Copper(I) Carbonyl Complex of a Trifluoromethylated Tris(pyrazolyl)borate Ligand

H. V. Rasika Dias* and Hui-Ling Lu

Department of Chemistry & Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019

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Introduction

Tris(pyrazolyl)borates are one of the most widely used ligands in chemistry.[1] However, the vast majority of studies involving the metal complexes of tris(pyrazolyl)borates are limited to either the parent ligand, $[HB(Pz)_3]^-$ or their alkylated analogs such as $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$. Very little has been done on systems which contain electron-withdrawing substituents.[2−4] Our interests have been focused on the development and study of the fluoroalkyl-substituted poly(pyrazolyl)borates.[5,6] Recently, we reported the synthesis and structural characterization of a tris(pyrazolyl)borate ligand containing six CF_3 substituents.[5] Here we report the synthesis of a copper(I) carbonyl complex using this highly fluorinated $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand, and show the effects of electron-withdrawing CF_3 groups on the structure and spectroscopic properties of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$, **1**.

Copper(I) adducts of carbon monoxide have been actively investigated largely due to their importance in catalysis and biochemistry.[7−11] Among the copper carbonyl adducts, the molecules involving tris(pyrazolyl)borate ligands are particularly interesting. There are several stable Cu(I)−CO complexes of tris(pyrazolyl)borates known to date.[12−16] In fact, $[HB(Pz)_3]CuCO$ is the first stable (and the first structurally characterized) copper carbonyl complex.[13,15] Compound **1** represents a unique addition to this group because it is the only example involving a highly electron deficient, polyfluorinated tris(pyrazolyl)borate ligand.[1]

Experimental Section

General Procedures. All operations 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 degassed twice prior to use. Glassware was oven-dried at 150 °C overnight. The ^1H and ^{13}C 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 analysis was performed at UTA using PE-2400 instrument. Bis(copper(I) trifluoromethanesulfonate)−benzene (Alfa) and CO (Metheson) were purchased and used as received. $[HB(3,5\text{-}(CF_3)_2Pz)_3]K{\bullet}DMAC$ was prepared according to the literature.[5]

Synthesis of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$. $2\text{-}[Cu(OTf)]{\cdot}C_6H_6$ (0.067 g, 0.134 mmol) was placed in a flask with thf (20 mL) and stirred for several minutes while bubbling CO. Solid $[HB(3,5\text{-}(CF_3)_2Pz)_3]K{\bullet}DMAC$ (0.210 g, 0.281 mmol) was added to this mixture and stirred overnight under an atmosphere of CO. The volatiles were removed and the residue was extracted into toluene and filtered, and the filtrate was concentrated to obtain **1** in 47% yield . X-ray quality crystals were grown from a toluene/hexane mixture at −20 °C. mp 146−147 °C, ^1H NMR (C_6D_6, 300 MHz, TMS) δ 6.06 (s, 3 H, Pz); ^{19}F NMR (C_6D_6, 282.36 MHz, external reference $CFCl_3$) δ −61.4, −58.8 (d, J = 3.2 Hz); IR (KBr) cm^{-1} 3160, 2960, 2923, 2851, 2634 (BH), 2137 (CO), 1668, 1556, 1494, 1396, 1367, 1276, 1251, 1166, 1145, 1080, 1047, 833, 780, 743, 692, 483, 414. Anal. Calcd for $C_{16}H_4BCuF_{18}N_6O$: C, 26.97; H, 0.57; N, 11.79. Found: C, 26.84; H, 0.62; N, 11.92.

Crystallographic Data Collection and Structure Determination

A colorless crystal of dimensions 0.68 × 0.66 × 0.03 mm was mounted on a glass fiber with a small amount of Paratone-N oil and placed in the dinitrogen cold stream of a Siemens P4 diffractometer equipped with a LT-2A device.[17] Cell parameters were determined using eight reflections taken from a 10 min rotation photograph, and verified with fractional search. An additional 18 high angle reflections, $24.49° < 2\theta < 25.02°$ were used to refine these parameters. Cell dimensions and structure refinement data are listed in Table 1. Intensity data were collected in the 2θ range 3.5−52°. Data were corrected for Lorentz, polarization and absorption 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 Siemens SHELXTL (PC version 4.2) software package.[18] Of the 3119 reflections measured, 2379 (R_i = 4.41%) were unique and 2067 had $F > 4\sigma(F)$. After anisotropic refinement of all non-hydrogen atoms, the H on B was located via difference Fourier map inspection. The remaining hydrogens were included at calculated positions with C−H = 0.96 Å, and fixed U_H. The final R and R_w values were 0.0398 and 0.0453, respectively ($w = [0.0008F^2 + \sigma^2(F)]^{-1}$). Final atomic positional parameters for non-hydrogen atoms are listed in Table 2. Selected bond lengths and angles are given in Table 3. Full crystallographic data, a complete list of bond distances and angles, anisotropic thermal parameters, and the hydrogen coordinates are presented in the Supporting Information.

Results and Discussion

The treatment of $[HB(3,5\text{-}(CF_3)_2Pz)_3]K{\bullet}DMAC$ (**2**)[5] (where $[HB(3,5\text{-}(CF_3)_2Pz)_3]$ = hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borate; DMAC = dimethylacetamide) with CuOTf under an atmosphere of CO leads to the title compound **1**. Compound **1** crystallizes from a toluene/hexane mixture as colorless thin plates. The ^1H, ^{19}F NMR, IR spectroscopic and the elemental analysis data agree with the proposed formulation. The ^1H NMR chemical shift value of the pyrazole ring protons in **1** is δ 6.06. This peak appears upfield from the corresponding signal

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Table 1. Crystal Data for $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$

formula	$C_{16}H_4BCuF_{18}N_6O$	V, Å^3	1169.0(4)
fw	712.6	Z	2
color/habit	colorless plates	D_{calc}, g cm^{-3}	2.024
cryst syst	monoclinic	T, °C	−80
space group	$P2_1/m$ (No. 11)	μ(Mo Kα), mm^{-1}	1.104
a, Å	8.080(2)	λ, Å	0.710 73
b, Å	14.992(3)	$2\theta_{max}$, deg	52.0
c, Å	9.907(2)	R^a	0.0398
β, deg	103.06(2)	$R_w{}^b$	0.0453

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

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

	x	y	z	U(eq)^a
Cu	9805(1)	2500	1035(1)	26(1)
C	9857(5)	2500	2869(4)	36(1)
O	9895(5)	2500	3996(3)	64(2)
N(11)	11636(4)	2500	−1180(3)	22(1)
N(12)	11904(4)	2500	223(3)	24(1)
N(21)	8849(3)	1649(1)	−1685(2)	23(1)
N(22)	8736(3)	1524(1)	−356(2)	24(1)
C(13)	13582(4)	2500	714(4)	27(1)
C(14)	14443(5)	2500	−352(4)	29(1)
C(15)	13164(4)	2500	−1534(4)	25(1)
C(16)	14297(5)	2500	2229(4)	34(1)
C(17)	13401(5)	2500	−2977(4)	37(1)
C(23)	7943(3)	736(2)	−336(3)	28(1)
C(24)	7526(4)	358(2)	−1639(3)	36(1)
C(25)	8122(3)	955(2)	−2470(3)	32(1)
C(26)	7595(4)	377(2)	977(3)	34(1)
C(27)	8025(5)	865(2)	−3990(3)	46(1)
F(16A)	15989(3)	2500	2516(3)	50(1)
F(16B)	13813(3)	1787(1)	2854(2)	50(1)
F(17A)	15057(3)	2500	−2965(3)	61(1)
F(17B)	12725(3)	1788(2)	−3701(2)	55(1)
F(26A)	6129(3)	667(2)	1204(3)	64(1)
F(26B)	7524(3)	−501(1)	944(3)	66(1)
F(26C)	8775(3)	593(2)	2088(2)	64(1)
F(27A)	7268(4)	95(2)	−4441(2)	84(1)
F(27B)	7170(3)	1524(2)	−4720(2)	61(1)
F(27C)	9558(3)	849(1)	−4275(2)	53(1)
B	9773(5)	2500	−2075(4)	22(1)

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

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$

	Bond Distances (Å)		
Cu−C	1.808(4)	C−O	1.110(5)
Cu−N(12)	2.035(3)	Cu−N(22)	2.061(2)
Cu−N(22A)	2.061(2)	B−N(11)	1.565(4)
B−N(21)	1.569(3)	B−N(21A)	1.569(3)
N(11)−N(12)	1.357(4)	N(21)−N(22)	1.354(3)
	Bond Angles (deg)		
Cu−C−O	179.8(4)	N(12)−Cu−N(22)	89.8(1)
N(12)−Cu−N(22A)	89.8(1)	N(22)−Cu−N(22A)	90.4(1)
C−Cu−N(12)	124.4(2)	C−Cu−N(22)	125.7(1)
C−Cu−N(22A)	125.7(1)	N(11)−B−N(21)	108.1(2)
N(11)−B−N(21A)	108.1(2)	N(21)−B−N(21A)	108.7(3)

of **2** (δ 6.38 in C_6D_6).[5] The ^{19}F NMR chemical shift values are very similar both in **1** and **2**.

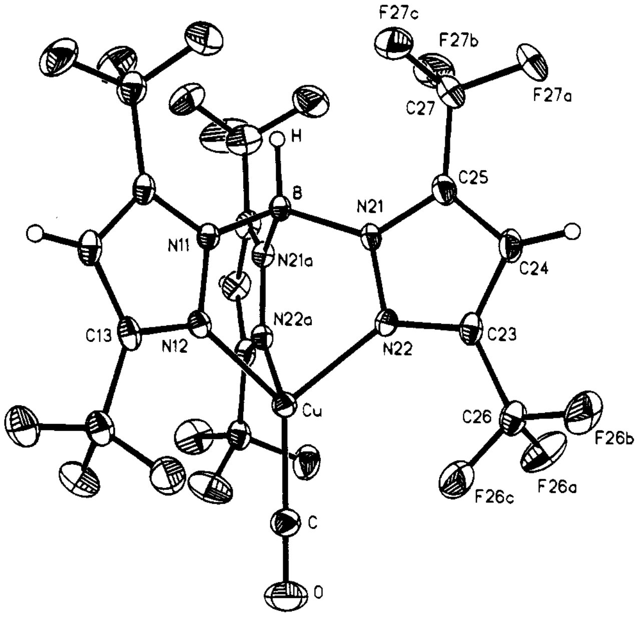

Figure 1. Molecular structure of compound **1** (ellipsoids are shown at the 30% probability level).

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

	ν_{CO} (cm^{-1})	Cu−C (Å)	C−O (Å)	ref
$[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$	2137	1.808(4)	1.110(5)	this work
$[HB(3,5\text{-}Ph_2Pz)_3]CuCO$	2086			12
$[HB(Pz)_3]CuCO$	2083	1.765(14)	1.120(6)	13,15
$[HB(3,5\text{-}(CH_3)_2Pz)_3]CuCO$	2066			14
$[HB(3,5\text{-}(i\text{-}Pr)_2Pz)_3]CuCO$	2056	1.769(8)	1.118(10)	12
$[HB(3\text{-}t\text{-}BuPz)_3]CuCO$	2069			16

The solid state IR spectrum of **1** shows a strong absorption at 2137 cm^{-1}, corresponding to the carbonyl stretching frequency. This value is considerably higher than the values observed for related tris(pyrazolyl)boratocopper(I) carbonyl complexes (Table 4).[12-16] However, the trend is consistent with the electron-donating ability of the substituents on the pyrazolylborate ligands.[19] The carbonyl stretching frequency of metal carbonyls has been used as an indirect probe to estimate the relative electron density on a metal ion.[20] The copper coordinated to the $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand bearing six electron-withdrawing CF_3 substituents would expect to have the lowest electron density among the complexes in Table 4. As a result the Cu to CO π-back-bonding would be at the lowest level in **1**, thus leading to a higher C−O stretching frequency. In fact, the ν_{CO} in **1** is very close to the value observed for free CO (2143 cm^{-1}).[21-23]

The structure of **1** was determined by X-ray crystallography. An ORTEP view of **1** is presented in Figure 1. Compound **1** crystallizes as well separated molecules in the $P2_1/m$ space group with a crystallographically imposed plane of symmetry containing one of the pyrazole rings, B, Cu, and the CO unit. The copper center adopts a distorted tetrahedral coordination.

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The Cu−C−O moiety is linear within experimental limits (179.8(4)°).

The critical feature in the X-ray crystal structure of **1** concerns the relatively long Cu−CO bond distance of 1.808(4) Å. Typical Cu(I)−CO distances are in the range of 1.75−1.78 Å (see Table 1 for related systems and references therein). 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}), carbonyl[glyoxal bis(2,4-dimethylpentyl-3-imine)](trifluoromethylsulfonato)copper, 1.820(6) Å (υ_{CO} = 2108 cm^{-1}), [(en)CuCO](BPh_4), 1.806(6) Å (υ_{CO} = 2117 cm^{-1}) or $[\{NH(py)_2CuCO](ClO_4)$, 1.802(2) Å (υ_{CO} = 2110 cm^{-1}).[24−28] The C−O bond length in **1** is 1.110(5) Å. Although, this value is relatively short, the bond shortening is not significant enough to draw any conclusions. Moreover, the C−O bond distance is not widely recognized as a reliable measure for comparing the bonding between various metal complexes.[20] Nevertheless, the general trends (in particular the relatively long Cu−C distance) are consistent with the results from the infrared study. The Cu−N distances and angles in **1** correspond closely to those previously observed for tris(pyrazolyl)boratocopper(I) complexes, while the B−N distances (1.565(4), 1.569(3), and 1.569(3) Å) are at the higher end of the typical values.[29]

In summary, compound **1** represents the first transition metal complex of the perfluoromethylated analog of $[HB(3,5\text{-}(CH_3)_2\text{-}Pz)_3]^-$ ligand. The structural and spectroscopic data show a notable difference between the fluorinated and nonfluorinated systems. For example, the CO stretching frequency of **1** is about 71 cm^{-1} higher than that of the methylated analog. We are currently pursuing the synthesis of other metal complexes of trifluoromethylated poly(pyrazolyl)borates, and are studying the effects of fluoro substituents on their physical properties and chemical reactivity.

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Supporting Information Available: Text giving crystallographic data and details of the structure determination and tables of atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **1** (6 pages). Ordering information is given on any current masthead page.

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