534(4)	1369(4)	169(2)
F16C	4944(4)	3596(3)	3413(4)	119(2)
C17	9179(5)	6928(5)	1811(5)	75(2)
F17A	9281(4)	6026(4)	669(3)	122(2)
F17B	9046(4)	8123(3)	1509(3)	100(1)
F17C	10649(3)	7029(4)	2721(3)	115(2)
C23	7404(5)	9676(4)	7711(4)	56(2)
C24	8608(5)	8833(4)	8036(4)	61(2)
C25	8982(5)	8307(4)	6812(4)	58(2)
C26	6514(6)	10532(6)	8626(5)	86(2)
F26A	4991(4)	10022(5)	8411(4)	143(2)
F26B	7188(5)	10650(5)	9922(3)	153(2)
F26C	6378(6)	11770(4)	8430(4)	152(3)
C27	10213(7)	7340(6)	6556(7)	86(3)
F27A	9679(19)	6334(12)	5532(9)	145(5)
F27B	11617(17)	7948(11)	6554(28)	131(7)
F27C	10635(15)	6794(13)	7613(11)	114(4)
F27D	9556(67)	6095(31)	5924(104)	240(51)
F27E	10827(57)	7447(57)	5497(50)	119(15)
F27F	11335(63)	7287(69)	7635(52)	218(23)
B	8047(8)	8713(5)	4298(5)	66(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3**

K−N12	2.819(4)	K−N22	3.043(3)
K−F16A	3.215(4)	K···KB	4.265(2)
K−N22A	2.858(4)	K−F16D	2.859(4)
K−F17D	2.874(3)	K−F26D	3.325(5)
K−F27H	2.812(55)	K−H2A	2.769(39)
N11−N12	1.341(5)	N21−N22	1.345(5)
N12−K−N22	75.9(1)	N12−K−F16A	53.1(1)
N22−K−F16A	125.6(1)	N12−K−F16d	74.8(1)
N12−K−N22A	109.7(1)	N22−K−N22A	87.5(1)
F16A−K−N22A	123.9(1)	N22−K−F16D	78.1(1)
F16A−K−F16D	72.0(1)	N22−K−F17D	163.8(1)
F16A−K−F17D	60.4(1)	F16D−K−F17D	117.5(1)
N12−K−F26D	64.6(1)	F16A−K−F27H	85.8(10)
N22−K−F26D	101.2(1)	F16A−K−F26D	75.3(1)
F16D−K−F26D	138.0(1)	F17D−K−F26D	64.5(1)
N12−K−F27H	137.1(11)	N22−K−F27H	133.5(9)
F16D−K−F27H	81.8(11)	F17D−K−F27H	58.0(9)
K−N12−N11	120.7(2)	K−N22−N21	98.8(2)
N12−N11−B	121.1(4)	N22−N21−B	119.1(3)
N11−B−N21	109.9(4)	H1−B−H2	112.1(33)

monochromator) radiation using the ω scan technique. Cell parameters were determined using 23 reflections. Data were corrected for Lorentz and polarization effects. An empirical absorption correction (using ψ scans) was also applied to the data set. The structure was solved by Patterson method followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using Siemens SHELXTL (PC Version 4.2) programs.[45] The copper atom lies on an inversion center. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on boron were located via difference Fourier map inspection. The remaining hydrogens were idealized and all the hydrogens were refined isotropically. Atomic positional parameters and selected bond lengths and angles of **4** are listed in Tables 4 and 5 respectively.

X-ray Structure Determination of $[H_2B(3,5-(CF_3)_2Pz)_2]_2Zn$ (5). Crystal data and data collection and refinement parameters are summarized in Table 1. A colorless single crystal of **5** was mounted on a glass fiber using 5-min epoxy. Data were collected on a Siemens P4 diffractometer at $T = 298$ K with Mo Kα ($\lambda = 0.710$ 73 Å, graphite monochromator) radiation using the ω scan technique. Cell parameters were determined using 29 reflections. Data were corrected for Lorentz and polarization effects. An empirical absorption correction (using ψ scans) was also applied to the data set. The structure was solved by Patterson method and refined using Siemens SHELXTL (PC Version 4.2) programs.[45] All non-hydrogen atoms were refined with anisotropic thermal parameters. A rotational disorder (over two sites) was observed for CF_3 fluorines of the C26, C36, and C46 carbons, and this disorder was modeled successfully. The hydrogens on boron were located via difference Fourier map inspection and refined with isotropic thermal parameters. The remaining hydrogens were included in calculated positions (C−H = 0.96 Å, fixed U_H). Atomic positional parameters and selected bond lengths and angles of **5** are listed in Tables 4 and 5 respectively.

X-ray Structure Determination of $[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$. X-ray quality crystals were obtained from Et_2O-CH_2Cl_2 at 0 °C. Crystal data and data collection and refinement parameters are summarized in Table 1. A colorless single crystal was mounted on a glass fiber using 5-min epoxy. Data were collected on a Siemens P4 diffractometer at $T = 298$ K with Mo Kα ($\lambda = 0.710$ 73 Å, graphite monochromator) radiation using the ω scan technique. Cell parameters were determined using 27 reflections. Data were corrected for Lorentz and polarization effects. The structure was solved by Patterson method and refined using Siemens SHELXTL (PC Version 4.2) programs.[45] The Zn atom resides on a 2-fold axis. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogens on boron were located via difference Fourier map inspection and refined with isotropic thermal parameters. The remaining hydrogens were included in calculated

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for Selected Atoms[a]

	x	*y*	*z*	*U*(eq)
		$[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Cu$		
Cu	2500	2500	0	51(1)
N11	1503(2)	2362(5)	230(3)	52(3)
N12	1673(2)	1674(5)	-276(3)	53(3)
N21	2687(2)	2744(5)	1780(3)	55(3)
N22	2980(3)	2094(5)	1438(3)	54(3)
B	2010(3)	3557(7)	993(5)	53(4)
		$[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Zn$		
Zn	267(1)	1461(1)	2798(1)	54(1)
N11	944(4)	-435(4)	1647(2)	54(1)
N21	2505(4)	1580(4)	1647(2)	58(1)
N22	1825(4)	2349(4)	2184(2)	56(1)
N31	−2307(4)	3368(4)	3394(2)	59(1)
N32	−1654(4)	3027(4)	2753(2)	56(1)
N41	−238(4)	2100(4)	4274(2)	54(1)
N42	851(4)	1431(4)	3830(2)	56(1)
B1	2571(6)	−135(6)	1692(3)	66(2)
B2	−1922(6)	2249(7)	4087(3)	64(2)
		$[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Zn$		
Zn	0	872(1)	2500	48(1)
N11	2462(5)	245(3)	3443(2)	50(2)
N12	1793(5)	77(3)	2820(2)	50(2)
N21	394(6)	1328(4)	3915(2)	56(2)
N22	−647(6)	1413(3)	3379(2)	52(2)
B	2196(9)	1191(6)	3779(4)	63(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

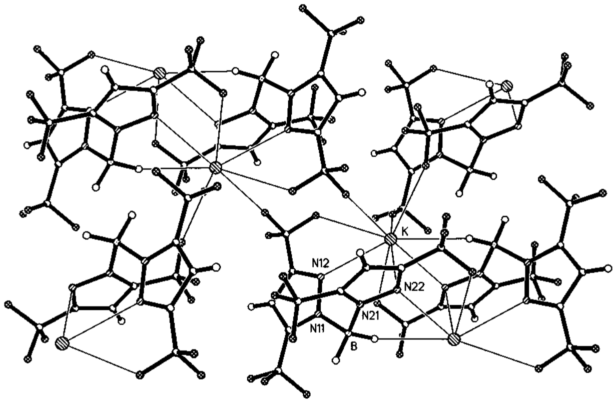

Figure 1. X-ray crystal structure of **3**.

positions (C−H = 0.96 Å, fixed U_H). Atomic positional parameters and selected bond lengths and angles are listed in Tables 4 and 5, respectively.

Table 5. Selected Bond Distances (Å) and Angles (deg)

	$[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Cu$		
Cu−N12	2.004(6)	Cu−N12A	2.004(6)
Cu−N22	1.997(5)	Cu−N22A	1.997(5)
N11−N12	1.357(10)	N21−N22	1.356(10)
N11−B	1.572(7)	N21−B	1.559(7)
Cu···H1	2.579		
N12−Cu−N22	87.1(2)	N12−Cu−N12A	180.0(1)
N22−Cu−N12A	92.9(2)	N12−Cu−N22A	92.9(2)
N22−Cu−N22A	180.0(1)	N12A−Cu−N22A	87.1(2)
Cu−N12−C13	140.4(6)	Cu−N22−C23	140.3(6)
Cu−N12−N11	113.1(3)	Cu−N22−N21	112.9(3)
N12−N11−B	115.9(6)	N22−N21−B	116.5(5)
C15−N11−B	135.7(7)	C25−N21−B	134.8(7)
N11−B−N21	105.7(5)	H1−B−H2	110.0(1)
	$[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Zn$		
Zn−N12	2.021(4)	Zn−N22	2.039(3)
Zn−N32	2.039(3)	Zn−N42	2.014(3)
N11−N12	1.363(5)	N21−N22	1.359(5)
N31−N32	1.362(5)	N41−N42	1.370(5)
N11−B1	1.566(7)	N21−B1	1.573(7)
N31−B2	1.570(6)	N41−B2	1.559(6)
N12−Zn−N22	100.0(1)	N12−Zn−N32	106.0(1)
N22−Zn−N32	106.8(1)	N12−Zn−N42	134.7(1)
N22−Zn−N42	106.4(1)	N32−Zn−N42	100.7(1)
Zn−N12−C13	134.5(3)	Zn−N22−C23	134.2(3)
Zn−N32−C33	135.3(3)	Zn−N42−C43	134.4(3)
Zn−N12−N11	117.0(3)	Zn−N22−N21	117.4(3)
Zn−N32−N31	116.7(3)	Zn−N42−N41	116.1(2)
N12−N11−B1	120.6(4)	N22−N21−B1	119.6(4)
N32−N31−B2	119.6(3)	N42−N41−B2	119.8(4)
C15−N11−B1	130.3(4)	C25−N21−B1	131.2(4)
C35−N31−B2	131.2(4)	C45−N41−B2	131.4(4)
N11−B1−N21	109.3(3)	N31−B2−N41	109.4(4)
	$[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Zn$		
Zn−N12	2.002(5)	Zn−N12A	2.002(5)
Zn−N22	2.007(5)	Zn−N22A	2.007(5)
N11−N12	1.382(6)	N21−N22	1.381(6)
N11−B	1.547(9)	N21−B	1.563(9)
N12−Zn−N22	99.2(2)	N12−Zn−N12A	109.6(3)
N22−Zn−N12A	106.9(2)	N12−Zn−N22A	106.9(2)
N22−Zn−N22A	134.0(3)	N12A−Zn−N22A	99.2(2)
Zn−N12−C13	132.2(4)	Zn−N22−C23	130.4(4)
Zn−N12−N11	118.9(4)	Zn−N22−N21	117.8(4)
N12−N11−B	119.1(5)	N22−N21−B	119.1(5)
C15−N11−B	132.2(5)	C25−N21−B	131.9(5)
N11−B−N21	109.7(5)		

Results and Discussion

The potassium salt of the bis(pyrazolyl)borate ligand **2** is readily prepared in toluene using KBH_4 and 3,5-bis(trifluoromethyl)pyrazole. This product has been isolated in high yield by extraction with Et_2O and characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and elemental analysis. Compound **3** is a white solid which melts around 189 °C. The ^{13}C NMR spectrum of **3** exhibits two sets of quartets for carbons of the CF_3 groups at δ 120.48 and 121.78, indicating two clearly different environments. The ^{13}C NMR spectrum of the starting material, 3,5-bis(trifluromethyl)pyrazole, shows only one quartet at δ 120.5 for the CF_3 carbons at 3- and 5-positions.[46] The ^{19}F NMR data for **3** show two singlet resonances for CF_3 in the normal region (δ −57.7, −59.7).

The X-ray crystal structure of **3**, which has an inversion center, is shown in Figure 1. It has a polymeric structure resulting from close contacts between the potassium ion and the nitrogens, some of the fluorines of the CF_3 groups on the 3- and 5-positions and hydrogen of the BH_2 moieties. The numbering scheme and the local geometry around potassium ion is illustrated in Figure 2. Each potassium center is coordinated to three nitrogens, five fluorines and to a hydrogen (K···H separation is 2.769(39) Å). The K−N (2.819(4)−3.043(3) Å) and K···F (2.812(55)−3.325(5) Å) distances of **3** are similar to those found in $\{[HB(3,5\text{-}(CF_3)_2Pz)_3]K(DMAC)\}_2$ (K−N, 2.811(9), 2.854(7), 2.99(1) Å, K···F, 3.07(1), 3.111(6), 3.82(1) Å) or $\{[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]K(DMAC)\}_2$ (K−N, 2.782(4), 2.867(5), 2.832(4) Å, K···F, 3.140(4), 3.000(4), 3.160(5) Å).[7,46]

Despite the importance and the wide utility of alkali metal poly(pyrazolyl)borates, only very few X-ray crystal structures have been reported in the literature. These include $\{[HB(3,5\text{-}(CF_3)_2Pz)_3]K(DMAC)\}_2$, $[HB(3,4,5\text{-}(CH_3)_3Pz)_3]K$ (crystallizes with three $3,4,5\text{-}(CH_3)_3PzH$ and 0.5 Et_2O), $[B(Pz)_4]K(H_2O)$, and $[B(Pz)_4]Na(H_2O)$.[7,47,48] Compounds with M···F−C interactions

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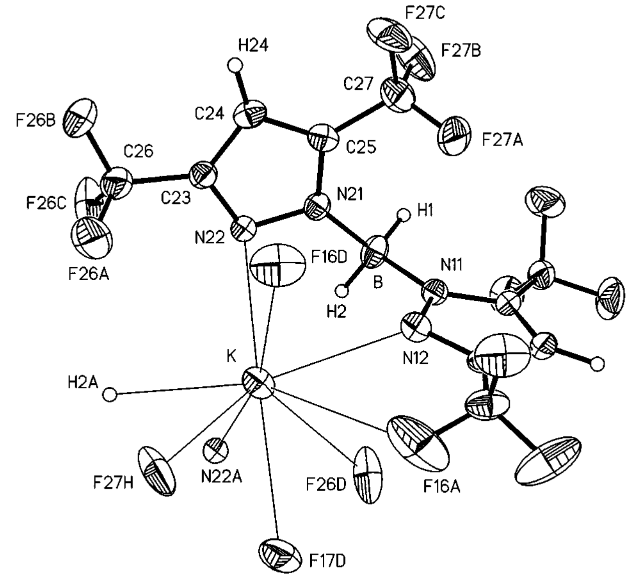
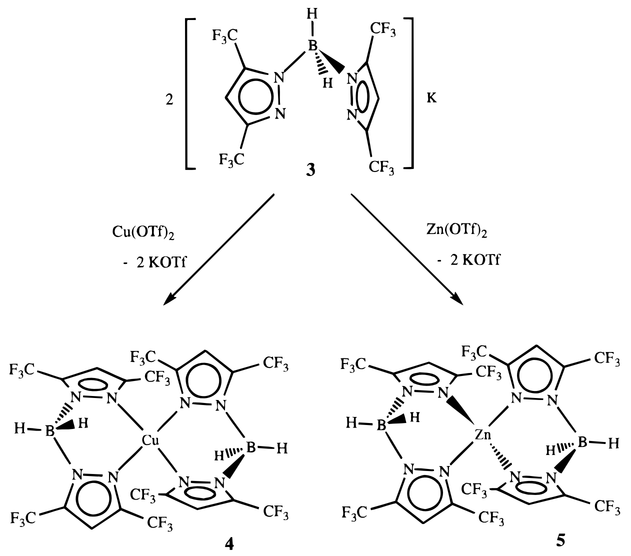


Figure 2. Interactions around the K atom and the ligand numbering scheme for **3**.

Scheme 1



are also of interest due to their importance in C−F activation processes.[3,49] For example, alkali metal salts of fluoroalkoxy ligands have been used as precursors for metal fluorides, e.g., NaF.[49] Close metal···F−C contacts are believed to be important in these C−F bond cleavage processes. However, the number of structurally characterized compounds with M···F−C (where M = alkali metal ion) interactions is very limited. Compound **3** is the first example with such interactions in the bis(pyrazolyl)borate family. Other structurally authenticated molecules with K···F−C contacts include $\{[HB(3,5\text{-}(CF_3)_2Pz)_3]K(DMAC)\}_2$, $\{[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]K(DMAC)\}_2$, $[K(OR)(thf)_2(\mu\text{-}thf)]_2$, and $[K(SR)(thf)]_x$, where R = $2,4,6\text{-}(CF_3)_3C_6H_2$.[7,14,46]

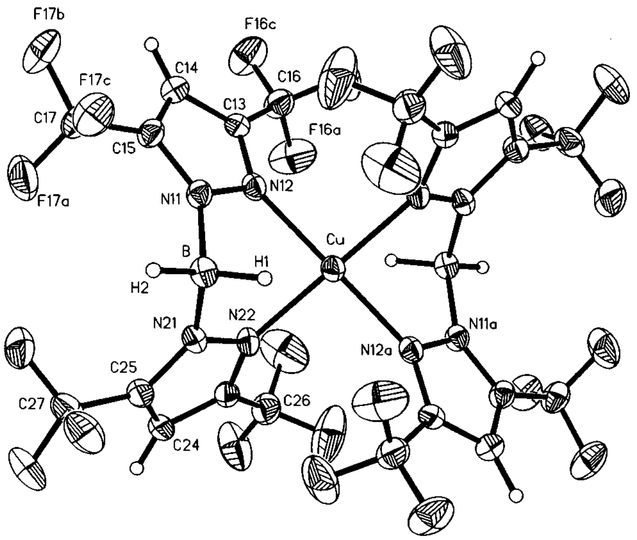


Figure 3. Molecular structure of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Cu$.

The potassium salt **3** has been used in the synthesis of Cu(II) and Zn(II) complexes as depicted in Scheme 1. Treatment of copper(II) trifloromethylsulfonate with two equivalents of **3** in Et_2O gave $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Cu$ (**4**), which was isolated as an air stable, paramagnetic, purple solid. The solubility of **4** is low in common solvents such as toluene, hexanes or Et_2O. Compound **4** melts at 234 °C and could be sublimed under vacuum around 80 °C (sublimed material had the same melting point). The corresponding methylated analog, $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Cu$, was reported to remain as a solid even at 268 °C.[44]

The structure of **4** was determined by X-ray crystallography (Figure 3). It crystallizes as discrete molecules with four nitrogen atoms coordinated to the copper in a square planar geometry (N−Cu−N angles are 87.1(2) and 92.9(2)°). The copper atom resides on an inversion center. The Cu−N distances average 2.00 Å. Such distances are typical for copper poly(pyrazolyl)borates.[50,51] For example, the Cu−N distances of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ or $\{[H_2B(3,5\text{-}(CF_3)_2Pz)_2]CuCNBu^t\}_2$ are 2.035(3) and 2.061(2) Å or 2.018(3) and 2.014(3) Å respectively.[26,52] These distances can also be compared to the Cu−N distances involving non-fluorinated tris(pyrazolyl)borates, $[HB(3,5\text{-}(i\text{-}Pr)_2Pz)_3]CuCO$ (2.019(5), 2.014(6), 2.022(6) Å), $[HB(Pz)_3]CuCO$ (2.039(4), 2.059(3) Å), or $[HB(3,5\text{-}(CH_3)_2Pz)_3]Cu(C_2H_4)$ (2.017(3), 2.041(3), 2.160(4) Å).[53−55] The $Cu(N-N)_2B$ unit in **4** adopts the characteristic boat conformation.[32] As a result, the endo hydrogens of each BH_2 moiety and the fluorines of CF_3 groups on the 3-position partially shield the copper center from above and below the CuN_4 plane as seen from Figures 3 and 4. These nonbonding Cu···H−B distances (average 2.58 Å) in **4** are much longer than the typical Cu−H bond distances (average 1.87 Å) observed in copper borohydride complexes.[56]

The zinc(II) complex, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Zn$ (**5**) was prepared in 56% yield by using $Zn(OTf)_2$ and **3** (Scheme 1). The ^{13}C and ^{19}F NMR spectra show chemical shift values very similar to those observed in **3**. Compound **5** is a colorless solid

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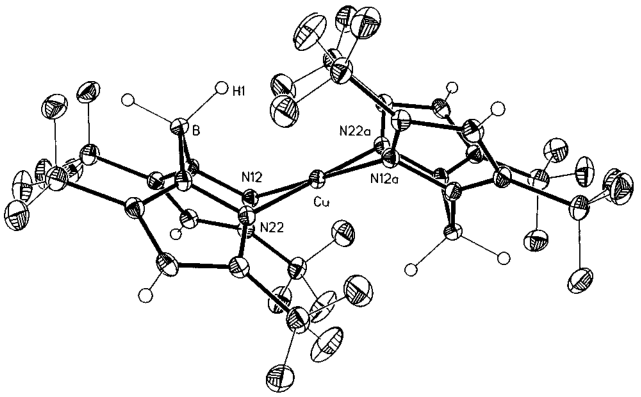

Figure 4. Molecular structure of $[H_2B(3,5-(CF_3)_2Pz)_2]_2Cu$.

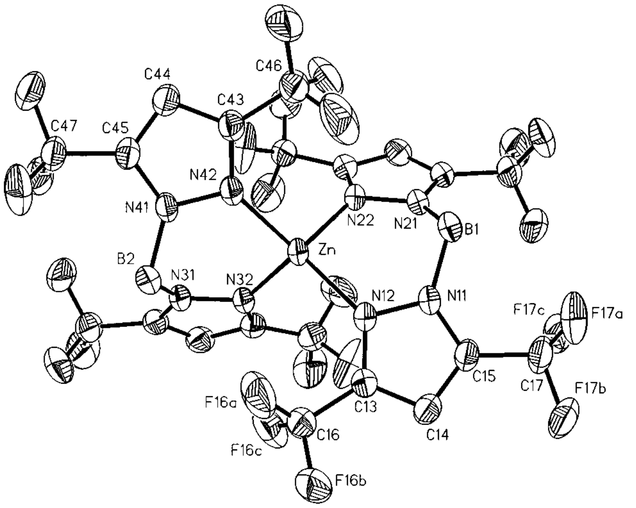

Figure 5. Molecular structure of $[H_2B(3,5-(CF_3)_2Pz)_2]_2Zn$ (hydrogen atoms omitted for clarity).

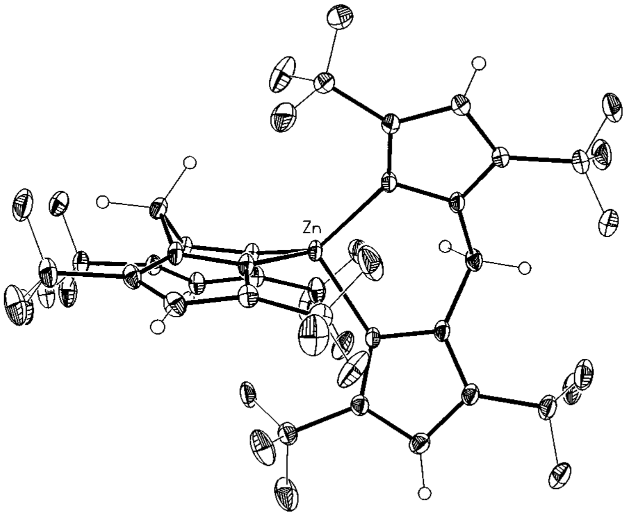

Figure 6. Molecular structure of $[H_2B(3,5-(CF_3)_2Pz)_2]_2Zn$.

which melts at a significantly lower temperature than that of the methylated analog, $[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$ (mp 235 °C).[44] The molecular structure of **5** was determined by X-ray diffraction, and two views are presented in Figures 5 and 6. The zinc atom adopts a distorted tetrahedral geometry (with N−Zn−N angles range from 100.0(1) to 134.7(1)°). Similar distortions from the regular tetrahedral geometry have been observed previously, e.g., $[\eta^2\text{-HB(3-PhPz)}_3]_2Zn$ (101.5−118.9° N−Zn−N angles), $[H_2B(Pz)_2]_2Co$ (96−122° N−Co−N angles).[57,58] The Zn−N distances range from 2.014(3) to 2.039(3) Å. These values are only marginally longer than the Cu−N distances observed for **4**. However, in contrast to **4**, Zn(N−N)₂B units adopt a significantly distorted (flattened at the Zn end) boat conformation. The Zn−X1a−X1b angle (where X1a or X1b is the centroid position between the nitrogens of pyrazole ring 2 position or nitrogens of pyrazole ring 1 position) in **5** is about 166° (see Figure 7 and Table 6). This distortion may be attributed to the steric effects of CF_3 substituents on the ligand and the demands of the tetrahedral geometry. Interestingly, zinc complexes involving bis(pyrazolyl)borates such as $[H_2B(3\text{-}(t\text{-}Bu)Pz)_2]ZnBu^t$ (contains a trigonal planar Zn center) and $\{[H_2B(3\text{-}(t\text{-}Bu)Pz)_2]Zn(\mu\text{-}OH)\}_3$ (with a tetrahedral zinc center but with two sterically less demanding OH donors) or the square planar copper(II) complex **4** display only minor distortions from the boat conformation. For example, the Cu-X1a-X1b angle of **4** is 129°.

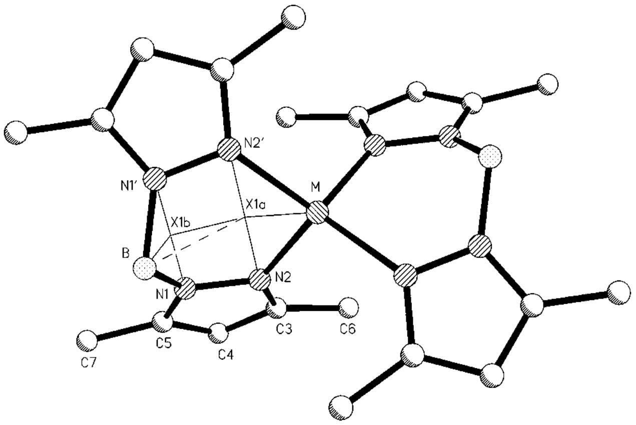

Figure 7. Diagram displaying the relative positions of X1a and X1b.

Table 6. Selected Nonbonded Distances (Å) and Angles (deg) for **4**, **5**, and $[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$

	5	$[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$	4
M−X1a−X1b	165.9	165.3	129.4
X1a−X1b−B	125.9	126.4	127.3
M−X1a−B	144.5	144.5	108.0
N2−N2′	3.11	3.06	2.76
N1−N1′	2.56	2.54	2.50
M−C6	3.60	3.46	3.66

The physical and chemical properties of metal complexes are closely related to the steric and electronic properties of the coordinated ligands. One of our current research efforts is focused on the study of ligand *electronic* effects on the physical and chemical properties of the metal adducts. Often, *steric* factors complicate the results from such investigations. The CF_3-substituted poly(pyrazolyl)borate systems are interesting due to their relationship to well-known CH_3 systems. The CF_3 bearing systems are believed to be sterically similar, but electronically very different from the analogous CH_3-substituted molecules.[59] In order to further explore the relative steric effects of CF_3 vs *CH*₃ susbstituents, we decided to study the X-ray crystal structure of $[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$ and compare it to the closely related fluorinated analog $[H_2B(3,5-(CF_3)_2Pz)_2]_2Zn$ (**5**).

$[H_2B(3,5-(CH_3)_2Pz)_2]_2Zn$ was prepared as described in the literature. X-ray quality crystals of this molecule were obtained from Et_2O-methylene chloride at 0 °C and the structure was characterized by X-ray diffraction (Figure 8). These [H₂B(3,5-

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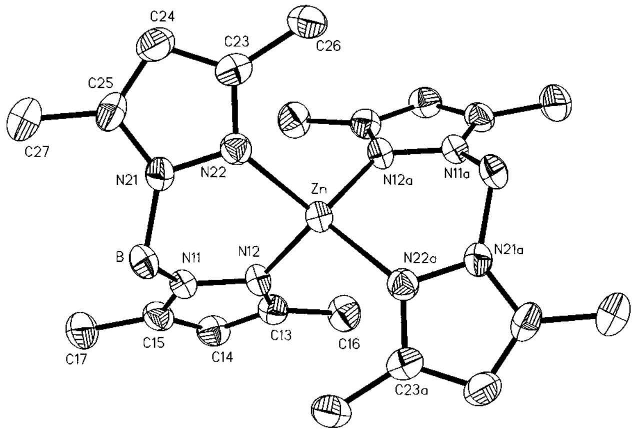

Figure 8. Molecular structure of $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Zn$ (hydrogen atoms omitted for clarity).

$(CH_3)_2Pz)_2]_2Zn$ molecules have a crystallographically imposed 2-fold axis. As in **5**, the Zn center adopts a tetrahedral geometry. The Zn−N distances (2.002(5), 2.007(5) Å) are very similar to those of $[\eta^2\text{-}HB(3\text{-}PhPz)_3]_2Zn$ (2.007, 2.018 Å) and only slightly shorter than those found in **5**, $[HB(3,5\text{-}(CH_3)_2Pz)_3]ZnMe$ (2.056(4), 2.048(6) Å), or $[H_2B(3\text{-}(t\text{-}Bu)Pz)_2]ZnBu^t$ (2.045(6), 2.040(5) Å).[57,60] In contrast, the six-coordinate Zn complex $[HB(3,5\text{-}(CH_3)_2Pz)_3]_2Zn$ has significantly longer Zn−N bonds (2.146(2), 2.183(2), 2.187(2) Å).[60] The $Zn(N{-}N)_2B$ moieties of $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Zn$ adopt a distorted boat conformation. Notably, as evident from the data listed in Table 6, the nature and the extent of this distortion are very similar to those found for the fluorinated analog, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]_2Zn$, suggesting very similar steric effects of having CH_3 or CF_3 substituents on the bis(pyrazolyl)borate ligand.

In summary, we have reported the synthesis and first structural characterization of a fluorinated bis(pyrazolyl)borate ligand as its potassium salt. Syntheses of **4** and **5** and their stability show that, despite the presence of four powerful electronegative CF_3 moieties, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ can serve as a useful ligand for metal ion coordination. On the basis of the bis(pyrazolyl)borate/β-diketone analogy, compound **4** may be compared to one of the most widely studied CVD copper precursors, $(CF_3COCHCOCF_3)_2Cu$.[21,32] Zinc(II) adducts of the fluoromethylated and methylated species $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ and $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]^-$ show very similar structures in the solid state. Poly(pyrazolyl)borates containing alkyl substituents have been found to be useful in obtaining volatile metal complexes.[32,44,61] Polyfluorinated ligands such as **2** may be even more useful in such applications. We are currently exploring the chemistry of this fluorinated ligand with other metal ions and their applications.

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Supporting Information Available: Text giving additional crystallographic information, tables of crystallographic data, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **3, 4, 5,** and $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]_2Zn$ and figures showing disorder models used for **3** and **5** (22 pages). Ordering information is given on any current masthead page.

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