Novel Tris(pyrazolyl)borates Bearing Perfluoroalkyl Pigtails. Syntheses and Characterization of the Sodium and Copper(I) Complexes of $[HB(3\text{-}(R)Pz)_3]^-$ ($R = C_2F_5$, C_3F_7; Pz = Pyrazolyl)

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3-(Pentafluoroethyl)pyrazole and 3-(heptafluoropropyl)pyrazole were synthesized and fully characterized. These pyrazoles react with $NaBH_4$ to yield sodium salts of $[HB(3\text{-}(C_2F_5)Pz)_3]^-$ and $[HB(3\text{-}(C_3F_7)Pz)_3]^-$. The X-ray crystal structure of $[HB(3\text{-}(C_2F_5)Pz)_3]Na(3\text{-}(C_2F_5)PzH)$ shows close contacts between the sodium atom and fluorine atoms of the $-C_2F_5$ substituents. The copper−carbon monoxide adducts $[HB(3\text{-}(C_2F_5)Pz)_3]CuCO$ and $[HB(3\text{-}(C_3F_7)Pz)_3]CuCO$ were prepared by the treatment of CuOTf with 1 equiv of the corresponding tris(pyrazolyl)boratosodium under CO. The copper and sodium complexes were characterized by ^1H, ^{13}C, and ^{19}F NMR and IR spectroscopies. IR spectroscopic data of $[HB(3\text{-}(CF_3)Pz)_3]CuCO$, $[HB(3\text{-}(C_2F_5)Pz)_3]CuCO$, and $[HB(3\text{-}(C_3F_7)Pz)_3]CuCO$ did not exhibit a significant difference in the υ_{CO} values, but they are notably lower than the corresponding υ_{CO} values of the 3,5-disubstituted analog $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$.

Introduction

Physical and chemical properties of metal adducts can be modulated by changing the ligands (e.g., $[\eta^5\text{-}C_5H_5]^-$ to $[HB(Pz)_3]^-$) on the metal ion or more conveniently by modifying the substituents on the ligand framework (e.g., replacing $[\eta^5\text{-}C_5H_5]^-$ with $[\eta^5\text{-}C_5Me_5]^-$).[1] Consequently, much effort has been directed toward the design, synthesis, and use of new ligands which contain substituents with a varying degree of steric and electronic properties.[2−8] Fluoroalkyl substituents are particularly interesting in this regard.[9−13] Metal adducts of the fluorinated ligands often show properties very different from their nonfluorinated counterparts. Polyfluorinated ligands commonly improve the volatility, oxidation resistance, and fluorocarbon solubility of metal complexes. They are known to increase the activity and affect the product distribution of certain metal-mediated reactions.[10,14,15] Ligands bearing fluorinated substituents are also desired for applications in fluorous biphase media and in supercritical carbon dioxide.[16−23]

One area of research focus in this laboratory is the synthesis and applications of fluorinated tris(pyrazolyl)borate ligands.[24−32] Tris(pyrazolyl)borates have been used extensively as a ligand in inorganic and organometallic chemistry.[6,33−35] In fact, complexes of tris(pyrazolyl)borates are now known for most of the metals in the periodic table. Ligands used in these studies are primarily the parent tris(pyrazolyl)borate $[HB(Pz)_3]^-$ or their alkyl-substituted analogs, e.g., $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$. Tris(pyrazolyl)borate ligands bearing fluoro

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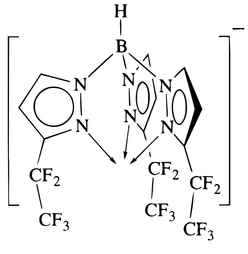
substituents are rare, and the examples in the literature include $[HB(3\text{-}(CF_3)Pz)_3]^-$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (where $HB(3,5\text{-}(CF_3)_2Pz)_3$ = hydrotris(3,5-bis(trifluoromethyl)-pyrazolyl)borate), and $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]^-$.[24,30,36,37] Ligands such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ are very electron-deficient and show interesting chemistry. For example, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ has been used in the stabilization of low-valent main group species such as $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]In$[27] and in the isolation of rare metal carbonyl complexes, e.g., $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$.[26,32] The partially trifluoromethylated $[HB(3\text{-}(CF_3)\text{-}5\text{-}(CH_3)Pz)_3]^-$ ligand has also shown to be useful in stabilizing a rare hydridovinyl species, $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]Ir(H)\text{-}(CO)(CH{=}CH_2)$.[36] These interesting results prompted us to extend our studies into the development of tris-(pyrazolyl)borate ligands with various other fluoro substituents.



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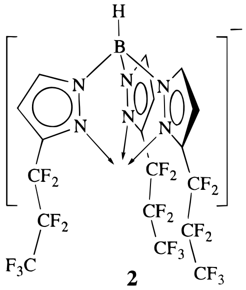

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In this paper, we describe the synthesis of two new tris(pyrazolyl)borate ligands containing $-C_2F_5$ and $-C_3F_7$ substituents on the pyrazolyl group 3-positions. In order to investigate the relative electronic properties of $[HB(3\text{-}(C_2F_5)Pz)_3]^-$ (**1**) and $[HB(3\text{-}(C_3F_7)Pz)_3]^-$ (**2**), we have synthesized their copper(I) carbonyl complexes and compared the C−O stretching frequency data to those of the previously reported tris(pyrazolyl)boratocopper(I) carbonyl complexes. The preparation of precursor pyrazoles, and the X-ray crystal structures of the sodium salt of ligand **1**, $[HB(3\text{-}(C_2F_5)Pz)_3]CuCO$, and $[HB(3\text{-}(C_3F_7)Pz)_3]CuCO$ are reported.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen using either standard Schlenk techniques or in a Vacuum Atmospheres single-station drybox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources, distilled from conventional drying agents, and twice degassed prior to use.[38] Glassware was oven-dried at 150 °C overnight. 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). Chemical shift for ^1H NMR spectra are relative to internal Me_4Si or residual protium in the deuterated solvents (C_6D_6, δ 7.15). ^{13}C NMR spectra were run with ^1H decoupling, and the chemical shifts are reported in ppm vs Me_4Si (C_6D_6, δ 128). ^{19}F NMR chemical shifts were referenced relative to an external $CFCl_3$ standard. IR spectra were recorded on a BioRad 40S spectrometer. Mass spectroscopic data were recorded on a Finnigan MAT TSQ 70 spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer Model 2400 CHN analyzer. Pentafluoropropionic anhydride (PCR), heptafluorobutyric anhydride (PCR). ethyl vinyl ether (Aldrich), hydrazine monohydrochloride (Aldrich), bis(copper(I) trifluoromethanesulfonate)−benzene (Alfa), CO (Matheson), and $NaBH_4$ (Aldrich) were purchased and used as received.

Preparation of 3-(Pentafluoroethyl)pyrazole. Pentafluoropropionic anhydride (25.0 g, 81 mmol) was added dropwise to a mixture of ethyl vinyl ether (4.5 g, 62 mmol) and pyridine (1.4 g, 50 mmol) in methylene chloride (30 mL) at 20 °C. This reaction mixture was stirred for 30 h. Methylene chloride was distilled off from the mixture, and ethyl ether and sodium carbonate (7.0 g) were added. After 10 min, the solution was filtered and ethyl ether was removed from the filtrate by distillation. Then the residue was distilled under vacuum to obtain 5-ethoxy-1,1,1,2,2-pentafluoro-4-penten-3-one as a brown-colored liquid at 50−51 °C (9.4 g, 70%). ^1H NMR ($CDCl_3$): δ 1.21 (q, J = 3.5 Hz, 2H, CH_2), 1.42 (t, J = 3.5 Hz, 3H, CH_3), 5.96 (d, J = 12.3 Hz, 1H, CH), 7.92 (d, J = 12.3 Hz, 1H, CH). ^{19}F NMR ($CDCl_3$): δ −124.7 (q, J = 15.2 Hz, 2F, CF_2), −82.9 (t, J = 15.2 Hz, 3F, CF_3). This was used immediately without further purification.

5-Ethoxy-1,1,1,2,2-pentafluoro-4-penten-3-one (9.4 g, 43 mmol) was added to hydrazine monohydrochloride (3.7 g, 54 mmol) in water (15 mL). Then sodium carbonate (3.2 g) was added in small portions over 20 min at 20 °C. The reaction mixture was stirred for 6 h. Then the solution was extracted with methylene chloride, and the organic layer was separated and dried with anhydrous magnesium sulfate (4.0 g). The mixture was filtered, the solvent was removed by distillation, and the resulting residue was distilled under vacuum at 99−101 °C to obtain 3-(pentafluoroethyl)pyrazole as a white low-melting solid (6.2 g, 77%). Mp: 29−30 °C. ^1H NMR ($CDCl_3$): δ 6.69 (d, J = 1.7 Hz, CH), 7.74 (d, J = 1.7 Hz, CH), 12.54 (br, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 105.31 (s, CH), 111.28 (tq, ^1J = 250.6 Hz, ^2J = 39.3 Hz, CF_2), 118.89 (qt, ^1J = 285.1 Hz, ^2J = 38.0 Hz, CF_3), 130.56 (s, CH), 140.93 (t, ^2J = 27.9 Hz, CCF_2). ^{19}F NMR (C_6D_6): δ −112.8 (br s, 2F, CF_2), −84.7 (t, J = 2.5 Hz, 3F, CF_3). EI-MS: m/z (rel intensity) 186 (80, M^+), 117 (100). Anal. Calcd for $C_5H_3F_5N_2$: C, 32.27; H, 1.62; N, 15.05. Found: C, 31.92; H, 1.60; N, 15.06.

Preparation of 3-(Heptafluoropropyl)pyrazole. Ethyl vinyl ether (1.25 g, 17 mmol) and pyridine (0.44 g) were dissolved in methylene chloride (10 mL). Pentafluoropropionic anhydride (10.00 g, 24 mmol) was added dropwise to this solution at 20 °C. The reaction mixture was stirred for 6 h. Methylene chloride was removed from the mixture by distillation, and ethyl ether and sodium carbonate (1.20 g) were added. After 5 min, the solution was filtered. The ethyl ether was removed by distillation, and the residue was distilled under vacuum to obtain 6-ethoxy-1,1,1,2,2,3,3-heptafluoro-5-hexen-4-one as an orange-brown liquid at 52−53 °C (3.22 g, 70%). This was used immediately in the following step without further purification.

6-Ethoxy-1,1,1,2,2,3,3-heptafluoro-5-hexen-4-one (3.22 g, 12 mmol) was added to hydrazine monohydrochloride (1.10 g, 16 mmol) in water (15 mL). Then sodium carbonate (0.40 g) was added in small portions over 15 min at 20 °C. The reaction mixture was stirred for 12 h. Then the mixture was extracted with methylene chloride, and the organic layer was separated and dried over anhydrous magnesium sulfate. The mixture was filtered, and the solvent was removed from the filtrate by distillation. The resulting residue was distilled under vacuum at 109−111 °C to obtain 3-(heptafluoropropyl)pyrazole as a low-melting white solid (1.98 g, 70%). Mp: 34−35 °C. ^1H NMR (C_6D_6): δ 6.12 (d, J = 1.9 Hz, CH), 6.67 (d, J = 1.9 Hz, CH), 12.07 (br, NH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 105.57 (s, CH), 107−124 (complex multiplet, CF_2, CF_2, CF_3), 130.24 (s, CH), 141.04 (t, ^2J = 28.4 Hz, CCF_2). ^{19}F NMR (C_6D_6): δ −127.2 (br s, 2F, CF_2), −110.4 (m, 2F, CF_2), −80.3 (t, J = 9.6 Hz, 3F, CF_3). Anal. Calcd for $C_6H_3F_7N_2$: C, 30.52; H, 1.28; N, 11.87. Found: C, 30.54; H, 1.57; N, 11.80.

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

	$[HB(3\text{-}(C_2F_5)Pz)_3]Na(3\text{-}(C_2F_5)Pz)\cdot 3\text{-}(C_2F_5)PzH$	$[HB(3\text{-}(C_2F_5)Pz)_3]CuCO$	$[HB(3\text{-}(C_3F_7)Pz)_3]CuCO$
formula	$C_{25}H_{13}BF_{25}N_{10}Na$	$C_{16}H_7BCuF_{15}N_6O$	$C_{19}H_7BCuF_{21}N_6O$
fw	962.25	658.63	808.7
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	12.019(2)	9.9106(14)	9.147(2)
b, Å	17.284(3)	11.589(2)	10.793(3)
c, Å	17.784(4)	11.857(2)	14.701(3)
α, deg	90	118.570(10)	83.36(2)
β, deg	96.294(12)	94.774(11)	87.05(2)
γ, deg	90	95.160(6)	70.69(2)
volume, Å^3	3672.3(12)	1178.6(3)	1360.3(5)
Z	4	2	2
ρ_{calc}, g/cm^3	1.740	1.856	1.974
μ, mm^{-1}	0.207	1.069	0.976
λ, Å	0.710 73	0.710 73	0.710 73
T, °C	-90(2)	−90(2)	−90(2)
R1, wR2^a	0.0594, 0.1527	0.0422, 0.1017	
R, Rw^b			0.0616, 0.0668

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. ^{b} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) for $[HB(3\text{-}(C_2F_5)Pz)_3]Na(3\text{-}(C_2F_5)PzH)$

Na−N12	2.383(4)	Na−N22	2.493(4)	B−N11	1.539(7)	B−N21	1.556(7)
Na−N32	2.457(4)	Na−N42	2.437(4)	B−N31	1.543(7)	N11−N12	1.353(5)
Na−F16A	2.921(4)	Na−F27A	2.957(4)	N21−N22	1.359(5)	N31−N32	1.354(5)
Na−F37A	2.883(6)	Na−46B	2.715(4)	N41−N42	1.351(6)		

Preparation of $[HB(3\text{-}(C_2F_5)Pz)_3]Na$ (3). 3-(Pentafluoroethyl)pyrazole (3.2 g, 17.2 mmol) and sodium borohydride (0.2 g, 5.3 mmol) were mixed in a round bottom flask and carefully heated for 4 h at 170 °C. The resulting solid was washed with petroleum ether and dried under vacuum to yield **3** as a white powder (2.5 g, 80%). Mp: 238−240 °C dec. ^{1}H NMR (DMSO-d_6): δ 6.53 (d, J = 1.7 Hz, C*H*), 7.52 (d, J = 1.7 Hz, C*H*). ^{13}C{^{1}H} NMR: (DMSO-d_6) δ 103.94 (s, *C*H), 111.64 (tq, ^1J = 248.2 Hz, ^2J = 38.2, *C*F$_2$), 118.91 (qt, ^1J = 285.6 Hz, ^2J = 39.1 Hz, *C*F$_3$), 135.04 (s, *C*H), 139.80 (t, ^2J = 27.6 Hz, *C*CF$_2$). ^{19}F NMR (DMSO-d_6): δ −109.8 (br d, 6F, C*F*$_2$), −83.5 (t, J = 2.9 Hz, 9F, C*F*$_3$). IR (KBr), cm^{-1}: 2404 (BH). EI-MS: *m/z* (rel intensity) 590 (100, M$^+$). Anal. Calcd for $C_{15}H_7BF_{15}N_6Na$: C, 30.53; H, 1.20; N, 14.24. Found: C, 30.16; H, 1.04; N, 14.00.

Preparation of $[HB(3\text{-}(C_3F_7)Pz)_3]Na$ (4). 3-(Heptafluoropropyl)pyrazole (0.90 g, 3.8 mmol) and sodium borohydride (38 mg, 1.0 mmol) were mixed in a small flask and carefully heated for 4 h at 170 °C. The resulting solid was washed with petroleum ether and dried under vacuum to obtain **4** as a white powder (0.41 g, 55%). Mp: 250−252 °C dec. ^{1}H NMR (DMSO-d_6): δ 6.52 (s, C*H*), 7.48 (s, C*H*). ^{13}C{^{1}H} NMR: (DMSO-d_6) δ 103.98 (s, *C*H), 108−120 (complex multiplet, *C*F$_2$, *C*F$_2$, *C*F$_3$), 134.78 (s, *C*H), 139.53 (t, ^2J = 27.8 Hz, *C*CF$_2$). ^{19}F NMR (DMSO-d_6): δ −124.6 (br s, 6F, C*F*$_2$), −108.6 (m, 6F, C*F*$_2$), −84.2 (t, J = 7.8 Hz, 9F, C*F*$_3$). IR (KBr), cm^{-1}: 2408 (BH). Anal. Calcd for $C_{18}H_7BF_{21}N_6Na$: C, 29.31; H, 0.95; N, 11.36. Found: C, 29.40; H, 0.96; N, 11.38.

Preparation of $[HB(3\text{-}(C_2F_5)Pz)_3]CuCO$ (5). $[HB(3\text{-}(C_2F_5)Pz)_3]Na$ (200 mg, 0.34 mmol) in THF (10 mL) was added to a CO-saturated THF (10 mL) solution of bis(copper(I) trifluoromethanesulfonate)−benzene (84 mg, 0.17 mmol) at room temperature. This mixture was stirred for 12 h under a CO atmosphere. The solvent was removed under vacuum, and the residue was extracted into *n*-hexane. The resulting mixture was filtered over Celite, and the filtrate was concentrated and cooled to −20 °C to obtain colorless crystals of **5** (130 mg, 59%). Mp: 141−143 °C. ^{1}H NMR (CDCl$_3$): δ 6.52 (d, J = 2.0 Hz, C*H*), 7.72 (d, J = 2.0 Hz, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 105.72 (s, *C*H), 110.74 (tq, ^1J = 252.4 Hz, ^2J = 39.8 Hz, *C*F$_2$), 118.68 (qt, ^1J = 285.7 Hz, ^2J = 38.4 Hz, *C*F$_3$), 136.53 (s, *C*H), 141.69 (t, ^2J = 28.1 Hz, *C*CF$_2$). ^{19}F NMR (CDCl$_3$): δ −113.88 (br s, 6F, C*F*$_2$), −85.27 (br s, 9F, C*F*$_3$). IR (KBr), cm^{-1}: 2519 (BH), 2110 (CO). Anal. Calcd for $C_{16}H_7BCuF_{15}N_6O$: C, 29.18; H, 1.07; N, 12.76. Found: C, 29.01; H, 0.82; N, 12.77.

Preparation of $[HB(3\text{-}(C_3F_7)Pz)_3]CuCO$ (6). $[HB(3\text{-}(C_3F_7)Pz)_3]Na$ (200 mg, 0.27 mmol) in THF (10 mL) was added to a CO-saturated THF (10 mL) solution of bis(copper(I) trifluoromethanesulfonate)−benzene (67 mg, 0.14 mmol) at room temperature. This mixture was stirred for 12 h under a CO atmosphere. The solvent was removed under reduced pressure, and the residue was extracted into *n*-hexane. The resulting mixture was filtered over Celite, and the filtrate was concentrated and cooled to −20 °C to obtain colorless crystals of **6** (120 mg, 56%). Mp: 120−122 °C. ^{1}H NMR (C$_6$D$_6$): δ 6.02 (d, J = 2.6 Hz, C*H*), 7.01 (d, J = 2.6 Hz, C*H*) . ^{19}F NMR (C$_6$D$_6$): δ −126.5 (br s, 6F, C*F*$_2$), −110.3 (m, 6F, C*F*$_2$), −80.5 (t, J = 9.2 Hz, 9F, C*F*$_3$). IR (KBr), cm^{-1}: 2515 (BH), 2102 (CO). Anal. Calcd for $C_{19}H_7BCuF_{21}N_6O$: C, 28.22; H, 0.87; N, 10.39. Found: C, 28.19; H, 0.81; N, 10.78.

X-ray Data Collection and Solution and Refinement of Structures. General Procedures. A suitable crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream.[39] Data collections were carried out at −90 °C on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite-monchromated Mo Kα radiation (λ = 0.710 73 Å). All the software programs and the sources of scattering factors are contained in the SHELXTL PC (Version 4.2 or 5.0) software package provided by Siemens Analytical X-ray Instruments, Inc.[40] Crystal data, data collection, and refinement parameters for compounds $[HB(3\text{-}(C_2F_5)Pz)_3]Na(3\text{-}(C_2F_5)PzH)\cdot 3\text{-}(C_2F_5)PzH$, $[HB(3\text{-}(C_2F_5)Pz)_3]CuCO$, and $[HB(3\text{-}(C_3F_7)Pz)_3]CuCO$ are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3. Further details are included with the Supporting Information.

$[HB(3\text{-}(C_2F_5)Pz)_3]Na(3\text{-}(C_2F_5)PzH)\cdot 3\text{-}(C_2F_5)PzH$. Crystals of the sodium salt were obtained from petroleum ether. The unit cell parameters were determined by least-square refinement of 30 reflections. Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. $[HB(3\text{-}(C_2F_5)Pz)_3]Na(3\text{-}(C_2F_5)PzH)$ crystallizes in the

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Copper Carbonyls Containing Fluorinated Tris(pyrazolyl)borates

	$[HB(3\text{-}(CF_3)Pz)_3]CuCO$	$[HB(3\text{-}(C_2F_5)Pz)_3]CuCO$	$[HB(3\text{-}(C_3F_7)Pz)_3]CuCO$
Cu−N	2.039(3)	2.064(3)	2.080(5)
	2.058(2)	2.086(3)	2.080(5)
	2.058(2)	2.074(3)	2.074(7)
Cu−C	1.790(4)	1.804(4)	1.799(10)
C−O	1.126(5)	1.115(5)	1.119(13)
B−N	1.558(6)	1.554(5)	1.573(10)
	1.547(3)	1.551(5)	1.561(9)
	1.547(3)	1.553(5)	1.565(9)
N−N	1.370(4)	1.362(4)	1.342(9)
	1.368(3)	1.362(4)	1.346(10)
	1.368(3)	1.367(4)	1.332(10)
Cu···B	3.062	3.063	3.079
Cu−C−O	179.0(4)	178.1(4)	178.7(6)
C−Cu−N	125.9(12)	124.3(2)	128.5(3)
	124.28(9)	127.2(2)	124.5(3)
	124.28(9)	123.1(2)	122.1(3)
N−Cu−N	91.73(12)	90.90(12)	88.2(2)
	90.07(9)	90.32(12)	91.1(2)
	90.07(9)	90.58(12)	91.8(2)
C−Cu···B	178.7	176.1	177.7

monoclinic, $P2_1/n$ space group with a molecule of free pyrazole (see Figure S1 in Supporting Information) in the asymmetric unit.[41] All the non-hydrogen atoms were refined anisotropically. The H atoms on boron and N41 and N51 were located from a difference map, and the position of the H atom on B was refined freely. These hydrogen atoms were refined isotropically. The hydrogens on the pyrazole ring were included in calculated positions with C−H = 0.93 Å and $U_H = 1.2U_C$. Refinement by the full-matrix least-squares technique based on F^2 converged to R1 = 0.0594.

$[HB(3\text{-}(C_2F_5)Pz)_3]CuCO$. X-ray quality crystals were obtained from hexane at −20 °C. The unit cell parameters were determined by least-squares refinement of 40 reflections. Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. Data were corrected for Lorentz and polarization effects and for absorption (using ψ scan data). The structure was solved by the Patterson method. All the nonhydrogen atoms were refined anisotropically. The H atom on boron was located from a difference map and refined with fixed U_H. The hydrogens on the pyrazole rings were included in calculated positions with the bond length of C−H = 0.93 Å and $U_H = 1.2U_C$. Refinement by the full-matrix least-squares technique based on F^2 converged to R1 = 0.0422.

$[HB(3\text{-}(C_3F_7)Pz)_3]CuCO$. X-ray quality crystals were obtained from hexane at −20 °C. The unit cell parameters were determined by least-square refinement of 39 reflections. Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. Data were corrected for Lorentz and polarization effects and for absorption (using ψ scan data). The structure was solved by the Patterson method. All the nonhydrogen atoms were refined anisotropically. The hydrogens were included in calculated positions with fixed U_H. Refinement by the full-matrix least-squares technique based on F converged to R = 0.0616.

Results and Discussion

Synthesis of Pyrazoles. Pyrazoles bearing pentafluoroethyl and heptafluoropropyl substitutents were synthesized by a two-step procedure similar to that reported for the 3-(trifluoromethyl)pyrazole.[42] The first step involves the preparation of the β-ethoxyvinyl fluoroalkyl ketone intermediates from the reaction between ethyl vinyl ether and the acid anhydride $(C_2F_5CO)_2O$ or $(C_3F_7CO)_2O$. These β-ethoxyvinyl fluoroalkyl ketones appear to be less stable relative to the trifluoromethylated analog $EtOC(H){=}C(H)COCF_3$.[43] Thus, they were used immediately in the second step, which involves the treatment with hydrazine to obtain the desired pyrazoles. These pyrazoles ($3\text{-}(C_2F_5)PzH$ and $3\text{-}(C_3F_7)PzH$) are low-melting solids with a strong pungent odor. They were characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopies, and elemental analyses (and also in the case of $3\text{-}(C_2F_5)PzH$ by mass spectral analysis). The ^{19}F NMR spectrum of $3\text{-}(C_2F_5)PzH$ consisted of a triplet (δ −84.7) and a broad singlet (δ −112.8), whereas $3\text{-}(C_3F_7)PzH$ displayed a triplet (δ −80.3), a complex multiplet (δ −110.4), and a broad singlet (δ −127.2). The $^{13}C\{^1H\}$ NMR resonances due to $-C_3F_7$ carbons in $3\text{-}(C_3F_7)PzH$ show a fairly complex structure while the related perfluoroethyl analog displayed two resonances with the expected splitting pattern for the $-C_2F_5$ moiety.

Sodium Complexes. The syntheses of the tris(pyrazolyl)boratosodium complexes $[HB(3\text{-}(C_2F_5)Pz)_3]Na$ (**3**) and $[HB(3\text{-}(C_3F_7)Pz)_3]Na$ (**4**) were accomplished by heating a mixture of perfluoroalkylpyrazole and $NaBH_4$ to 170 °C. They were isolated as white solids in 80% and 55% yields, respectively. These sodium complexes do not show high solubility in hydrocarbons such as hexanes or toluene but dissolve fairly well in THF and DMSO. Compounds **3** and **4** were characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopies and elemental analyses. The proposed composition of $[HB(3\text{-}(C_2F_5)Pz)_3]Na$ (**3**) was also supported by EI-MS. The peak observed at m/z 590 was assigned to the $\{[HB(3\text{-}(C_2F_5)Pz)_3]Na\}^+$ ion.

When the synthesis of **3** was carried out in kerosene under similar conditions, the isolated yield was relatively poor. This may be due to an incomplete reaction as supported by the isolation of the $3\text{-}(C_2F_5)PzH$ adduct of **3** (along with unreacted pyrazole) from the resulting mixture. In contrast to **3** which was obtained under solvent free conditions, this pyrazole adduct of **3** is more soluble in organic solvents and forms colorless crystals. It was characterized by X-ray crystallography (Figure 1). The sodium atom in $[HB(3\text{-}(C_2F_5)Pz)_3]Na(3\text{-}(C_2F_5)PzH)$ is coordinated to four nitrogens and to four fluorines. The Na−N distances between the tris(pyrazolyl)borate ligand and pyrazole nitrogens are 2.383(4), 2.493(4), 2.457(4), and 2.437(4) Å, respectively. Interestingly, the pyrazole coordinates to the sodium via the nitrogen atom that is closer to the perfluoroethyl group. The Na···F separations of 2.921(4), 2.957(4), 2.883(6), and 2.715(4) Å are short, suggesting fairly strong interactions. These distances are well within the sum of van der Waals radii of Na and F atoms (3.80 Å).

Compounds with metal···F−C interactions are of interest due to their importance in C−F activation processes.[11] However, structurally authenticated mol-

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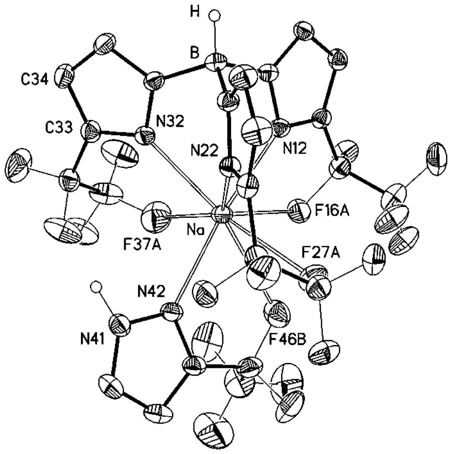

Figure 1. Molecular structure of $[HB(3-(C_2F_5)Pz)_3]Na(3-(C_2F_5)PzH)$. Hydrogens on pyrazolyl carbons have been removed for clarity.

ecules with such interactions are rare.[11,24,28,30,44] Furthermore, only a very few structures of alkali metal tris(pyrazolyl)borates have been reported in the literature.[24,30,45-47] $[HB(3-(C_2F_5)Pz)_3]Na(3-(C_2F_5)PzH)$ is, therefore, an important new addition to these two categories.

Copper Carbonyl Complexes. Copper(I) complexes of carbon monoxide have been actively studied due to their importance in catalysis and biochemistry.[48-52] Tris(pyrazolyl)borate ligands play an important role in this regard. In fact, the first stable copper(I) carbonyl complex was isolated by Bruce and coworkers using the tris(pyrazolyl)borate ligand $[HB(Pz)_3]^-$.[53,54] We have recently reported the use of a $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand to stabilize a Cu−CO species.[25] As a part of our investigation into the chemistry of fluorinated tris(pyrazolyl)borate ligands, we have synthesized the copper carbonyl complexes **1** and **2** and examined their spectroscopic and structural features.

The treatment of the tris(pyrazolyl)boratosodium salts with CuOTf in the presence of CO led to the copper(I) carbonyl adducts $[HB(3-(C_2F_5)Pz)_3]CuCO$ (**5**) and $[HB(3-(C_3F_7)Pz)_3]CuCO$ (**6**) in 59% and 56% isolated yields, respectively (Scheme 1). They are colorless, air- and moisture-stable solids. They show good solubility in a variety of solvents such as hexanes, toluene, THF, or $CHCl_3$. Compounds **5** and **6** were characterized by NMR and IR spectroscopies and X-ray crystallography. The solid state IR spectrum of **5** shows a strong absorption at 2110 cm^{-1}, corresponding to the carbonyl stretching frequency. The ν_{CO} for **6** is marginally lower (2102 cm^{-1}). These ν_{CO} values in **5** and **6** are lower than that observed for the free CO (2143 cm^{-1}),[55] indicating some degree of Cu → CO back-bonding.[3]

Scheme 1

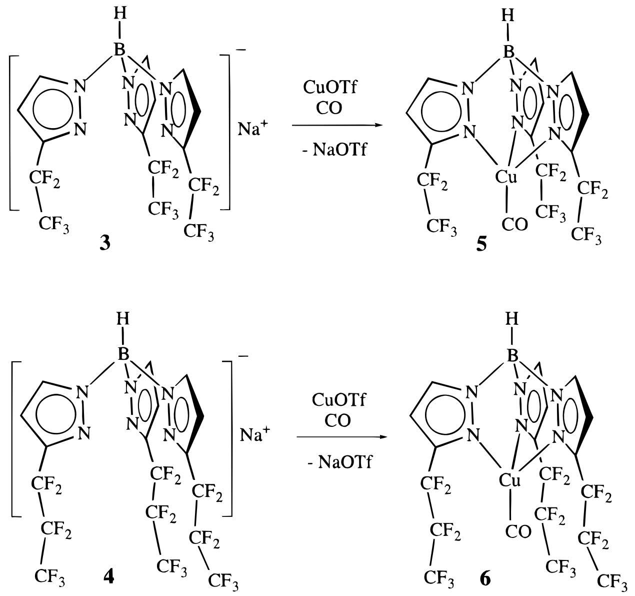

Table 4. Selected IR Spectroscopic Data for Tris(pyrazolyl)boratocopper(I) Carbonyl Complexes

compound	ν_{CO} (cm^{-1})	ref
$[HB(3,5-(i-Pr)_2Pz)_3]CuCO$	2056	56
$[HB(3,5-(CH_3)_2Pz)_3]CuCO$	2066	57
$[HB(Pz)_3]CuCO$	2083	53
$[HB(3,5-(Ph)_2Pz)_3]CuCO$	2086	56
$[HB(3-(CF_3)Pz)_3]CuCO$	2100	29
$[HB(3-(C_3F_7)Pz)_3]CuCO$	2102	this work
$[HB(3-(C_2F_5)Pz)_3]CuCO$	2110	this work
$[HB(3,5-(CF_3)_2Pz)_3]CuCO$	2137	25
CO	2143	55

The C−O stretching frequencies of a series of closely related tris(pyrazolyl)boratocopper(I) carbonyl complexes are presented in Table 4. These ν_{CO} data can be used as an indirect measure of the relative electron density of the copper atom in these complexes or to evaluate the relative electron donor properties of the tris(pyrazolyl)borate ligand. The data in Table 4 show that, compared to the 3,5-disubstituted analog $[HB(3,5-(CF_3)_2Pz)_3]CuCO$,[25] compounds **6**, **5**, and $[HB(3-(CF_3)Pz)_3]CuCO$ show relatively low ν_{CO} values. These data suggest that there is a significant effect from the perfluoroalkyl substituents in the pyrazolyl ring 5-position on the electronic properties of the copper center. A similar effect was also noted in the [tris(pyrazolyl)borato]manganese systems.[29] Furthermore, the ligand's electronic effects resulting from the change of substituent from $-CF_3$ to $-C_3F_7$ in these ligand systems appear to be minor (at least in copper systems).

Fluorinated tris(pyrazolyl)boratocopper(I) carbonyls in general display considerably higher carbonyl stretching frequencies relative to nonfluorinated analogs (Table 4). The overall trend is consistent with the electron-

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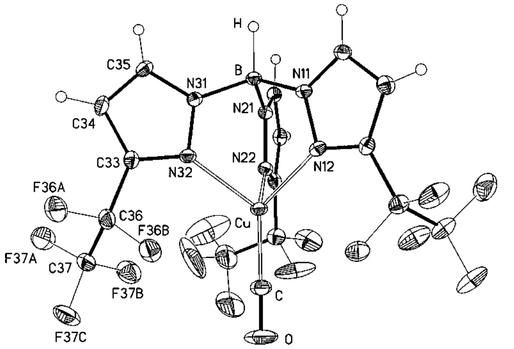

Figure 2. Molecular structure of $[HB(3-(C_2F_5)Pz)_3]CuCO$.

donating ability of the substituents on the pyrazolyl groups.[58] Interestingly, the values of the C−O stretching frequencies of **5** and **6** are comparable to the those observed for the cationic [tris(pyrazolyl)methane]copper carbonyl complexes $\{[HC(3,5-(CH_3)_2Pz)_3]CuCO\}^+$ (2113 cm^{-1}) and $\{[HC(3-(Ph)Pz)_3]CuCO\}^+$ (2104 cm^{-1}).[59]

The X-ray crystal structure of **5** is illustrated in Figure 2. The copper center adopts a distorted tetrahedral coordination. The Cu−C−O moiety is linear within experimental limits (178.1(4)°). The important feature in the X-ray crystal structure of **5** concerns the relatively long Cu−CO bond distance of 1.804(4) Å, which is very similar to that observed for $[HB(3,5-(CF_3)_2Pz)_3]CuCO$ (1.808(4) Å) or $[HB(3-(CF_3)Pz)_3]CuCO$ (1.790(4) Å).[25,29] Typical Cu(I)−CO distances are in the range of 1.75−1.78 Å. However, there are rare examples with long Cu−CO distances as in $[Cu(CO)Cl]_n$, 1.86(2) Å (υ_{CO} = 2127 cm^{-1} in Nujol or 2157 cm^{-1} in Ar matrix),[60] carbonyl[glyoxal bis(2,4-dimethylpentyl-3-imine)](trimethylsulfonato)copper, 1.820(6) Å (υ_{CO} = 2108 cm^{-1}),[61] or $[\{NH(py)_2\}CuCO](ClO_4)$, 1.808(2) Å ($\upsilon_{CO}$ = 2110 cm^{-1}).[62] The C−O bond length in **1** is 1.115(5) Å. The Cu−N bond distances and angles in **5** are typical for a [tris(pyrazolyl)borato]copper(I) complex.[30]

The solid state structure of **6** is shown in Figure 3. Three perfluoropropyl chains in the pyrazolyl group 3-position create a cavity which is occupied by the linear Cu−CO moiety. The Cu−C and C−O bond lengths are 1.799(10) and 1.119(13) Å, respectively. As evident from the data shown in Table 3, the difference in structural parameters between **5** and **6** is not significant.

In summary, we have described the synthesis of two new tris(pyrazolyl)borate ligands containing fluorinated "pigtails" [63] in the 3-position of the pyrazolyl groups. They allow the isolation of stable copper(I) carbon monoxide adducts **5** and **6**. We are currently investigating the chemistry of ligands **1** and **2** with other metal ions. The overall procedure described for the synthesis of **1** and **2** may also be applicable for the synthesis of tris(pyrazolyl)borates with even longer perfluoroalkyl chains.

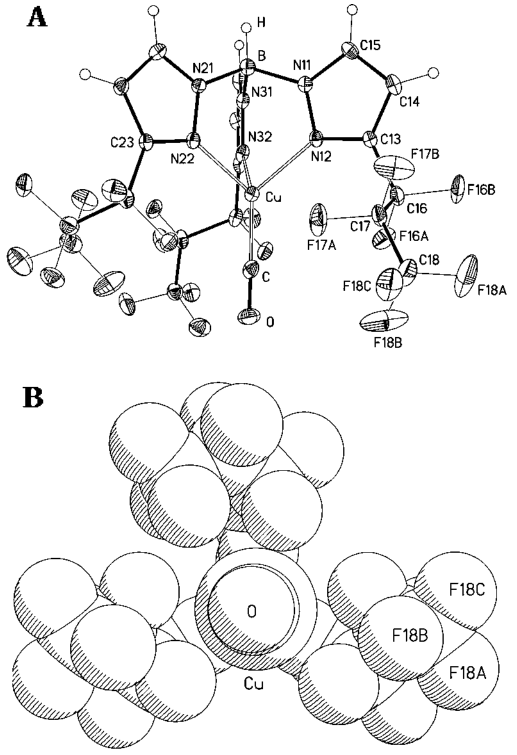

Figure 3. Molecular structure of $[HB(3-(C_3F_7)Pz)_3]CuCO$ (A) ORTEP diagram and (B) a view down the O−C bond (space-filling model).

Acknowledgment. Financial support received from The Robert A. Welch Foundation is gratefully acknowledged. We also thank U.T.A. for providing funds to purchase the Siemens P4 single-crystal X-ray diffractometer. The CHN analyzer was purchased through a grant from the Defense Advanced Research Projects Agency monitored by the Office of Naval Research. We also thank Mr. Mark Land for obtaining the mass spectral data and Mrs. Shamini Dias for helpful discussions.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and complete bond distances and angles for $[HB(3-(C_2F_5)Pz)_3]Na-(3-(C_2F_5)PzH)\cdot 3-(C_2F_5)PzH$, **5,** and **6** (20 pages). Ordering information is given on any current masthead page.

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