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Polyfluorinated Tris(pyrazolyl)borates. Syntheses and Spectroscopic and Structural Characterization of Group 1 and Group 11 Metal Complexes of $[HB(3,5-(CF_3)_2Pz)_3]^-$ and $[HB(3-(CF_3)Pz)_3]^-$

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The fluorinated tris(pyrazolyl)borate ligands $[HB(3,5-(CF_3)_2Pz)_3]^-$ and $[HB(3-(CF_3)Pz)_3]^-$ (where Pz = pyrazolyl) have been synthesized as their sodium salts from the corresponding pyrazoles and $NaBH_4$ in high yield. These sodium complexes and the related $[HB(3,5-(CF_3)_2Pz)_3]K(DMAC)$ were used as ligand transfer agents in the preparation of the copper and silver complexes $[HB(3,5-(CF_3)_2Pz)_3]Cu(DMAC)$, $[HB(3,5-(CF_3)_2Pz)_3]CuPPh_3$, $[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$, and $[HB(3-(CF_3)Pz)_3]AgPPh_3$. Metal complexes of the fluorinated $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand have highly electrophilic metal sites relative to their hydrocarbon analogs. This is evident from the formation of stable adducts with neutral oxygen donors such as H_2O, dimethylacetamide, or thf. Furthermore, the metal compounds derived from fluorinated ligands show fairly long-range coupling between fluorines of the trifluoromethyl groups and the hydrogen, silver, or phosphorus. The solid state structures show that the fluorines are in close proximity to these nuclei, thus suggesting a possible through-space coupling mechanism. Crystal structures of the sodium adducts exhibit significant metal−fluorine interactions. The treatment of $[HB(3,5-(CF_3)_2Pz)_3]Na(H_2O)$ with Et_4NBr led to $[Et_4N][HB(3,5-(CF_3)_2Pz)_3]$, which contains a well-separated $[Et_4N]^+$ cation and the $[HB(3,5-(CF_3)_2Pz)_3]^-$ anion in the solid state. Crystal data with Mo Kα (λ = 0.710 73 Å) at 193 K: $[HB(3,5-(CF_3)_2Pz)_3]Na(H_2O)$, $C_{15}H_6BF_{18}N_6NaO$, a = 7.992(2) Å, b = 15.049(2) Å, c = 9.934(2) Å, β = 101.16(2)°, monoclinic, $P2_1/m$, Z = 2; $[\{HB(3-(CF_3)Pz)_3\}Na(thf)]_2$, $C_{32}H_{30}B_2F_{18}N_{12}Na_2O_2$, a = 9.063(3) Å, b = 10.183(2) Å, c = 12.129(2) Å, α = 94.61(1)°, β = 101.16(2)°, γ = 95.66(2)°, triclinic, $P\bar{1}$, Z = 1; $[HB(3,5-(CF_3)_2Pz)_3]Cu(DMAC)$, $C_{19}H_{13}BCuF_{18}N_7O$, a = 15.124(4) Å, b = 8.833(2) Å, c = 21.637(6) Å, β = 105.291(14)°, monoclinic, $P2_1/n$, Z = 4; $[HB(3,5-(CF_3)_2Pz)_3]CuPPh_3$, $C_{33}H_{19}BCuF_{18}N_6P$, a = 9.1671(8) Å, b = 14.908(2) Å, c = 26.764(3) Å, β = 94.891(1)°, monoclinic, $P2_1/c$, Z = 4; $[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3\cdot 0.5C_6H_{14}$, $C_{36}H_{26}AgBF_{18}N_6P$, a = 13.929(2) Å, b = 16.498(2) Å, c = 18.752(2) Å, β = 111.439(6)°, monoclinic, $P2_1/c$, Z = 4; $[Et_4N][HB(3,5-(CF_3)_2Pz)_3]$, $C_{23}H_{24}BF_{18}N_7$, a = 10.155(2) Å, b = 18.580(4) Å, c = 16.875(5) Å, β = 99.01(2)°, monoclinic, $P2_1/n$, Z = 4.

Introduction

Metal adducts of the fluorinated ligands often show very different physical and chemical properties relative to their nonfluorinated analogs.[1−5] Polyfluorinated ligands commonly improve the volatility, oxidation resistance, and fluorocarbon solubility of their metal adducts. They have also been known to improve the activity of certain metal-catalyzed reactions.[2,6−9] As a result, fluorinated ligands have been highly desired for a variety of applications. There are several different types of polyfluorinated ligands currently used in chemistry.[1,2,4,5,7,8,10−41] They include β-diketones, phosphines, porphyrins, cyclopentadienes, alkyls, aryls, and alkoxides. Some of the weakly coordinating, fluorine-containing anions such as BF_4^-, PF_6^-, $SO_3CF_3^-$, $B(C_6F_5)_4^-$, $OTeF_5^-$, etc. also play a significant role in chemistry.[42]

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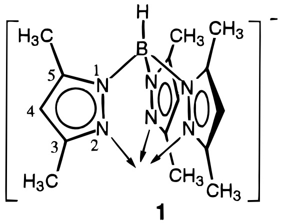
One area of focus in our laboratory is the development of fluorinated poly(pyrazolyl)borates.[43,44] Poly(pyrazolyl)borates constitute one of the most widely used ligands in chemistry.[45−48] In fact, complexes of these ligands are now known for most of the elements in the periodic table. A vast majority of these studies involves the use of either the parent tris(pyrazolyl)borate, $[HB(Pz)_3]^-$, or its alkyl-substituted-ligand systems, e.g., $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$ (**1**).[45,46] The fluorinated analogs remain largely unexplored.[43−45,49] Recently, we reported the synthesis and the structural characterization of the potassium complex of a tris(pyrazolyl)borate ligand, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$, **2** (where $[HB(3,5\text{-}(CF_3)_2Pz)_3]$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate), bearing six electron-withdrawing CF_3 substituents.[43]



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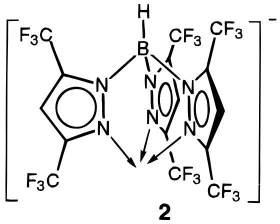

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This ligand has enabled the isolation of several unique compounds such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ in stable, crystalline form.[50,51] The use of **1** to generate $[HB(3,5\text{-}(CH_3)_2Pz)_3]In$ has resulted in a slow disproportionation leading to an In(III) species.[52] Spectroscopic and structural data for the copper carbonyl complex $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]CuCO$ show significant differences relative to the nonfluorinated analogs.[53] For example, the carbonyl stretching frequency of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ is the highest observed for a [tris(pyrazolyl)borato]copper(I) complex, and it is about 71 cm^{-1} higher than that for the copper(I) carbonyl species derived from the methylated ligand **1**.[54] The Cu−CO bond length in $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ is also longer than the corresponding distance in nonfluorinated analogs. The partially trifluoromethylated $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]^-$ ligand has also been shown to be useful in stabilizing a rare hydrido vinyl species, $[HB(3\text{-}(CF_3)\text{-}5\text{-}(CH_3)Pz)_3]Ir(H)(CO)(CH{=}CH_2)$.[49]

Here we report full details of the synthesis and structural characterization of the sodium salts of two highly fluorinated ligand systems, hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate and hydrotris(3-(trifluoromethyl)pyrazolyl)borate. Their uses in the synthesis of several new copper and silver complexes are also described along with some interesting NMR spectroscopic results and X-ray crystallographic data.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of purified nitrogen either with 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 degassed twice prior to use.[55] Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at room temperature on a Bruker MSL-300 spectrometer (^1H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.36 MHz; ^{31}P, 121.49 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 (C_6D_6, 7.15 ppm). ^{13}C NMR spectra were run with ^1H decoupling, and the chemical shifts are reported in ppm vs Me_4Si (C_6D_6 at 128.0 ppm). ^{19}F NMR and ^{31}P NMR chemical shifts were referenced to an external $CFCl_3$ and an 85% H_3PO_4 standard, respectively. The ^{31}P NMR spectroscopic data were accumulated with ^1H decoupling. 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 at The University of Texas at Arlington using a PE-2400 CHN analyzer.

3,5-Bis(trifluoromethyl)pyrazole and 3-(trifluoromethyl)pyrazole were prepared by literature methods.[56,57] $NaBH_4$ (Aldrich), PPh_3 (Aldrich), bis(copper(I) trifluoromethanesulfonate)−benzene (Alfa), silver(I) trifluoromethanesulfonate (Strem), Et_4NCN (Aldrich), and Et_4NBr (Alfa) were purchased and used as received.

Synthesis of $[HB(3,5\text{-}(CF_3)_2Pz)_3]K(DMAC)$ (3). This was synthesized from 3,5-bis(trifluoromethyl)pyrazole and KBH_4 as described previously.[43] ^1H NMR (C_6D_6): δ 1.46 (s, CH_3) 1.96 (s, CH_3), 2.38 (s, CH_3), 6.38 (s, C*H*). ^{19}F NMR (C_6D_6): δ −61.4, −58.9. IR (KBr), cm^{-1}: 1618 (CO), 2583 (BH).

Synthesis of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$ (4). $NaBH_4$ (0.40 g, 10.6 mmol) and 3,5-bis(trifluoromethyl)pyrazole (7.55 g, 37 mmol) were mixed in a minimum amount of kerosene. The mixture was slowly heated to 180−190 °C and kept for 4 h at 190 °C. During this period, a white solid slowly precipitated. The mixture was allowed to cool to room temperature, and the resulting white solid was collected by suction filtration (in air). It was washed several times with petroleum ether and sucked dry in air to obtain **4** as a white solid (yield 76% based on $NaBH_4$). Mp: 107−109 °C. ^1H NMR (C_6D_6): δ 0.75 (s, 2H, H_2O), 6.25 (s, 3H, C*H*). ^{19}F NMR (C_6D_6): δ −62.2 (s), −58.5 (d, $^5J(H,F)$ = 3.5 Hz). ^1H NMR (DMSO-d_6): δ 5.0 (b, 2H, H_2O), 7.18 (s, 3H, C*H*). ^{19}F NMR (DMSO-d_6): δ −60.1, −58.9. $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 105.93 (s, *C*H), 120.05 (q, $^1J(C,F)$ = 268.9 Hz, CF_3), 121.39 (q, $^1J(C,F)$ = 268.3 Hz, CF_3), 136.32 (q, $^2J(C,F)$ = 38.9 Hz, CCF_3), 140.57 (q, $^2J(C,F)$ = 37.1Hz, CCF_3). IR (solid), cm^{-1}: 2612 (BH). Anal. Calcd for $C_{15}H_6N_6BF_{18}O$: C, 27.21; H, 0.91; N, 12.69. Found: C, 27.18; H, 0.98; N, 12.66.

Synthesis of $[DB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$. This was prepared using $NaBD_4$ and 3,5-bis(trifluoromethyl)pyrazole and the same procedure described for **4**.

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Synthesis of [HB(3-(CF_3)Pz)$_3$]Na (5). 3-(Trifluoromethyl)pyrazole (5.0 g, 36.74 mmol) and sodium borohydride (0.408 g, 10.79 mmol) were mixed in 5 mL of kerosene. The mixture was heated for 4 h at 180 °C to obtain a yellow solid. The solid was collected, washed with petroleum ether, and dried under vacuum. This solid was suspended in hexanes (30 mL), and the suspension was refluxed for 2 h and filtered to obtain **5** in 85% yield. Mp: 280 °C, dec. ^{1}H NMR (DMSO-d_6): δ 6.52 (s, 3H, C*H*), 7.53 (s, 3H, C*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 102.76 (s, *C*H), 122.42 (q, ^1J(C,F) = 267.8 Hz, *C*F$_3$), 134.94 (s, *C*H), 141.31 (q, ^2J(C,F) = 35.2 Hz, *C*CF$_3$). ^{19}F NMR (DMSO-d_6): δ −59.2 (s). Anal. Calcd for $C_{12}H_7N_6BF_9Na$: C, 32.76; H, 1.60; N, 19.10. Found: C, 32.88; H, 1.41; N, 18.52. The thf adduct [HB(3-(CF_3)Pz)$_3$]Na(thf) was prepared by dissolving **5** in a minimum amount of warm thf−toluene followed by slow cooling to 0 °C. [HB(3-(CF_3)Pz)$_3$]Na(thf) was isolated as a colorless, crystalline solid. ^{1}H NMR ($CDCl_3$): δ 1.89 (m, 4H, C*H*$_2$), 3.80 (m, 4H, C*H*$_2$), 6.39 (d, J = 1.72 Hz, 3H, C*H*), 7.69 (d, J = 1.77 Hz, 3H, C*H*). ^{19}F NMR ($CDCl_3$): δ -62.3 (s).

Synthesis of [HB(3,5-(CF_3)$_2$Pz)$_3$]Cu(DMAC) (6). A thf (10 mL) solution of [HB(3,5-(CF_3)$_2$Pz)$_3$]K(DMAC) (0.200 g, 0.268 mmol) was added to the bis(copper(I) trifluoromethanesulfonate)−benzene complex (0.067 g, 0.134 mmol) in thf (10 mL) at room temperature. The mixture was refluxed for 12 h and cooled to room temperature, and the solvent was removed under reduced pressure. The resulting mixture was filtered, and the product was recrystallized from toluene at −25 °C to give 130 mg of **6** (63% yield). Mp: 170−171 °C. ^{1}H NMR (C_6D_6): δ 1.86 (s, C*H*$_3$), 1.98 (s, C*H*$_3$), 2.58 (s, C*H*$_3$), 6.31 (s, C*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.64 (s, *C*H$_3$), 34.96 (s, *C*H$_3$), 37.48 (s, *C*H$_3$), 106.52 (s, *C*H), 119.84 (q, ^1J(C,F) = 270.1 Hz , *C*F$_3$), 120.89 (q, ^1J(C,F) = 269.4 Hz, *C*F$_3$), 139.27 (q, ^2J(C,F) = 42.1 Hz, *C*CF$_3$), 142.36 (q, ^2J(C,F) = 39.0 Hz, *C*CF$_3$), 172.53 (s, *C*O). ^{19}F NMR (C_6D_6): δ −61.4 (s), −58.3 (d, ^5J(H,F) = 3.2 Hz). IR (KBr), cm^{-1}: 1616 (CO), 2613 (BH). Anal. Calcd for $C_{19}H_{13}N_7F_{18}BCuO$: C, 29.57; H, 1.70; N, 12.71. Found: C, 30.06; H, 1.49; N, 12.30.

Synthesis of [HB(3,5-(CF_3)$_2$Pz)$_3$]CuPPh$_3$ (7). To a mixture of the bis(copper(I) trifluoromethanesulfonate]−benzene complex (0.067 g, 0.134 mmol) and thf (15 mL) were added [HB(3,5-(CF_3)$_2$Pz)$_3$]K(DMAC) (0.200 g, 0.268 mmol) and PPh$_3$ (0.070 g, 0.268 mmol) at room temperature. The resulting mixture was refluxed overnight. The solution was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was extracted into toluene, the extract was filtered, and the filtrate was dried under vacuum to obtain **7** in 79% yield. Crystals suitable for X-ray experiments were obtained from toluene−hexane at −25 °C. Mp: 179−181 °C. ^{1}H NMR (C_6D_6): δ 6.31 (s, 3H, C*H*), 7.13 (d, J = 7.8 Hz, 9H, *Ho,p*), 7.67 (m, 6H, *Hm*). ^{13}C{^{1}H}NMR (C_6D_6): δ 107.69 (br s, *C*H), 119.69 (q, ^1J(C,F) = 271 Hz, *C*F$_3$), 120.10 (q, ^1J(C,F) = 270 Hz, *C*F$_3$), 128.68 (d, ^3J(C,P) = 10 Hz, *Cm*), 130.51 (br, s, *Cp*), 132.99 (d, ^1J(C,P) = 39 Hz, *Ci*), 134.67 (d, ^2J(C,P) = 15 Hz, *Co*), 140.21 (q, ^2J(C,F) = 42 Hz, *C*CF$_3$), 144.37 (q, ^2J(C,F) = 39 Hz, *C*CF$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 7.2 (br s). ^{19}F NMR (C_6D_6): δ −59.6 (d, ^5J(P,F) = 6.5 Hz), −58.2 (d, ^5J(H,F) = 2.6 Hz). IR (KBr), cm^{-1}: 2600 (BH). Anal. Calcd for $C_{33}H_{19}N_6F_{18}BCuP$: C, 41.86; H, 2.02; N, 8.88. Found: C, 41.89; H, 2.09; N, 8.74.

Synthesis of [HB(3,5-(CF_3)$_2$Pz)$_3$]AgPPh$_3$ (8). A mixture of **4** (0.558 mmol) and PPh$_3$ (0.146 g, 0.558 mmol) in thf (30 mL) was added to silver(I) triflate (0.143 g, 0.558 mmol) in thf (20 mL) at 0 °C. After the addition, the solution was stirred overnight at room temperature. The volatile materials were removed under reduced pressure, and the residue was extracted into toluene. Filtration through Celite followed by the removal of toluene from the filtrate gave **8** (92%, 0.515 mmol) as a pure white solid. Clear, colorless crystals were grown from hexane at −25°C but easily became opaque at room temperature. Mp: 186.5−188 °C. ^{1}H NMR (C_6D_6): δ 6.30 (s, 3H, C*H*), 7.09−7.17 (m, 9H, *Ho,p*), 7.61−7.68 (m, 6H, *Hm*). ^{13}C{^{1}H} NMR (C_6D_6): δ 106.91 (s, *C*H), 119.91 (q, ^1J(C,F) = 270.7 Hz, *C*F$_3$), 120.69 (q, ^1J(C,F) = 268.8 Hz, *C*F$_3$), 129.1 (d, ^3J(C,P) = 9.8 Hz, *Cm*), 130.97 (s, *Cp*), 131.80 (dd, ^1J(C,P) = 36.9 Hz, ^2J(C,Ag) = 4.6 Hz, *Ci*), 134.30 (d, ^2J(C,P) = 16.2 Hz, *Co*), 140.47 (q, ^2J(C,F) = 42.2 Hz, *C*CF$_3$) , 144.18 (q, ^2J(C,F) = 38.4 Hz, *C*CF$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 17.8 (^1J(P,^{107}Ag) = 657.5 Hz, ^1J(P,^{109}Ag) = 758.8 Hz, ^5J(P,F) = 8.3 Hz). ^{19}F NMR (C_6D_6): δ −60.4 (dd, ^5J(F,P) = 8.1 Hz, ^4J(F,Ag) = 1.4 Hz), −58.3 (d, ^5J(F,H) = 2.5 Hz). IR, cm^{-1}: 2606 (BH). Anal. Calcd for $C_{33}H_{19}N_6BF_{18}PAg$: C, 39.99; H, 1.93; N, 8.48. Found: C, 40.13; H, 1.41; N, 8.38.

Synthesis of [HB(3-(CF_3)Pz)$_3$]AgPPh$_3$ (9). Compound **5** (0.137 g, 0.311 mmol) was dissolved in thf, and PPh$_3$ (0.082 g, 0.313 mmol) in thf (10 mL) was added. This mixture was then added to AgOTf (0.080 g, 0.311 mmol) in thf (10 mL) at 0 °C. After 1 h, the solution was allowed to warm to room temperature and stirred for 30 min. The solvent was removed under vacuum, and the residue was extracted into benzene. After filtration, the volatile materials were removed under reduced pressure to obtain a white powder. This solid was washed with *n*−hexane and dried under vacuum to obtain **9** as a white powder in 81.7% yield. Mp: decomposed at 105 °C without melting. ^{1}H NMR (C_6D_6): δ 6.16 (d, J = 2.06 Hz, 3H, C*H*), 7.07 (m, 9H, C*H*), 7.31 (d, J = 1.53 Hz, 3H, C*H*), 7.70 (m, 6H, C*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 103.97 (s, *C*H), 122.07 (q, ^1J(C,F) = 268.6 Hz, *C*F$_3$), 128.99 (d, ^3J(C,P) = 10 Hz, *Cm*), 130.47 (s, *Cp*), 133.49 (br, *Ci*), 134.51 (d, ^2J(C,P) = 17.1 Hz, *Co*), 137.21 (s, *C*H), 144.54 (q, ^2J(C,F) = 37.4 Hz, *C*CF$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 17.6 (br dd, ^1J(P,^{107}Ag) = 631.6 Hz, ^1J(P,^{109}Ag) = 734.7 Hz). ^{19}F NMR (C_6D_6): δ −60.1 (dd). IR, cm^{-1}: 2535 (BH). Anal. Calcd for $C_{30}H_{22}N_6BF_9PAg$; C, 45.77; H, 2.82; N, 10.68. Found: C, 45.36; H, 2.47; N, 10.05.

Synthesis of [Et$_4$N][HB(3,5-(CF_3)$_2$Pz)$_3$] (10). [HB(3,5-(CF_3)$_2$Pz)$_3$]Na(H_2O) (0.922 g, 1.39 mmol) and tetraethylammonium bromide (0.293 g, 1.39 mmol) were mixed in CH_2Cl_2 at room temperature. A white precipitate formed immediately. The mixture was filtered, and the solvent was removed from the filtrate to obtain **10** in quantitative yield. It was recrystallized from methylene chloride−hexane to obtain colorless crystals. Mp: 113−114.5 °C. ^{1}H NMR (C_6D_6): δ 0.39 (t, C*H*$_3$), 2.08 (q, C*H*$_2$), 6.73 (s, C*H*). ^{19}F NMR (C_6D_6): δ −60.4 (s), −59.6 (br). IR, cm^{-1}: 2532 (BH). Anal. Calcd for $C_{23}H_{24}N_7F_{18}B$: C, 36.77; H, 3.22; N, 13.05. Found: C, 36.64; H, 3.17; N, 12.72.

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.[58] Data collections were carried out at −80 °C on the 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) software package provided by Siemens Analytical X-ray Instruments, Inc.[59] Crystal data, data collection and refinement parameters for compounds **4,** [{HB(3-(CF_3)Pz)$_3$}Na(thf)]$_2$, **6**−**8**, and **10** are summarized in Table 1. Atomic coordinates for important atoms are provided in Tables 2−7. Selected bond lengths and angles are listed in Table 8. Further details are included with the supporting material.

[HB(3,5-(CF_3)$_2$Pz)$_3$]Na(H_2O) (4). The crystals of **4** were obtained from toluene at room temperature. The unit cell parameters were determined by least-squares refinement of 20 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, polarization, and absorption effects (using ψ scan data). The structure was solved by direct methods and standard difference map techniques using an IBM-compatible PC. Compound **4** crystallizes in the monoclinic $P2_1/m$ space group with a crystallographically imposed mirror plane containing Na, O, B, H, two fluorines of the CF$_3$, and one of the pyrazole rings. All the non-hydrogen atoms were refined anisotropically. The H on boron and oxygen were located from a difference map, and the position of the H on oxygen was refined freely. The hydrogens on the pyrazole ring were included in calculated positions with C−H = 0.96 Å. All the hydrogen atoms were refined isotropically. Refinement by full-matrix least-squares techniques based

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(58) Hope, H. In *Experimental Organometallic Chemistry;* ACS Symposium Series 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; p 257.

(59) *Siemens SHELXTL (PC version 4.2)*; Siemens Industrial Automation, Inc.: Madison, WI.

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

	4	$\{5\cdot thf\}_2$	**6**	**7**	**8**$\cdot 0.5C_6H_{14}$	**10**
formula	$C_{15}H_6BF_{18}N_6NaO$	$C_{32}H_{30}B_2F_{18}N_{12}Na_2O_2$	$C_{19}H_{13}BCuF_{18}N_7O$	$C_{33}H_{19}BCuF_{18}N_6P$	$C_{36}H_{26}AgBF_{18}N_6P$	$C_{23}H_{24}AgBF_{18}N_7$
fw	662.1	1024.2	771.7	946.9	1034.3	751.3
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	7.992(2)	9.063(3)	15.124(4)	9.1671(8)	13.929(2)	10.155(2)
b, Å	15.049(2)	10.183(2)	8.833(2)	14.908(2)	16.498(2)	18.580(4)
c, Å	9.934(2)	12.129(2)	21.637(6)	26.764(3)	18.752(2)	16.875(5)
α, deg	90	94.61(1)	90	90	90	90
β, deg	101.16(2)	101.16(2)	105.291(14)	94. 890(1)	111.439(6)	99.01(2)
γ, deg	90	95.66(2)	90	90	90	90
V, $Å^3$	1172.0(4)	1087.2(5)	2783.3(12)	3644.5(8)	4011.6(9)	3144.5(13)
Z	2	1	4	4	4	4
ρ(calcd), g/cm^3	1.876	1.564	1.838	1.726	1.712	1.587
μ, mm^{-1}	0.235	0.171	0.934	0.772	0.663	0.172
T, K	193	193	193	193	193	193
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
R, R_w, %[a]	3.61, 4.06	4.61, 5.00	4.08, 4.42	3.79, 4.28	3.83, 3.94	4.81, 4.96

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

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ × 10^3) for $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$

	x	*y*	*z*	*U*(eq)[a]
Na	4772(2)	2500	1576(1)	35(1)
N(11)	3936(2)	1655(1)	−1587(2)	24(1)
N(12)	3748(2)	1501(1)	−279(2)	25(1)
N(21)	6750(3)	2500	−1084(3)	22(1)
N(22)	7053(3)	2500	308(3)	26(1)
C(13)	2962(3)	723(2)	−287(3)	29(1)
C(14)	2600(3)	357(2)	−1593(3)	41(1)
C(15)	3240(3)	964(2)	−2390(3)	33(1)
C(16)	2553(3)	381(2)	1004(3)	38(1)
C(17)	3212(4)	887(2)	−3882(3)	49(1)
C(23)	8743(4)	2500	712(3)	28(1)
C(24)	9571(4)	2500	−388(3)	31(1)
C(25)	8274(4)	2500	−1506(3)	27(1)
C(26)	9488(5)	2500	2201(4)	39(1)
C(27)	8488(4)	2500	−2950(4)	37(1)
F(16A)	3562(2)	735(1)	2106(2)	58(1)
F(16B)	955(2)	569(1)	1136(2)	55(1)
F(16C)	2716(2)	−494(1)	1106(2)	59(1)
F(17A)	2439(3)	135(2)	−4360(2)	94(1)
F(17B)	2404(2)	1555(2)	−4606(2)	69(1)
F(17C)	4767(2)	860(1)	−4182(2)	59(1)
F(26A)	11184(3)	2500	2418(2)	59(1)
F(26B)	9028(2)	1791(1)	2843(2)	59(1)
F(27A)	10142(3)	2500	−3005(3)	64(1)
F(27B)	7804(2)	1789(1)	−3661(2)	56(1)
B	4891(5)	2500	−1929(4)	24(1)
O	5188(6)	2500	3810(3)	90(2)

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

on *F* converged to $R = 0.0361$ and $R_w = 0.0406$. The GOF was 1.24, max $\Delta/\sigma = 0.046$, and the largest difference peak was 0.27 e $Å^{-3}$.

[{HB(3-(CF$_3$)Pz)$_3$}Na(thf)]$_2$. X-ray-quality crystals were obtained from toluene at 0 °C. The unit cell parameters were determined by least-square refinement of 14 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 but not for absorption. The structure was solved by direct methods. $[\{HB(3\text{-}(CF_3)Pz)_3\}Na(thf)]_2$ crystallizes as dimers with a center of inversion in the triclinic $P\bar{1}$ space group. All the non-hydrogen atoms were refined anisotropically. The disordered (over two positions) fluorines of the CF_3 group attached to C(16) were modeled successfully, and the occupancies were refined to 60% and 40%. The H on boron was located from a difference map. The hydrogens on the pyrazole ring and thf were included in calculated positions with C−H = 0.96 Å and fixed U_H. Refinement by full-matrix least-squares techniques based on *F* converged to $R = 0.0461$ and $R_w = 0.0500$. The GOF was 1.51, max $\Delta/\sigma = 0.011$, and the largest difference peak was 0.44 e $Å^{-3}$.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ × 10^3) for $[\{HB(3\text{-}(CF_3)Pz)_3\}Na(thf)]_2$

	x	*y*	*z*	*U*(eq)[a]
Na	1199(1)	1868(1)	2598(1)	36(1)
N(11)	−297(3)	4588(2)	1932(2)	29(1)
N(12)	1067(3)	4119(2)	2017(2)	33(1)
N(21)	−2176(3)	2520(2)	1472(2)	28(1)
N(22)	−1396(3)	1442(2)	1531(2)	31(1)
N(31)	−1306(3)	3534(2)	3510(2)	29(1)
N(32)	−187(3)	2798(3)	3917(2)	32(1)
C(13)	1936(4)	5061(3)	1650(3)	34(1)
C(14)	1165(4)	6122(3)	1330(3)	38(1)
C(15)	−252(4)	5782(3)	1520(3)	34(1)
C(16)	3530(5)	4875(4)	1646(4)	57(2)
C(23)	−2168(3)	568(3)	692(3)	29(1)
C(24)	−3431(4)	1052(3)	77(3)	35(1)
C(25)	−3393(3)	2301(3)	612(3)	32(1)
C(26)	−1732(4)	−796(3)	559(3)	40(1)
C(33)	−203(4)	2780(3)	5012(3)	33(1)
C(34)	−1310(4)	3489(3)	5331(3)	38(1)
C(35)	−1983(4)	3958(3)	4351(3)	36(1)
C(36)	914(4)	2076(3)	5715(3)	42(1)
F(16A)	4406(11)	5941(7)	1793(10)	91(4)
F(16B)	3644(6)	4489(9)	491(5)	80(3)
F(16C)	3996(11)	3925(11)	2135(11)	105(6)
F(16D)	4311(18)	5764(18)	1328(19)	135(10)
F(16E)	3853(16)	3760(11)	1439(19)	111(9)
F(16F)	4393(9)	5053(18)	2859(8)	105(5)
F(26A)	−1886(3)	−1255(2)	−526(2)	67(1)
F(26B)	−299(3)	−871(2)	1049(2)	58(1)
F(26C)	−2583(3)	−1666(2)	1004(2)	60(1)
F(36A)	1584(3)	1273(3)	5109(2)	82(1)
F(36B)	303(3)	1325(3)	6392(2)	89(1)
F(36C)	2007(3)	2874(2)	6402(2)	81(1)
B	−1677(4)	3829(4)	2268(3)	30(1)
O	3331(3)	805(2)	3050(2)	50(1)
C(1)	3325(4)	−584(4)	3122(4)	56(2)
C(2)	4923(5)	−882(4)	3219(4)	63(2)
C(3)	5836(5)	403(5)	3304(5)	78(2)
C(4)	4847(5)	1398(5)	3314(5)	89(2)

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

[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Cu(DMAC) (6). The crystals of **6** were obtained from toluene−hexane at −25 °C. The unit cell parameters were determined by least-square refinement of 26 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, polarization, absorption (using SHELXA),[60] and extinction effects. The structure was solved by Patterson and standard difference map techniques using an IBM-compatible PC. All the non-hydrogen atoms were refined anisotropically. The H on boron was located from a

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[HB(3,5-(CF_3)_2Pz)_3]Cu(DMAC)$

	x	y	z	U(eq)[a]
Cu	4734(1)	4327(1)	7226(1)	33(1)
N(11)	4571(2)	3615(4)	8512(2)	25(1)
N(12)	4173(2)	4529(4)	8000(2)	31(1)
N(21)	6214(2)	3672(4)	8400(2)	23(1)
N(22)	6098(2)	4423(4)	7830(2)	27(1)
N(31)	5160(2)	1454(4)	7947(2)	25(1)
N(32)	4830(2)	1943(4)	7328(2)	26(1)
O(1S)	4580(2)	5461(4)	6424(2)	42(1)
N(1S)	4085(3)	6365(5)	5424(2)	38(1)
C(1S)	2956(3)	5279(7)	5931(3)	50(2)
C(2S)	3922(3)	5706(5)	5939(2)	34(2)
C(3S)	3365(4)	6823(7)	4845(3)	54(2)
C(4S)	5036(4)	6823(7)	5433(3)	53(2)
B	5429(3)	2612(6)	8507(2)	26(2)

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

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[HB(3,5-(CF_3)_2Pz)_3]CuPPh_3$

	x	y	z	U(eq)[a]
Cu	4720(1)	7691(1)	4050(1)	30(1)
P	5265(1)	7890(1)	3266(1)	25(1)
N(11)	5581(3)	7282(2)	5138(1)	27(1)
N(12)	6221(3)	7410(2)	4702(1)	29(1)
N(21)	3232(3)	6523(2)	4791(1)	27(1)
N(22)	3250(4)	6593(2)	4286(1)	27(1)
N(31)	3275(4)	8195(2)	4966(1)	27(1)
N(32)	3605(4)	8540(2)	4520(1)	28(1)
C(41)	6262(4)	8909(3)	3114(1)	26(1)
C(51)	3666(4)	7944(3)	2808(1)	28(1)
C(61)	6391(4)	6996(3)	3033(1)	25(1)
B	3900(5)	7262(3)	5148(2)	28(1)

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

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$

	x	y	z	U(eq)[a]
Ag	2110(1)	2382(1)	1334(1)	33(1)
P	3925(1)	2578(1)	1824(1)	29(1)
N(11)	−198(3)	2720(2)	1279(2)	26(2)
N(12)	730(3)	3115(2)	1520(2)	26(2)
N(21)	7(3)	1284(2)	905(2)	25(2)
N(22)	1001(3)	1235(3)	1389(2)	29(2)
N(31)	−139(3)	2422(2)	−31(2)	27(2)
N(32)	861(3)	2344(2)	31(2)	29(2)
C(41)	4499(4)	2706(3)	2860(3)	30(2)
C(51)	4384(4)	3464(3)	1462(3)	32(2)
C(61)	4606(4)	1722(3)	1618(3)	31(2)
B	−500(5)	2112(4)	608(3)	31(2)

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

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Et_4N][HB(3,5-(CF_3)_2Pz)_3]$

	x	y	z	U(eq)[a]
N(11)	−1433(4)	2049(2)	−1164(2)	32(2)
N(12)	−2515(4)	2031(2)	−791(2)	37(2)
N(21)	−846(4)	3279(2)	−561(2)	33(2)
N(22)	−1009(4)	3346(2)	219(2)	39(2)
N(31)	743(4)	2231(2)	−225(2)	33(2)
N(32)	651(4)	1516(2)	−89(2)	35(2)
C(13)	−3284(5)	1519(3)	−1164(3)	40(2)
C(14)	−2723(6)	1199(3)	−1771(3)	42(2)
C(15)	−1541(5)	1548(3)	−1755(3)	37(2)
C(16)	−4608(6)	1369(3)	−953(3)	53(2)
C(17)	−550(7)	1448(3)	−2295(3)	52(2)
C(23)	−1494(5)	3999(3)	278(3)	41(2)
C(24)	−1663(5)	4369(3)	−448(3)	44(2)
C(25)	−1243(5)	3893(3)	−974(3)	33(2)
C(26)	−1753(9)	4267(3)	1054(4)	70(3)
C(27)	−1237(6)	3995(3)	−1838(3)	43(2)
C(33)	1764(5)	1339(3)	398(3)	36(2)
C(34)	2606(5)	1928(3)	585(3)	43(2)
C(35)	1924(5)	2484(3)	168(3)	35(2)
C(36)	1986(6)	584(3)	658(3)	42(2)
C(37)	2389(6)	3233(3)	147(4)	48(2)
F(16A)	−4573(3)	939(2)	−306(2)	72(1)
F(16B)	−5412(4)	1044(2)	−1545(2)	82(2)
F(16C)	−5236(3)	1965(2)	−772(2)	71(1)
F(17A)	707(4)	1373(2)	−1924(2)	76(2)
F(17B)	−842(4)	870(2)	−2759(2)	80(2)
F(17C)	−519(4)	2002(2)	−2806(2)	71(1)
F(26A)	−573(6)	4357(3)	1588(3)	126(3)
F(26B)	−2370(5)	3844(2)	1465(3)	118(2)
F(26C)	−2226(6)	4916(2)	1032(2)	117(2)
F(27A)	−1878(3)	3476(2)	−2295(2)	59(1)
F(27B)	−6(3)	4023(2)	−2035(2)	60(1)
F(27C)	−1829(3)	4614(2)	−2089(2)	63(1)
F(36A)	3234(3)	485(2)	1044(2)	72(1)
F(36B)	1815(4)	124(2)	62(2)	83(2)
F(36C)	1213(4)	366(2)	1171(2)	74(1)
F(37A)	3712(3)	3274(2)	326(2)	72(1)
F(37B)	1922(4)	3671(2)	666(2)	79(2)
F(37C)	2067(4)	3543(2)	−566(2)	75(1)
B	−282(6)	2586(3)	−896(3)	34(2)
N	1635(4)	8445(2)	7998(2)	39(2)
C(1)	444(5)	8093(3)	8293(3)	48(2)
C(2)	−194(6)	7478(3)	7789(3)	60(2)
C(3)	2794(5)	7921(3)	8061(3)	46(2)
C(4)	3420(6)	7718(3)	8913(3)	63(3)
C(5)	1318(6)	8656(3)	7120(3)	56(2)
C(6)	179(7)	9172(4)	6918(4)	94(3)
C(7)	1974(6)	9089(3)	8543(3)	59(2)
C(8)	3164(7)	9526(3)	8367(4)	77(3)

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

difference map, and the positionial and isotropic thermal parameters were allowed to refine freely. All other hydrogens were included in calculated positions with C−H = 0.96 Å and refined isotropically. Refinement by full-matrix least-squares techniques based on F converged to $R = 0.0408$ and $R_w = 0.0442$. The GOF was 1.30, max $\Delta/\sigma = 0.095$, and the largest difference peak was 0.43 e $Å^{-3}$.

$[HB(3,5-(CF_3)_2Pz)_3]CuPPh_3$ (7). The crystals of **7** were obtained from toluene−hexane at −25 °C. The unit cell parameters were determined by least-square refinement of 21 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 but not for absorption effects. The structure was solved by direct methods and standard difference map techniques using an IBM-compatible PC. All the non-hydrogen atoms were refined anisotropically. The H on boron was located from a difference map. All other hydrogens were included in calculated positions with C−H = 0.96 Å and refined with fixed U_H. Refinement by full-matrix least-squares techniques based on F converged to $R = 0.0379$ and $R_w = 0.0428$. The GOF was 1.36, max $\Delta/\sigma = 0.000$, and the largest difference peak was 0.51 e $Å^{-3}$.

$[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$ (8). The crystals of **8** were obtained from hexane at −25 °C. The unit cell parameters were determined by least-square refinement of 22 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, polarization, and absorption (using SHELXA)[60] effects. The structure was solved by Patterson and standard difference map techniques using an IBM-compatible PC. Compound **8** crystallizes in the monoclinic $P2_1/c$ space group with 0.5

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(60) Sheldrick, G. M. *SHELXA*; University of Göttingen: Göttingen, Germany, 1993.

Table 8. Selected Bond Lengths (Å) and Angles (deg)

	4	{**5**·thf}$_2$	**6**	**7**	**8**	**10**
(M−X)	(Na−O)	(Na−O)	(Cu−O)	(Cu−P)	(Ag−P)	
M−X	2.179(4)	2.303(3)	1.963(3)	2.219(1)	2.376(1)	
M−N	2.396(2) 2.409(3) 2.396(2)	2.458(3) 2.434(3) 2.408(3)	2.075(4) 2.134(3) 2.119(4)	2.168(3) 2.243(3) 2.108(3)	2.401(4) 2.469(4) 2.427(3)	
B−N	1.554(3) 1.558(4) 1.554(3)	1.544(5) 1.555(4) 1.539(5)	1.575(6) 1.576(6) 1.556(6)	1.544(6) 1.548(6) 1.565(6)	1.542(7) 1.545(7) 1.547(9)	1.552(6) 1.548(6) 1.557(6)
X−M−N	123.4(1) 138.2(1) 138.2(1)	127.3(1) 140.3(1) 125.9(1)	133.8(1) 113.0(1) 126.0(1)	127.4(1) 123.5(1) 130.0(1)	132.1(1) 133.0(1) 131.5(1)	
N−M−N	77.2(1) 77.7(1) 77.2(1)	84.4(1) 79.2(1) 78.1(1)	92.1(1) 91.9(1) 87.0(1)	89.4(1) 86.8(1) 86.4(1)	80.4(1) 80.9(1) 78.0(1)	
N−B−N	109.8(2) 109.8(2) 109.8(3)	109.2(3) 111.1(2) 110.6(3)	108.7(3) 109.3(3) 109.2(4)	110.3(3) 108.5(3) 109.0(3)	109.2(4) 110.4(4) 109.6(5)	109.7(4) 109.7(4) 109.3(4)

molecule of *n*−hexane in the asymmetric unit. The H on boron was located from a difference map. All other hydrogens were included in calculated positions with C−H = 0.96 Å and refined with fixed U_H. Refinement by full-matrix least-squares techniques based on F converged to $R = 0.0383$ and $R_w = 0.0394$. The GOF was 1.13, max $\Delta/\sigma = 0.001$, and the largest difference peak was 0.43 e Å^{-3}.

[Et$_4$N][HB(3,5-(CF$_3$)$_2$Pz)$_3$] (10). The crystals of **10** were obtained from CH_2Cl_2−hexane at −25 °C. 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, polarization, and absorption (using SHELXA)[60] effects. The structure was solved by direct methods and standard difference map techniques using an IBM-compatible PC. All the non-hydrogen atoms were refined anisotropically. The H on boron was located from a difference map and refined isotropically. All other hydrogens were included in calculated positions with C−H = 0.96 Å and refined with fixed U_H. Refinement by full-matrix least-squares techniques based on F converged to $R = 0.0481$ and $R_w = 0.0496$. The GOF was 1.29, max $\Delta/\sigma = 0.000$, and the largest difference peak was 0.59 e Å^{-3}.

Results and Discussion

Alkali Metal Complexes. Potassium and sodium salts of the [HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$ were prepared by the treatment of 3,5-bis(trifluoromethyl)pyrazole with either KBH_4 (in dimethylacetamide at 180 °C) or $NaBH_4$ (in kerosene at 190 °C). The properties of the potassium salt, which was isolated as the dimethylacetamide adduct, [HB(3,5-(CF$_3$)$_2$Pz)$_3$]K(DMAC) (**3**), have been described elsewhere.[43] It was found to adopt a dimeric structure in the solid state (Figure 1).

The sodium salt [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Na was isolated as its H_2O adduct and characterized using X-ray crystallography, NMR, IR, and elemental analysis. [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Na(H$_2$O) **4** is a colorless solid which melts around 107−109 °C. Compound **4** can be purified by vacuum sublimation. However, this results in some loss of coordinated H_2O. The treatment of **4** with either thf or Et_2O results in the formation of the corresponding ether adduct.

X-ray-quality crystals of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Na(H$_2$O) **4** were obtained from toluene. Compound **4** crystallizes with a crystallographically imposed mirror plane containing one of the pyrazole rings, B, Na, and the O. A perspective drawing of **4** is given in Figure 2 with the numbering scheme. The Na atom in **4** is coordinated to the three nitrogens of the tris(pyrazolyl)borate ligand and to the oxygen of the water molecule. The Na−N (three) and Na−O bond lengths are 2.396(2), 2.396(2), 2.409(3), and 2.179(4) Å, respectively. In addition, there are two Lewis acid-base interactions (2.909(2) Å) between the sodium and two fluorine atoms from two of the CF_3 groups on the pyrazole 3-positions.

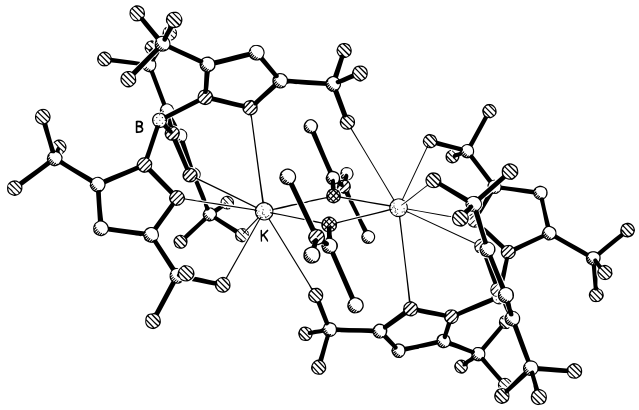

Figure 1. Molecular structure of [{HB(3-(CF$_3$)Pz)$_3$}K(DMAC)]$_2$ with H atoms omitted (Reprinted with permission from ref 43. Copyright 1995 American Chemical Society).

The crystal packing diagram of **4** (Figure 3) shows intermolecular F•••HO contacts (2.374, 2.531 Å) between the hydrogens of coordinated H_2O and the fluorines of CF_3 on the pyrazole 5-positions. These distances are within the sum of the van der Waals radii of H and F (2.70 Å) but are longer than the typically observed distances for H-bonded species involving F and H (1.70 Å).[61,62]

The sodium salt of [HB(3-(CF$_3$)Pz)$_3$]$^-$ was synthesized in a manner similar to that for **4** using 3-(CF$_3$)PzH and $NaBH_4$. [HB(3-(CF$_3$)Pz)$_3$]Na was isolated as a white solid. The elemental analysis and IR data indicate [HB(3-(CF$_3$)Pz)$_3$]Na to be free of coordinated water. Unlike **4**, [HB(3-(CF$_3$)Pz)$_3$]Na is significantly less soluble in organic solvents such as toluene, ether, or thf. [HB(3-(CF$_3$)Pz)$_3$]Na did not provide good-quality crystals for an X-ray crystallographic study. However, we were able to obtain large colorless crystals of its thf adduct from toluene−thf and characterize it using X-ray diffraction (Figure 4). [HB(3-(CF$_3$)Pz)$_3$]Na(thf) crystallizes as dimeric units with the center of the dimer residing upon a center of inversion. Each sodium center is five-coordinate with Na−N (three) and Na−O distances of 2.458(3), 2.408(3), 2.434(3), and 2.303(3) Å, respectively. In addition, one of the fluorines of the neighboring CF_3 coordinates to Na (2.744(3) Å), forming the bridge holding the dimer. The lack of CF_3 substituents on the pyrazole ring 5-positions allows the tris(pyrazolyl)borate ligand framework to open easily around the metal center. This is reflected in relatively long N−Na distances in [{HB(3-(CF$_3$)Pz)$_3$}Na(thf)]$_2$ compared to those of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Na(H$_2$O).

Interestingly, despite 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-(CF$_3$)$_2$-Pz)$_3$}K(DMAC)]$_2$, [{H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$}K]$_n$, [HB(3,4,5-(CH$_3$)$_3$-Pz)$_3$]K (crystallizes with three 3,4,5-(CH$_3$)$_3$PzH and 0.5 Et$_2$O), [HB(3,5-(*t*-Bu)$_2$Pz)$_3$]K(C$_6$H$_6$), [HB(3,5-(*t*-Bu)$_2$Pz)$_3$]Cs, [B(Pz)$_4$]K(H$_2$O), and [B(Pz)$_4$]Na(H$_2$O).[43,44,63−65] The Na−N distances (2.396(2), 2.396(2), 2.409(3) Å) and Na−OH$_2$ distance (2.179(4)

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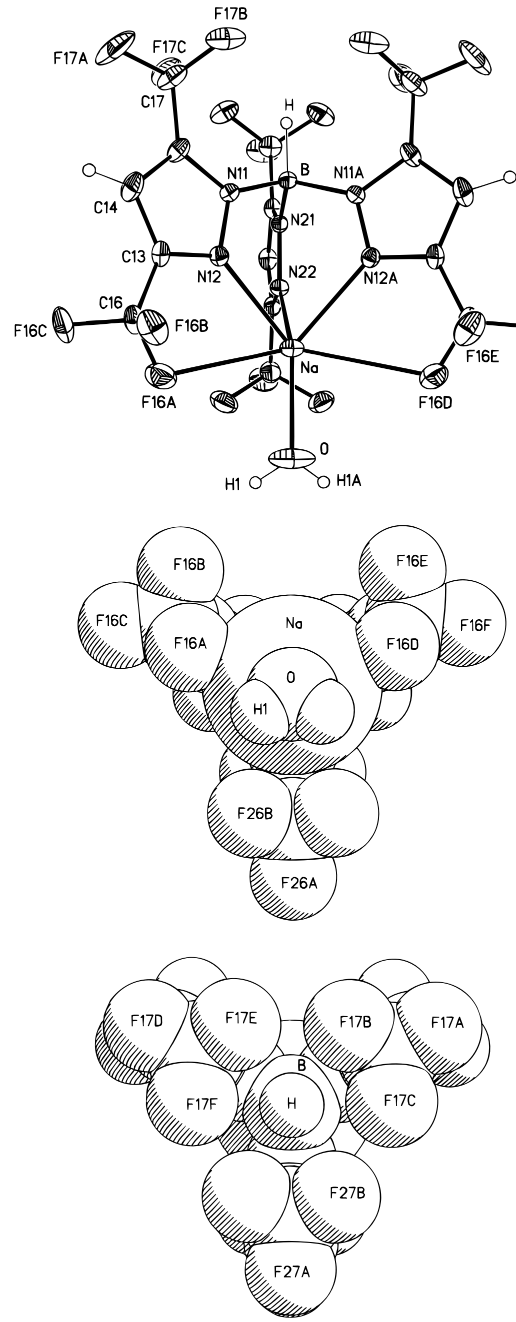

Figure 2. Molecular structure of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$: (a) ORTEP drawing with atom-numbering scheme (thermal ellipsoids for non-hydrogen atoms at 30% probability level); (b) view down the O−Na bond axis (space-filling model); (c) view down the H−B bond axis (space-filling model).

Å) of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$ are significantly shorter than those found in $[B(Pz)_4]Na(H_2O)$ (Na−N 2.458(3)−2.617(2) Å; Na−O 2.443(3), 2.536 Å).[63]

Compounds with M···F−C interactions are of interest due to their importance in C−F activation processes.[3] For example, alkali metal salts of fluoroalkoxy ligands have been used as precursors for metal fluorides, e.g., NaF.[3,66,67] 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.[3] Weak Na···F−C interactions have been previously seen in the sodium salts of various other fluorinated ligands (e.g.: sodium fluoropyruvate, Na···F−C 2.470(1) Å; $[Na(OCH(CF_3)_2]_4$, Na···F−C 2.635(2)−3.750(2) Å; $[(2,4,6\text{-}(CF_3)_3C_6H_2O)Na(thf)_2]_2$, Na···F−C 2.664-(7)−2.720(7) Å).[67−69] Compounds **4** and **5** are the first examples with such interactions in the bis(pyrazolyl)borate family.

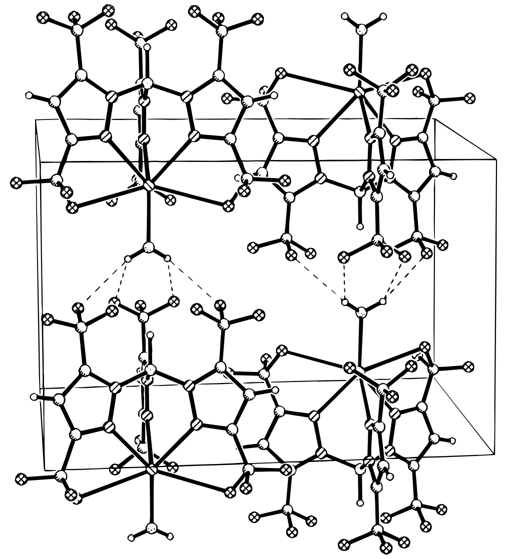

Figure 3. View of the arrangement of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$ molecules in the crystal lattice.

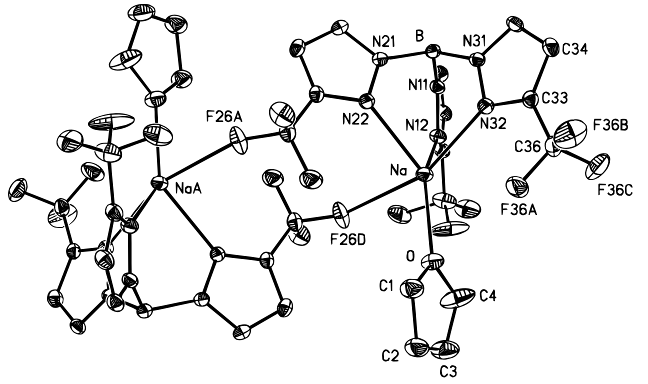

Figure 4. ORTEP drawing (at 30% probability level) of $[\{HB(3\text{-}(CF_3)\text{-}Pz)_3\}Na(thf)]_2$.

The ^{19}F NMR spectrum of **4** in C_6D_6 consisted of two signals with chemical shift values of δ −58.5 and −62.2. The ^{19}F NMR spectrum of $[HB(3\text{-}(CF_3)Pz)_3]Na$ exhibits just a singlet at −59.2 ppm (Table 9). These chemical shifts are in the expected region for the CF_3 groups.[70] The downfield signal at −58.5 ppm for compound **4** could be assigned to the trifluoromethyl groups at pyrazole ring 5-positions. Interestingly, this signal appears as a doublet with J = 3.5 Hz. The most likely cause for this splitting is the intramolecular spin−spin coupling with the hydrogen on the boron atom. In fact, the ^{19}F NMR spectrum of the deuterated analog, $[DB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$, dis-

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Table 9. Selected NMR Spectroscopic Data[a] (Solvent C_6D_6)

	^1H	^{19}F	^{31}P
$[HB(3,5-(CF_3)_2Pz)_3]K(DMAC)$ (**3**)	6.38	−58.9 −61.4	
$[HB(3,5-(CF_3)_2Pz)_3]Na(H_2O)$ (**4**)	6.25	−58.5 (d, $J_{F,H}$ = 3.5) −62.2	
$[HB(3-(CF_3)Pz)_3]$ Na (**5**)[b]	6.52 7.53	−59.2	
$[HB(3,5-(CF_3)_2Pz)_3]Cu(DMAC)$ (**6**)	6.31	−58.3 (d, $J_{F,H}$ = 3.2) −61.4	
$[HB(3,5-(CF_3)_2Pz)_3]CuPPh_3$ (**7**)	6.31	−58.2 (d, $J_{F,H}$ = 2.6) −59.6 (d, $J_{F,P}$ = 6.5)	7.2 (br)
$[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$ (**8**)	6.30	−58.3 (d, $J_{F,H}$ = 2.5) −60.4 (dd, $J_{F,P}$ = 8.1, $J_{F,Ag}$ = 1.4)	17.8 (ddm, $J_{Ag,P}$ = 657.5, $J_{Ag,P}$ = 758.8, $J_{F,P}$ = 8.3)
$[HB(3-(CF_3)Pz)_3]AgPPh_3$ (**9**)	6.16 7.31	−60.1 (br dd)	17.6 (br dd, $J_{Ag,P}$ = 631.7, $J_{Ag,P}$ = 734.7)
$[HB(3,5-(CF_3)_2Pz)_3]Ag(thf)$	6.34	−58.4 (d, $J_{F,H}$ = 2.9) −61.2	
$[Et_4N][HB(3,5-(CF_3)_2Pz)_3]$ (**10**)	6.73	−59.6 (br) −60.4	

[a] Chemical shifts are given in ppm; coupling constants are given in Hz. [b] NMR data for **5** in DMSO-d_6.

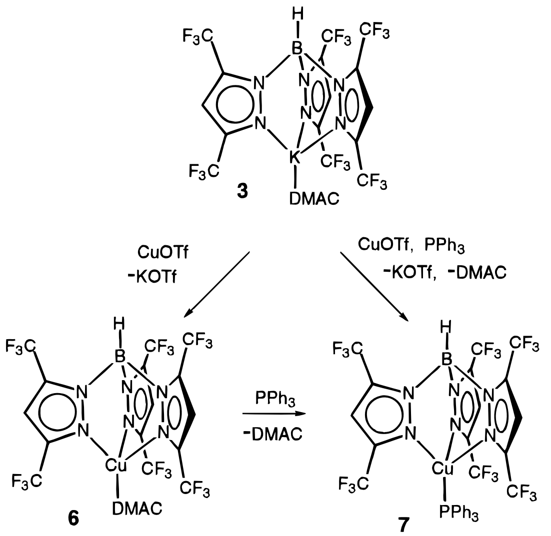
played only a singlet for the trifluoromethyl groups on the 5-positions (peaks were not sharp enough to observe D−F coupling, which was estimated to be about 0.5 Hz using J_{DF}/J_{HF} = 0.154).[71] Furthermore, the ^1H-decoupled ^{19}F NMR spectrum of **4** shows only two singlets, suggesting that the splitting may indeed be due to the hydrogen on boron.[72] Unfortunately, the signal due to the *H*−B is too broad (due to quadrupolar broadening) and could not be detected in the ^1H NMR spectrum.[73]

Long-range H−F coupling has been reported for various fluorocarbon molecules with close through space H···F contacts.[74,75] In fact, X-ray crystallographic data for **4** show that the closest nonbonded H···F distance between the H on boron and fluorines of the CF_3's on the pyrazole 5-positions is 2.64 Å. In this structure, the hydrogen atom on boron lies on a plane which dissects the F−C−F angle (see Figure 2). However, because of the free rotation of CF_3 moieties, this H···F separation would expected to be even smaller in solution. In fact, it is possible to calculate the closest approach of F to *H*−B in **4** on the basis of the X-ray data, and it was found to be about 1.9 Å. This separation is well within the sum of the van der Waals radii of F and H and supports the possibility of detecting spin−spin H−F coupling. The ^1H and ^{13}C NMR spectra of the alkali metal salts $[HB(3,5-(CF_3)_2Pz)_3]K(DMAC)$, $[HB(3,5-(CF_3)_2Pz)_3]Na(H_2O)$, and $[HB(3-(CF_3)Pz)_3]Na$ are not exceptional.

Coinage Metal Complexes. The alkali metal salts of $[HB(3,5-(CF_3)_2Pz)_3]^-$ were used in the preparation of the copper complexes $[HB(3,5-(CF_3)_2Pz)_3]Cu(DMAC)$ (**6**) and $[HB(3,5-(CF_3)_2Pz)_3]Cu(PPh_3)$ (**7**) as depicted in Scheme 1. The treatment of **3** with CuOTf in the presence of PPh_3 led to **7** in good yield. In the absence of PPh_3, the reaction between **3** and CuOTf resulted in the copper dimethylacetamide adduct **6** in 63% yield. Similar behavior was observed in the silver(I) analog. For example, the reaction between **4** and AgOTf in thf gave $[HB(3,5-(CF_3)_2Pz)_3]Ag(thf)$ in very good yield.[51] Interestingly, copper(I) complexes derived from the parent tris(pyrazolyl)borate or the alkyl-substituted analogs show different behavior. For example, $[HB(Pz)_3]Cu$ and $[HB(3,5-(i\text{-}Pr)_2Pz)_3]Cu$ have been synthesized in aqueous solutions or in the presence of neutral oxygen donors such as methanol and acetone and have been isolated as solids free of any coordinated solvent.[76,77] In general, they tend to form dimers in the solid state.[54,78,79] The formation of DMAC adduct **6** can be attributed to the increased Lewis acidity of the copper center and to the reduced nucleophilicity of the ligand due to the presence of highly electron-withdrawing CF_3 substituents. In fact, the copper complex of the 3,5-diphenyl-substituted tris(pyrazolyl)borate shows some affinity for acetone and has been isolated as a stable acetone adduct.[77]

Selected NMR spectroscopic data for **6** and **7** are presented in Table 9. ^1H and ^{19}F NMR chemical shift values and the ν_{CO} for $[HB(3,5-(CF_3)_2Pz)_3]Cu(DMAC)$ do not vary signifi-

Scheme 1



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[73] The observation of *H*−B would also be complicated by coupling to nine equivalent fluorine atoms as well as by partially collapsed coupling to boron-11. These two effects, superimposed, would smear out the *H*−B signal even further than the quadrupolar effect of boron alone.

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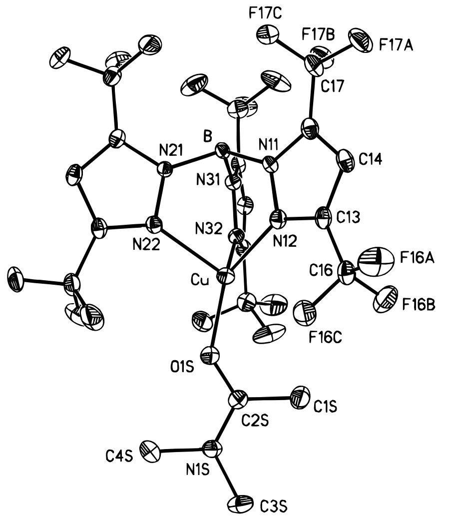

Figure 5. ORTEP drawing (at 30% probability level) of [HB(3,5-$(CF_3)_2Pz)_3$]Cu(DMAC) with H atoms omitted.

cantly from the corresponding values for [HB(3,5-$(CF_3)_2Pz)_3$]K-(DMAC). The ^{19}F NMR spectrum of the triphenylphosphine adduct **7** shows two doublets at −58.2 and −59.6 ppm. The splitting may be attributed to the spin−spin coupling to H (on B) and P nuclei, respectively. The coupling to H (as discussed in detail for compound **4**) was confirmed by a ^{1}H-decoupled ^{19}F NMR experiment. Further evidence comes from the ^{19}F NMR spectra of the closely related copper complexes [DB(3,5-$(CF_3)_2Pz)_3$]CuCO and [HB(3,5-$(CF_3)_2Pz)_3$]CuCO.[53] Although we did not confirm the involvement of phosphorus in the splitting of the resonance centered at −59.6 ppm, ^{31}P NMR data for the closely related silver analog **8** (see Figure 7) support this possibility.

The $^{31}P\{^{1}H\}$ NMR spectrum of **7** exhibits a broad peak (too broad to observe fluorine coupling) at 7.2 ppm. Interestingly, the chemical shift value does not differ significantly from that of the closely related nonfluorinated analog, [HB(3,5-$(CH_3)_2$-$Pz)_3$]$CuPPh_3$.[80] ^{1}H NMR spectra of **6** and **7** show a singlet around 6.3 ppm, which could be assigned to hydrogen atoms on the pyrazole ring 4-positions. Corresponding signals for [HB(3,5-$(CH_3)_2Pz)_3$]$CuPPh_3$ and [HB(3,5-(*i*-Pr)$_2$Pz)$_3$]$CuPPh_3$ complexes appear at significantly lower frequencies, 5.62 and 5.82 ppm, respectively.[77,80]

The structures of compounds **6** and **7** were confirmed by X-ray crystallography (Figures 5 and 6). Both compounds show monomeric structures with pseudotetrahedral copper centers. The Cu−N distances of **6** and **7** (Table 8) can be compared to the corresponding bond lengths in [HB(3,5-$(CF_3)_2Pz)_3$]CuCO (2.035-(3), 2.061(2), 2.061(3) Å), [HB(3,5-$(CF_3)_2Pz)_3$]$CuCNBu^t$ (2.072(5), 2.093(4), 2.093(4) Å), [HB(3,5-(*i*-Pr)$_2$Pz)$_3$]CuCO (2.019(5), 2.014(6), 2.022(6) Å), [HB(3,5-$(CH_3)_2Pz)_3$]$CuPPh_3$ (2.106(14), 2.101(10), 2.086(13) Å), or [HB(3,5-$(CH_3)_2Pz)_3$]Cu-(C_2H_4) (2.017(3), 2.041(3), 2.160(4) Å).[53,77,80−82] No significant difference in Cu−N separation is evident between the fluorinated and nonfluorinated tris(pyrazolyl)borate systems of copper(I).

The Cu−O distance in dimethylacetamide adduct **6** (1.963-(3) Å) is slightly longer than those found in [HB(3,5-$(CH_3)_2$-$Pz)_3$]$CuOS(O)_2CF_3$ (1.947(7) Å) and [HB(3,5-$(CH_3)_2Pz)_3$]-$CuOOC(Me)_2Ph$ (1.816(4), 1.814(4) Å).[83,84] However, in

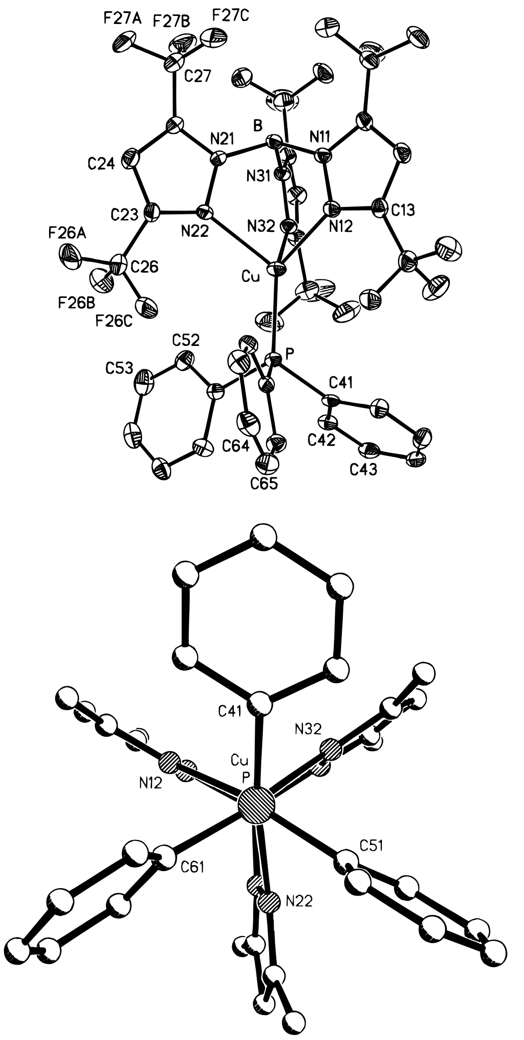

Figure 6. Molecular structure of [HB(3,5-$(CF_3)_2Pz)_3$]$CuPPh_3$: (a) ORTEP drawing (at 30% probability level) with H atoms omitted; (b) view down the P−Cu bond axis with H and F atoms omitted.

contrast to **6**, these examples represent copper in the formally II oxidation state. Compound [HB(3,5-$(CF_3)_2Pz)_3$]$CuPPh_3$ (**7**) can be compared with the phosphine adduct, [HB(3,5-$(CH_3)_2$-$Pz)_3$]$CuPPh_3$.[80] The most important feature, the Cu−P separation in **7**, is 2.219(1) Å, whereas the corresponding value in the methylated analog is 2.166(6) Å. Both these compounds contain sterically somewhat similar tris(pyrazolyl)borate ligands. Therefore, the slight lengthening of the copper-phosphorus bond may be a consequence of reduced π-back-bonding in **7**. A similar trend has been observed in the related copper(I) carbonyls. For example, the Cu−C distance in [HB(3,5-$(CF_3)_2$-$Pz)_3$]CuCO (1.808(4) Å) is longer than that in [HB(3,5-(*i*-Pr)$_2$Pz)$_3$]CuCO (1.769(8) Å).[53,77]

The closest nonbonded intramolecular F···P distance in **7** is 3.41 Å. However, the closest separation in solution would be even less because, in the crystal structure, Cu and P atoms lie on a plane which dissects the F−C−F angle of the CF_3 groups. The F···P separation in solution was estimated to be about 3.19 Å. Such close contacts are within the sum of van der Waals radii of F and P (3.40 Å) and may explain the observed splitting in the ^{19}F NMR spectrum.[61,74,85]

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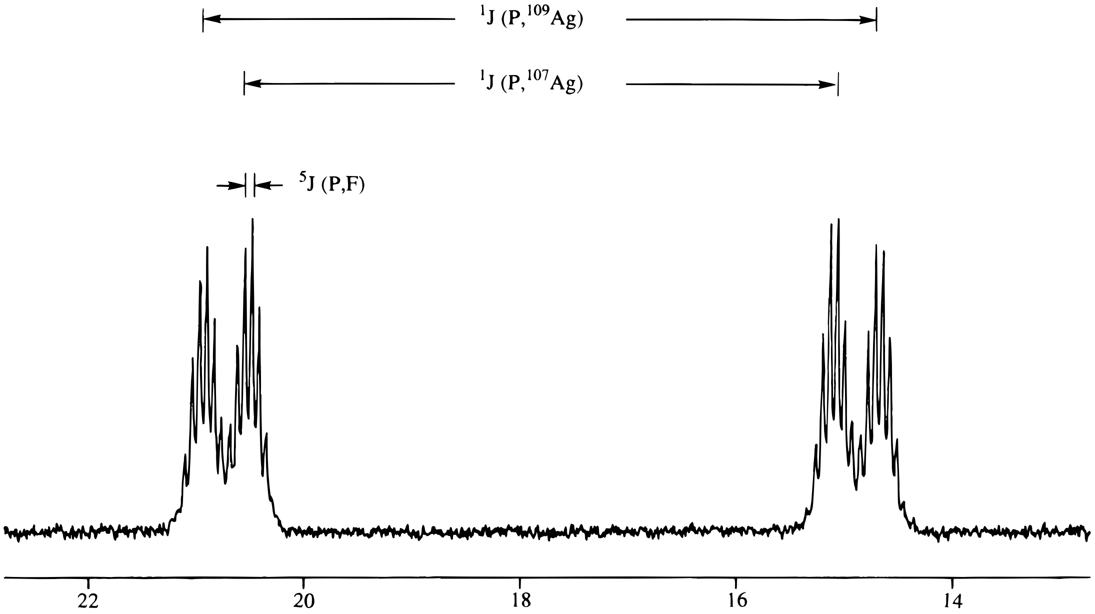

Figure 7. $^{31}P\{^{1}H\}$ NMR spectrum of $[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$.

The silver(I) complex **8**, $[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$, was prepared directly by treating **4** with AgOTf and 1 equiv of PPh_3. This somewhat light-sensitive compound was isolated as colorless crystals and characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The ^{19}F NMR spectrum of **8** exhibits a doublet at δ −58.3 and a doublet of doublets at δ −60.4. The appearance of a doublet at −58.3 ppm can be attributed to the long-range $^{19}F-^{1}H$ coupling (as established in compound **4**). This was further supported by the ^{19}F NMR data from the closely related silver(I) adduct $[HB(3,5-(CF_3)_2Pz)_3]$-Ag(thf) and its deuterated analog $[DB(3,5-(CF_3)_2Pz)_3]Ag(thf)$.[51] The signal centered at −60.4 ppm, which corresponds to CF_3's at 3-positions, is coupled to both P and Ag, and the $^{5}J(P-F)$ and $^{4}J(F-Ag)$ ($^{107/109}Ag$ not resolved) values are 8.1 and 1.4 Hz, respectively. The $^{31}P\{^{1}H\}$ NMR spectrum of **8** (Figure 7) shows coupling to ^{107}Ag and ^{109}Ag and to fluorine atoms of the CF_3 groups on pyrazole 3-positions. The observed Ag−P coupling constants ($J(^{107}Ag-^{31}P) = 657.5$ and $J(^{109}Ag-^{31}P) = 758.8$ Hz) are relatively higher than the values reported for various other silver phosphine complexes (typically $^{1}J(Ag-P)$ coupling constants range from 200 to 500 Hz), but the ratio $J(^{109}Ag-^{31}P)/J(^{107}Ag-^{31}P)$ is consistent with the $^{109}Ag/^{107}Ag$ gyromagnetic ratio of 1.149.[86,87] The ^{1}H NMR signal of the pyrazole ring hydrogens appears as a singlet at 6.31 ppm. The chemical shifts of these protons are very similar to those observed for corresponding protons in the copper complex **7** (Table 9). $[HB(3-(CF_3)Pz)_3]AgPPh_3$ (**9**) was prepared from **5**, AgOTf, and PPh_3. The fluorines on the substituents at 3-position appear at δ −60.1 in the ^{19}F NMR spectrum. The ^{31}P NMR spectrum of **9** is similar to that of **8**, with P−Ag coupling constants of 631.6 and 734.7 Hz. However, the resonances in the ^{31}P and ^{19}F NMR spectra are broad and the P−F splittings are not well resolved.

$[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$ (**8**) was crystallized from hexane as colorless crystals. It crystallizes as discrete molecules with 0.5 *n*−hexane per molecule of **8** in the crystal lattice. An ORTEP diagram of the structure of $[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$ is shown in Figure 8.[88] The silver atom adopts a pseudo tetrahedral geometry. The Ag−P bond length is 2.376(1) Å. This value is slightly shorter than the typical Ag−P distances observed for silver(I) triphenylphosphine complexes (average

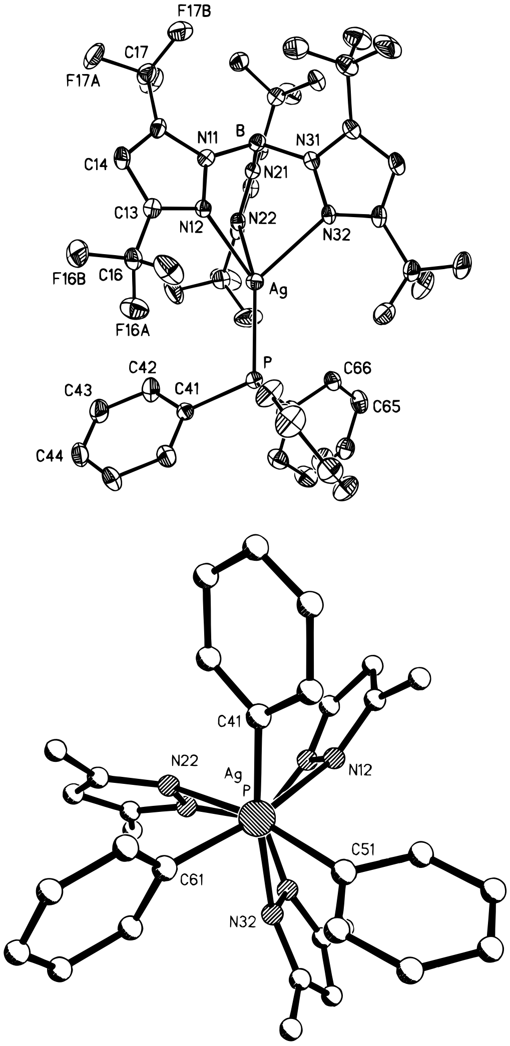

Figure 8. Molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$: (a) ORTEP drawing (at 30% probability level) with H atoms omitted; (b) view down the P−Ag bond axis with H and F atoms omitted.

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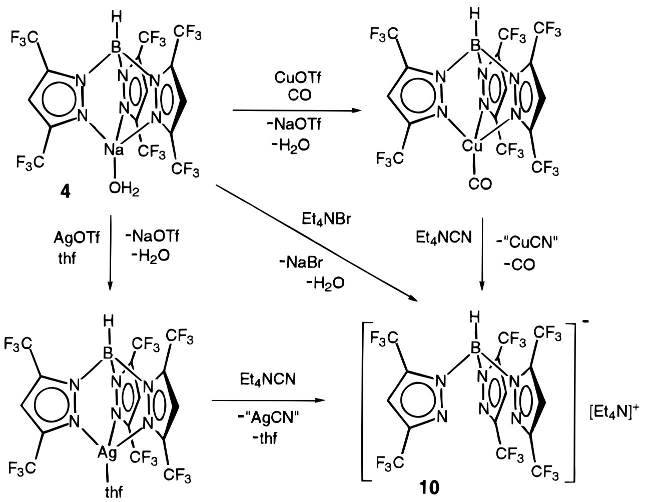
Scheme 2



2.419 Å for 27 compounds).[89] Unlike those of Cu(I), structurally characterized poly(pyrazolyl)borato complexes of Ag(I) are limited.[45,46] These include $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCNBu^t$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(thf)$, $[HB(3\text{-}(2\text{-}pyridyl)Pz)_3]_2Ag_3ClO_4$, and a bis(pyrazolyl)borate complex $[Ph_2B(Pz)_2]AgP(4\text{-}MeC_6H_4)_3$.[50,51,90,91] The $[Ph_2B(Pz)_2]AgP(4\text{-}MeC_6H_4)_3$ complex has a pseudo-three-coordinate silver center, and the Ag−P bond distance is 2.351(1) Å. The Ag−N separation in $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgPPh_3$ (Table 8) can also be compared to the corresponding bond distances in $[Ph_2B(Pz)_2]AgP(4\text{-}MeC_6H_4)_3$ (2.194(4), 2.411(4) Å).[91]

One striking difference between **7** and **8** is the relative orientation of the pyrazole rings. Compound **7** features a pseudo-C_{3v} symmetry (except for the orientation of one of the phenyl groups), whereas **8**, due to its propeller-shaped arrangement of pyrazole and phenyl rings, shows a pseudo-C_3 symmetry. The views down the P−metal···B axis for compounds **7** and **8** are presented in Figures 6 and 8, respectively.

Metal-Free Ligand. The attempted synthesis of $[\{HB(3,5\text{-}(CF_3)_2Pz)_3\}AgCN]^-$ using $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(thf)$ and Et_4NCN led to $[Et_4N][HB(3,5\text{-}(CF_3)_2Pz)_3]$ (**10**), presumably through the precipitation of AgCN. The treatment of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(CO)$ with Et_4NCN also resulted in the immediate formation **10**. Compound **10** was obtained conveniently by treating **4** with Et_4NBr as illustrated in Scheme 2. This air- and moisture-stable, colorless solid was characterized by NMR spectroscopy and X-ray diffraction (Figure 9). The ^1H NMR signal of the pyrazole ring hydrogens shows a significant downfield shift compared to the corresponding resonance of the metal adducts (Table 9). The X-ray crystal structure of **10** shows well-separated $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[Et_4N]^+$. The B−N distances of the free ligand are very similar to the B−N lengths found in the metalated systems (Table 8).

Summary and Conclusion

We have reported the syntheses of two polyfluorinated tris(pyrazolyl)borate ligands in high yield and their utility in the preparation of several new copper and silver complexes containing neutral oxygen and phosphorus donor ligands. The crystal structures of the sodium and potassium salts of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[HB(3\text{-}(CF_3)Pz)_3]^-$ show significant metal−fluorine interactions. Such interactions are of interest due to their importance in the activation of C−F bonds and in the deposition of metal fluorides from the metal precursors containing fluoro ligands in chemical vapor deposition processes. Structurally authenticated sodium, potassium, or silver tris(pyrazolyl)borates are also very rare. The compounds **3**, **4**, $[\{HB(3\text{-}(CF_3)Pz)_3\}Na(thf)]_2$, and **8** represent four such molecules. Metal complexes of the fluorinated $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand have highly electrophilic metal sites relative to their hydrocarbon analogs. This is evident from the formation of stable adducts with neutral oxygen donors such as H_2O, dimethylacetamide, or thf. Furthermore, the metal compounds derived from fluorinated ligands show fairly long-range coupling between fluorines of the trifluoromethyl groups and the hydrogen, silver, or phosphorus. The solid state structures show that the fluorines are in close proximity to these nuclei, thus suggesting possible through-space coupling mechanisms. We have also described a convenient route to a "naked" tris(pyrazolyl)borate anion. The ease of formation of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and its stability may be attributable to the presence of highly electron-withdrawing CF_3 substituents on the pyrazole rings.

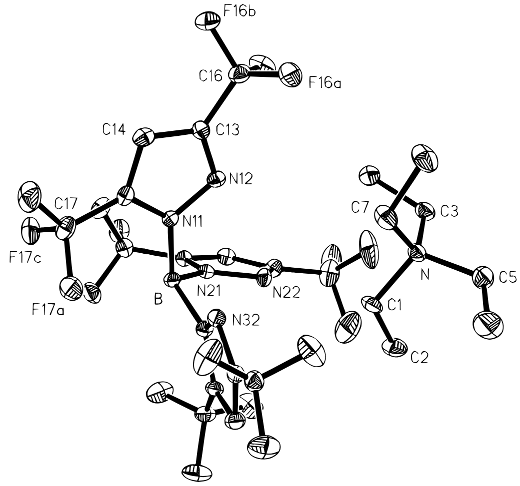


Figure 9. ORTEP drawing (at 30% probability level) of $[Et_4N][HB(3,5\text{-}(CF_3)_2Pz)_3]$ with H atoms omitted.

Copper complexes of tris(pyrazolyl)borates have been studied extensively because of their importance in the preparation of model compounds for various metalloproteins, ability to generate stable species such as copper carbonyl, nitrosyl, and olefin complexes, and their role in the carbene and nitrene transfer catalysis.[45,82,92−94] Compared to the case of the copper compounds, very little is known about the related silver complexes. Interestingly, almost all known group 11 metal complexes of poly(pyrazolyl)borates involve relatively electron-rich tris(pyrazolyl)borates such as methyl- or isopropyl-substituted ligands. The copper and silver compounds we report here are very different in that they involve highly fluorinated, "electron-poor" ligand systems. Furthermore, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ or $[HB(3\text{-}(CF_3)Pz)_3]^-$ systems are sterically somewhat similar to the corresponding methlylated analogs.[28,44] This enables the study of ligand electronic effects on various reactions without significant interference from the steric factors. Although several

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such studies have been carried out in metal−cyclopentadiene chemistry, very few similar investigations have been reported for poly(pyrazolyl)borates.[27−29,49,95] Hydrotris(pyrazolyl)borate ligands are often considered as cyclopentadienyl analogs in that both classes are monoanionic 6-electron donors capable of occupying three coordination sites around a metal center.[45] Cyclopentadienyl ligands involving CF_3 substituents are difficult to synthesize, and their metal complexes have been largely unexplored compared to the electron-rich alkylated analogs.[22−24,27,28] Therefore, ligands such as $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]^-$ or $[HB(3\text{-}(CF_3)Pz)_3]^-$, in addition to having their own unique properties and coordination chemistry, would also be valuable as reasonable models for CF_3-substituted cyclopentadienyl ligands. These ligands would also be useful for applications in supercritical CO_2 or fluorous media.[19,96−98] We are currently exploring the coordination chemistry of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[HB(3\text{-}(CF_3)Pz)_3]^-$ and the synthesis of other fluoroalkyl-substituted tris(pyrazolyl)borate ligands.

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Supporting Information Available: Tables of crystallographic data, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles (27 pages). Ordering information is given on any current masthead page.

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