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Notes

Copper(I) Isocyanide Complexes of Highly Fluorinated Poly(pyrazolyl)borates

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Introduction

Poly(pyrazolyl)borate ligands have been used widely in inorganic, organometallic, and bioinorganic chemistry.[1,2] However, most of these studies involve either the parent poly(pyrazolyl)borate or their alkylated analogs such as hydrotris(3,5-dimethylpyrazolyl)borate, $[HB(3,5-(CH_3)_2Pz)_3]^-$ or dihydrobis(3,5-dimethylpyrazolyl)borate, $[H_2B(3,5-(CH_3)_2Pz)_2]^-$.[1−3] Very little has been done on poly(pyrazolyl)borate systems bearing electron-withdrawing substituents such as trifluoromethyl groups.[1,4] Recently, we reported the synthesis of two such ligands, $[HB(3,5-(CF_3)_2Pz)_3]^-$ and $[H_2B(3,5-(CF_3)_2Pz)_2]^-$, containing six and four CF_3 substituents, respectively.[5,6] Here we describe the use of these highly fluorinated ligands in copper(I) isocyanide chemistry, and the structural characterization of a novel hydrogen-bridged dimer.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of purified nitrogen using either standard Schlenk techniques or 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. Glassware was oven-dried at 150 °C overnight. The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker MSL-300 spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed at UTA using a PE-2400 instrument. Bis(copper(I) trifluoromethanesulfonate)−benzene (Alfa) and Bu^tNC (Aldrich) were purchased and used as received. $[HB(3,5-(CF_3)_2Pz)_3]K\cdot DMAC$ and $[H_2B(3,5-(CF_3)_2Pz)_2]K$ were prepared according to the literature.[5,6]

Synthesis of $[HB(3,5-(CF_3)_2Pz)_3]CuCNBu^t$ (1). $2[Cu(OTf)]\cdot C_6H_6$ (40 mg, 0.08 mmol) was placed in a flask with thf (10 mL) and Bu^tNC (14 mg, 0.17 mmol), and solid $[HB(3,5-(CF_3)_2Pz)_3]K\cdot DMAC$ (120 mg, 0.161 mmol) was added at room temperature. This mixture was stirred overnight, and the volatiles were removed under vacuum. The residue was extracted into toluene, the extract was filtered, and the volatiles were removed from the filtrate to obtain **1** as a white solid. X-ray-quality crystals were grown from hexane at −25 °C: yield 53%; mp 185−187 °C; NMR (C_6D_6) ^1H (300 MHz) δ 1.06 (s, 9H, CH_3), 6.21 (s, 3H, CH); $^{13}C\{^1H\}$ (75.47 MHz) δ 29.65 (s, CH_3), 56.18 (s, $C(CH_3)_3$), 106.62 (s, *C*H), 119.65 (q, $^1J(C,F) = 270.5$ Hz, CF_3), 120.70 (q, $^1J(C,F) = 269.7$ Hz, CF_3), 139.26 (q, $^2J(C,F) = 43$ Hz, CCF_3) 139.65 (s, br, CN), 143.11 (q, $^2J(C,F) = 38.8$ Hz, CCF_3); ^{19}F (282.36 MHz, external reference $CFCl_3$) δ −61.03 (s), −58.50 (d, $^5J(F,H) = 2.9$ Hz); IR (KBr) 2196 (CN), 2616 cm^{-1} (BH). Anal. Calcd for $C_{20}H_{13}N_7BF_{18}Cu$: C, 31.29; H, 1.71; N, 12.77. Found: C, 31.15; H, 1.26; N, 12.44.

Synthesis of $\{[H_2B(3,5-(CF_3)_2Pz)_2]CuCNBu^t\}_2$ (2). $2[Cu(OTf)]\cdot C_6H_6$ (100 mg, 0.20 mmol) was placed in a flask with thf (10 mL) and Bu^tNC (0.40 mg, 0.48 mmol). Solid $[H_2B(3,5-(CF_3)_2Pz)_2]K$ (200 mg, 0.44 mmol) was added to the mixture at room temperature. The resulting mixture was stirred overnight, and the volatiles were removed under vacuum. The residue was extracted into Et_2O, the extract was filtered, and the volatiles were removed from the filtrate to obtain **2** as a colorless solid. X-ray quality crystals were grown from Et_2O−hexane at −25 °C: yield 58%; mp 124−126 °C; NMR (C_6D_6) ^1H (300 MHz) δ 0.76 (s, 9H, CH_3), 6.32 (s, 2H, C*H*); $^{13}C\{^1H\}$ (75.5 MHz) δ 29.03 (s, CH_3), 56.57 (s, $C(CH_3)_3$), 105.81 (s, *C*H), 119.75 (q, $^1J(C,F) = 270.1$ Hz, CF_3), 120.69 (q, $^1J(C,F) = 269.3$ Hz, CF_3), 134.25 (br s, CN), 139.04 (q, $^2J(C,F) = 42.5$ Hz, CCF_3), 141.81 (q, $^2J(C,F) = 38.1$ Hz, CCF_3); ^{19}F (282.36 MHz, external reference $CFCl_3$) δ −60.32 (s), −58.98 (br s); IR (KBr) 2196 (CN), 2303, 2344, 2568 cm^{-1} (BH). Anal. Calcd for $\{C_{15}H_{13}N_5BF_{12}Cu\}_2$: C, 31.85; H, 2.32; N, 12.38. Found: C, 31.80; H, 1.97; N, 12.47.

Crystallographic Data Collection and Structure Determination. A colorless crystal of **1** with dimensions 0.10 × 0.45 × 0.47 mm was mounted on a glass fiber with a small amount of Paratone-N oil/grease and placed in the dinitrogen cold stream of a Siemens P4 diffractometer equipped with an LT-2A device. Cell parameters were determined using 20 reflections. Data were corrected for Lorentz and polarization effects. The space group determination was based upon a check of Laue symmetry and symmetric absences present and was confirmed by the structure solution. The structure was solved by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the Siemens SHELXTL (PC version 4.2) software package. The molecule crystallizes in the $P2_1/m$ space group with a crystallographically imposed mirror plane containing H, B, one of the pyrazole rings, Cu, and the isocyanide group. All the F atoms behaved nicely. While all F atom positions were ordered, a rotational disorder (over two sites) was observed for carbons of the Bu^t group. This disorder was modeled successfully with 50% occupancy for each $C-Me_3$ unit. All non-hydrogen atoms, except for two of the disordered carbons, C4A and C4B, were refined anisotropically. The H on B was located from the difference map. The pyrazole ring hydrogens were included in calculated positions (C−H = 0.96 Å) and were refined isotropically. Due to disorder, the hydrogens on the Me groups were not included in the refinement.

A colorless crystal of **2** with dimensions 0.22 × 0.47 × 0.57 mm was used. Cell parameters were determined using 19 reflections. Data were corrected for Lorentz and polarization effects and for absorption effects. Compound **2** crystallized in $P\bar{1}$ with the center of the molecule lying on an inversion center. The structure was solved by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the Siemens SHELXTL (PC version 4.2) software package. Minor disorder was noted for some of the Bu^t carbons. However, a reasonable model could not be obtained from the peaks of the difference map. All the non-hydrogen atoms were refined anisotropically. The two hydrogens on B were located from the difference map, and the positions and the isotropic thermal parameters were refined successfully. The remaining hydrogens were included in the calculated positions. The pyrazole ring hydrogens were refined isotropically. The remaining hydrogens were given fixed U_H. Cell dimensions and structure refinement details are listed in Table 1. Final atomic positional parameters for selected atoms are listed in Table 2, and selected bond lengths and angles are given in Table 3.

Results and Discussion

$[HB(3,5-(CF_3)_2Pz)_3]CuCNBu^t$, **1**, has been synthesized by treating $[HB(3,5-(CF_3)_2Pz)_3]K\cdot DMAC$ with CuOTf and *tert-*

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Table 1. Crystal Data for **1** and **2**[a]

formula	$C_{20}H_4BCuF_{18}N_7$ (**1**)	$C_{30}H_{26}B_2Cu_2F_{24}N_{10}$ (**2**)
fw	758.7	1131.3
color/habit	colorless, diamond-shaped rods	colorless blocks
crystal system	monoclinic	triclinic
space group	$P2_1/m$	$P\bar{1}$
a, Å	8.093(2)	9.142(2)
b, Å	14.992(4)	10.616(1)
c, Å	13.273(3)	11.795(2)
α, deg	90	76.36(1)
β, deg	105.70(2)	85.09(2)
γ, deg	90	87.29(1)
V, Å^3	1550.3(7)	1108.0(3)
Z	2	1
D_{calc}, g cm^{-3}	1.625	1.695
T, °C	−80	−80
μ(Mo Kα), mm^{-1}	0.836	1.098
λ, Å	0.710 73	0.710 73
$2\theta_{max}$, deg	48.0	48.0
R, R_w	0.0498, 0.0533	0.0420, 0.0482

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [0.0008F^2 + \sigma^2(F)]^{-1}$

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

	x	y	z	U(eq)[a]
		$[HB(3,5-(CF_3)_2Pz)_3]CuCNBu^t$ (**1**)		
Cu	991(1)	2500	869(1)	35(1)
N11	−2297(6)	2500	−774(3)	28(2)
N12	−1657(6)	2500	288(3)	29(2)
N21	113(4)	1653(2)	−1226(2)	30(1)
N22	1107(4)	1514(2)	−227(3)	30(1)
B	−1031(9)	2500	−1478(5)	32(2)
N	2730(8)	2500	3153(5)	78(3)
C1	2085(9)	2500	2267(5)	48(3)
C2	3480(14)	2500	4310(6)	107(6)
H	−1617	2500	−2378	32(16)
		$\{[H_2B(3,5-(CF_3)_2Pz)_2]CuCNBu^t\}_2$ (**2**)		
Cu	2978(1)	9621(1)	1299(1)	32(1)
N11	2677(3)	10393(3)	−1241(2)	28(1)
N12	2364(3)	9448(3)	−258(2)	28(1)
N21	3411(3)	12178(3)	−286(2)	30(1)
N22	3256(3)	11551(3)	858(2)	31(1)
B	3851(4)	11408(4)	−1245(3)	31(1)
N	2468(3)	7801(3)	3661(2)	36(1)
C1	2595(4)	8526(3)	2762(3)	35(1)
C2	2456(4)	6867(3)	4787(3)	40(1)
H1	4876(45)	10840(34)	−1029(31)	41(10)
H2	3964(39)	12061(31)	−2072(28)	30(9)

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

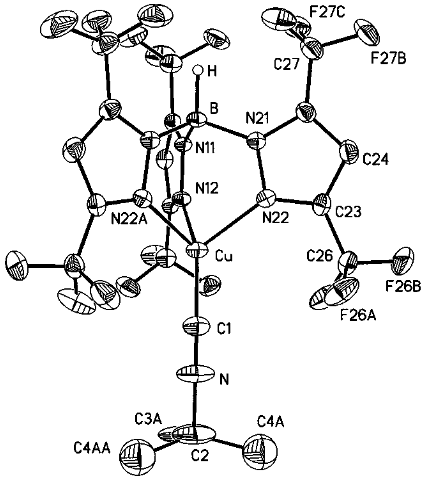

Figure 1. Molecular structure of **1**. The hydrogens on the pyrazole rings and Bu^t group have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg)

	$[HB(3,5-(CF_3)_2Pz)_3]CuCNBu^t$ (**1**)		
	Bond Distances		
Cu−C1	1.827(6)	C1−N	1.151(8)
Cu−N12	2.072(5)	Cu−N22	2.093(4)
Cu−N22A	2.093(4)	B−N11	1.562(9)
B−N21	1.554(5)	B−N21A	1.554(5)
N11−N12	1.363(6)	N21−N22	1.368(4)
	Bond Angles		
Cu−C1−N	178.1(7)	C1−N−C2	177.2(9)
N12−Cu−N22	88.7(1)	N12−Cu−N22A	88.7(1)
N22−Cu−N22A	89.8(2)	C1−Cu−N22A	127.2(1)
C1−Cu−N12	123.1(3)	C1−Cu−N22	127.2(1)
N11−B−N21	108.7(3)	N21−B−N21A	109.7(5)
	$\{[H_2B(3,5-(CF_3)_2Pz)_2]CuCNBu^t\}_2$ (**2**)		
	Bond Distances		
Cu−C1	1.855(3)	C1−N	1.155(4)
Cu−N12	2.018(3)	Cu−N22	2.014(3)
B−N11	1.555(5)	B−N21	1.561(5)
N11−N12	1.362(3)	N21−N22	1.356(3)
B−H1	1.105(39)	B−H2	1.055(30)
Cu−H1A	2.017(40)	N−C2	1.457(4)
	Bond Angles		
Cu−C1−N	174.5(3)	C1−N−C2	174.7(4)
N12−Cu−N22	97.1(1)	C1−Cu−H1A	98.9(9)
C1−Cu−N12	128.4(1)	C1−Cu−N22	129.7(1)
N11−B−N21	110.6(3)	B−H−CuA	154.3(26)

butyl isocyanide and isolated in moderate yield. Compound **1** is an air- and moisture-stable colorless solid melting at 185−187 °C. The IR stretching bands corresponding to the isocyanide and B−H moieties appear at 2196 and 2616 cm^{-1}, respectively. The ν_{CN} is much higher than the value observed for $[B(Pz)_4]CuCNBu^t$ (2140 cm^{-1}), $[HB(Pz)_3]CuCNBu^t$ (2155 cm^{-1}), $[(C_5H_5)Co\{P(OMe)_2O\}_3]CuCNBu^t$ (2148 cm^{-1}), ^{t}-BuOCuCNBu^t (2102 cm^{-1}), or the free ligand (2138 cm^{-1}).[7−10] The unusually high C−N stretching frequency for **1** in the IR spectrum is a direct result of the fluorination of the tris(pyrazolyl)borate ligand. The X-ray crystal structure of **1** depicted in Figure 1 shows well-separated molecules with a Cu−C distance of 1.827(6) Å and a C−N−Bu^t angle of 177.2(9)°. This Cu−C distance can be compared to the corresponding bond length observed for the closely related carbonyl complex $[HB(3,5-(CF_3)_2Pz)_3]CuCO$ (1.808(4) Å) or for various other copper isocyanides (Cu−C(av) = 1.896 Å).[11,12] The copper center adopts a pseudotetrahedral geometry. The Cu−N bond distances of **1** (2.072(5), 2.093(4) Å) are somewhat similar to those of $[HB(3,5-(CF_3)_2Pz)_3]CuCO$ (2.035(3), 2.061(2) Å)[11] but longer than the Cu−N distances observed in the square planar Cu(II) complex $[H_2B(3,5-(CF_3)_2Pz)_2]_2Cu$ (2.004(6), 1.997(5) Å).[6]

The bis[(pyrazolyl)borato]copper complex $\{[H_2B(3,5-(CF_3)_2Pz)_2]CuCNBu^t\}_2$ (**2**) was prepared in a manner similar to that for **1** using $[H_2B(3,5-(CF_3)_2Pz)_2]K$, CuOTf, and *tert*-butyl isocyanide. Interestingly, the X-ray crystal structure of **2** revealed a novel dimeric species. This compound crystallizes

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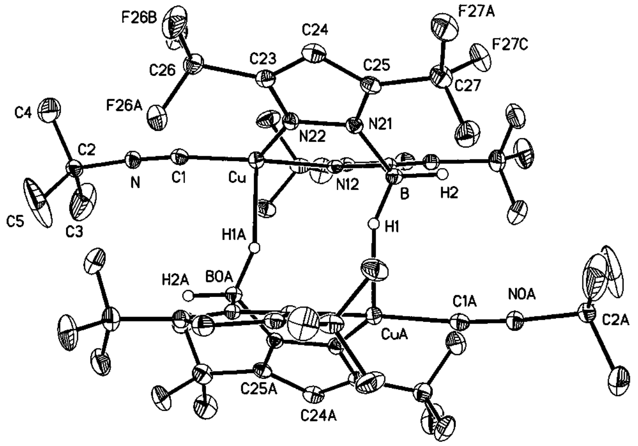

Figure 2. Molecular structure of **2**. The hydrogens on the pyrazole rings and Bu^t group have been omitted for clarity.

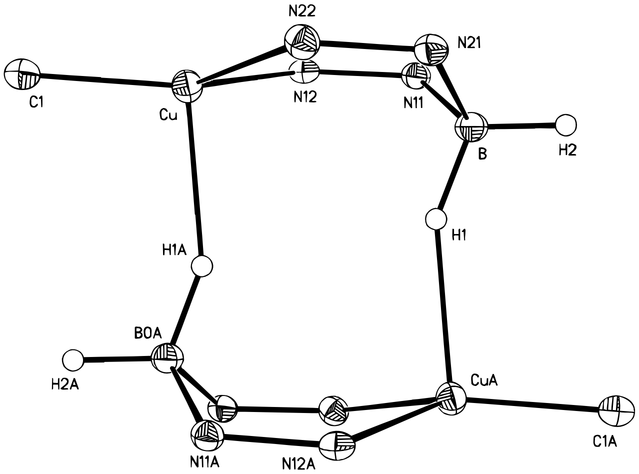

Figure 3. Molecular structure of **2**, showing only the atoms bonded to copper and boron.

in the $P\bar{1}$ space group with the center of the dimer residing upon a center of inversion (Figure 2). The two units are held together by the bridging hydrogen atoms (Figure 3). The copper center adopts a distorted, pseudotetrahedral geometry. The bis(pyrazolyl)borate ligand displays a boat conformation.[6] The Cu−C−N−Bu^t moiety is almost linear (Cu−C−N = 174.5(3)°, C−N−Bu^t = 174.7(4)°). The Cu−C bond distance of 1.855(3) Å in **2** is longer than the corresponding bond length in **1**. The Cu−H, B−H(bridging), and B−H(terminal) distances are 2.02(4), 1.11(4), and 1.05(3) Å, respectively. The Cu−H and Cu···B (3.050 Å) separations are longer than the typically observed values for various copper borohydrides involving Cu−H−B interactions.[13−15] However, Cu−H distances of similar magnitude have been observed in complexes such as $\{(PPh_3)_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$.[16]

The IR band corresponding to ν_{CN} appeared at a position identical to that observed for **1**. In addition, several strong bands were detected in the IR spectrum at 2303, 2344, and 2568 cm^{-1}, the first two of which may be assigned to ν_{CuHB}.[8] Similar absorptions are also seen for $Cu_2B_{10}H_{10}$ systems (e.g., $Cu_2B_{10}H_{10}$, $\{(PPh_3)_2Cu\}_2B_{10}H_{10}$) which contain Cu−H−B bridges.[16,17] The ^{1}H NMR signals due to B−H are too broad and could not be observed for either **1** or **2**.

In summary, we have reported the synthesis and first structural characterization of the isocyanide adducts involving poly(pyrazolyl)borato complexes of copper(I) and the use of two highly fluorinated ligands in copper chemistry. Compound **2** shows a novel mode of coordination for a bis(pyrazolyl)borate ligand. Bis(pyrazolyl)borate ligands are known to display intramolecular M−H−B interactions.[2] However, to our knowledge, intermolecular M−H−B bonding has not been reported with these systems. We are currently extending the chemistry of fluorinated poly(pyrazolyl)borates to other elements and exploring the reactivity of **1** and **2** with various nucleophiles.

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Supporting Information Available: Text giving details of the structure determinations and tables of crystallographic data, data collection and refinement details, atomic positional and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles and a diagram of **1** showing the disorder in the *tert*-butyl group (13 pages). Ordering information is given on any current masthead page.

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