Direct Synthesis of a Bis(pyrazolyl)boratocopper(I) Complex: Synthesis and Characterization of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ Displaying an Unusual Coordination Mode for a Poly(pyrazolyl)borate Ligand

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Introduction

Poly(pyrazolyl)borates are one of the most widely used ligands in coordination chemistry.[1−5] Complexes of these ligands are known for most of the elements in the periodic table. Syntheses of poly(pyrazolyl)boratometal complexes generally require the use of alkali-metal poly(pyrazolyl)borates as starting material.[6] The alkali-metal derivatives are synthesized by heating a mixture of an alkali-metal tetrahydroborate and a pyrazole.[3]

There are many non-alkali-metal tetrahydroborates known.[7,8] This has prompted us to investigate the possibility of using some of these salts in poly(pyrazolyl)borate chemistry. The following work describes the synthesis of a copper(I) bis(pyrazolyl)borate, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$, directly from a copper tetrahydroborate salt and $3,5\text{-}(CF_3)_2PzH$ (where $3,5\text{-}(CF_3)_2PzH$ = 3,5-bis(trifluoromethyl)pyrazole), thereby circumventing the need for an alkali-metal derivative such as $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]K$.[9]

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen either using standard Schlenk techniques or in a Vacuum Atmospheres single-station drybox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources and distilled from conventional drying agents prior to use. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded at 25 °C on a Bruker MSL-300 spectrometer (^{1}H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.36 MHz; ^{31}P, 121.49 MHz). Proton and carbon chemical shifts are reported in parts per million vs Me_4Si. ^{19}F and ^{31}P NMR chemical shifts were referenced relative to an external $CFCl_3$ and an 85% H_3PO_4 standard, respectively. Infrared 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 Perkin-Elmer model 2400 CHN analyzer. Synthesis of $3,5\text{-}(CF_3)_2PzH$ was carried out as reported previously.[10] $(PPh_3)_2CuBH_4$ was purchased from commercial sources and used as received.

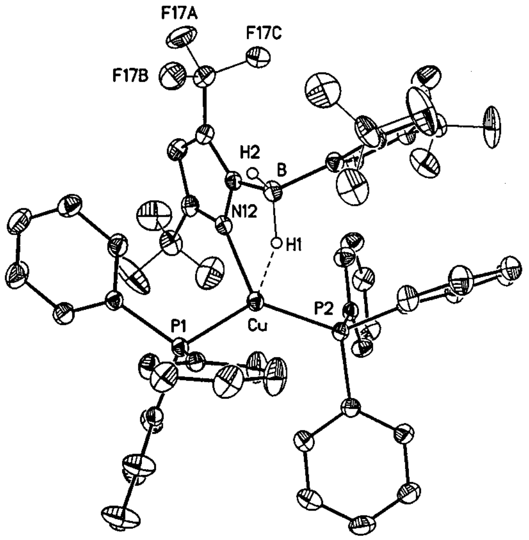

Figure 1. Structure of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ (all hydrogen atoms except H on boron are omitted for clarity). Selected bond lengths (Å) and angles (deg): Cu−N12 2.057(2), Cu−P1 2.2388(7), Cu−P2 2.2690(7), Cu···H 2.01(2), Cu···B 2.891, B−H1 1.16(2), B−H2 1.07-(2), B−N11 1.555(4), B−N12 1.556(4), N12−Cu−P1 105.83(6), N12−Cu−P2 120.13(6), P1−Cu−P2 132.91(3).

Synthesis of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$. A mixture of $(PPh_3)_2CuBH_4$ (0.368 g, 0.610 mmol), $3,5\text{-}(CF_3)_2PzH$ (0.436 g, 2.14 mmol), and kerosene (∼5 mL) was gradually heated (over a period of 3 h) to 175−180 °C. The mixture was kept at this temperature for 1 h and cooled to −20 °C to obtain a white precipitate. The precipitate was separated and extracted into warm hexane. The hexane extract was kept in a −20 °C freezer overnight to obtain a colorless solid. It was dried under vacuum for several hours to obtain $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ in 60% yield. X-ray-quality crystals were grown from a hexane−toluene mixture at −20 °C. Mp: 143−145 °C. ^{1}H NMR (C_6D_6): δ 6.42 (s, 2H, pyr-H), 6.96 (d, 6H, H_p), 6.97 (d, 12H, H_o), 7.34 (m, 12H, H_m). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 106.3 (br s, CH), 120.5 (q, $^1J_{C,F}$ = 269 Hz, CF_3), 121.4 (q, $^1J_{C,F}$ = 269 Hz, CF_3), 128.9 (d, $^3J_{C,P}$ = 9 Hz, C_m), 130.1 (br s, C_P), 132.7 (d, $^1J_{C,P}$ = 28 Hz, C_i), 133.7 (d, $^2J_{C,P}$ = 15 Hz, C_O), 138.2 (q, $^2J_{C,F}$ = 41 Hz, CCF_3), 141.3 (q, $^2J_{C,F}$ = 38 Hz, CCF_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −25.72 (br s). ^{19}F NMR (C_6D_6): δ −60.65 (s), −59.57 (br s). IR (KBr), cm^{-1}: selected 3163 (CH), 3147 (CH), 2505, 2261 (sh), 2215 (br). Anal. Calcd for $C_{46}H_{34}BCuF_{12}N_4P_2$: C, 54.86; H, 3.40; N, 5.56. Found: C, 54.99; H, 3.14; N, 5.55.

Crystallographic Data Collection and Structure Determination. A colorless crystal of dimensions 0.51 mm × 0.43 mm × 0.34 mm was chosen, mounted in inert oil and transferred to the cold gas stream of the Siemens P4 diffractometer. The structure was solved using direct methods and refined by full-matrix least squares on F^2. All non-hydrogens were refined anisotropically. Hydrogens on boron were located and refined. Others were included at calculated positions.

Results and Discussion

The reaction between $(PPh_3)_2CuBH_4$ and $3,5\text{-}(CF_3)_2PzH$ at ∼180 °C results in the formation of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$. It has been characterized by X-ray diffraction (Figure 1, Table 1), and NMR and IR spectroscopy. The X-ray crystal structure of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ displays an unusual mode of coordination for a bis(pyrazolyl)borate (Figure 2).

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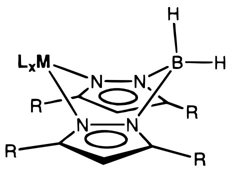
Table 1. Crystal Data for $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2 \cdot 0.5$ *n*-Hexane

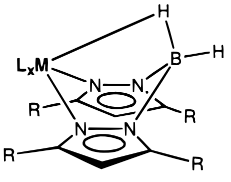
empirical formula	$C_{49}H_{41}BCuF_{12}N_4P_2$	V, Å^3	2437.2(5)
fw	1050.15	Z	2
temp, K	183	λ(Mo Kα), Å	0.710 73
cryst syst	triclinic	D_c, Mg/m^3	1.431
space group	$P\bar{1}$	μ(Mo Kα), mm^{-1}	0.598
a, Å	13.486(2)	GOF (on F^2)	1.053
b, Å	13.672(1)	R1, wR2 ($I > 2\sigma(I)$)[a]	0.0342, 0.0840
c, Å	13.909(1)	R1, wR2 (all data)[a]	0.0423, 0.0884
α, deg	80.288(8)		
β, deg	82.151(9)		
γ, deg	75.677(8)		

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Unlike the more common bonding mode **A**,[3,4,9] or somewhat rare **B**,[1,5,11,12] $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ ligand in $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ coordinates to copper through only one nitrogen atom (type **C**). The geometry at the copper may be described as trigonal planar with a Cu−N bond length of 2.057(2) Å and Cu−P distances of 2.2388(7) and 2.2690(7) Å. One of the hydrogens on boron also shows a weak interaction with the copper atom (Cu−H = 2.01(2) Å; Cu···B = 2.891 Å). This contact is not strong enough to distort the geometry at copper from trigonal planar as evident from the sum of the angles at Cu, 358.8°. The Cu−H distance of 2.01(2) Å is at the higher end of the typical Cu−H bond lengths observed in copper borohydrides (average 1.87 Å; range 1.70−2.08 Å).[13−15] It is very similar to the Cu−H contact of the H-bridged dimer $\{[H_2B(3,5\text{-}(CF_3)_2Pz)_2]CuCNBu^t\}_2$ (bonding mode **D**; Cu−H = 2.02(2) Å, Cu···B = 3.050 Å). Interestingly, unlike in the title compound, copper sites of $\{[H_2B(3,5\text{-}(CF_3)_2Pz)_2]CuCNBu^t\}_2$ show significant deviations from planarity as a result of the Cu−H bond (sum of the angles at Cu 355.2°).[16]



A



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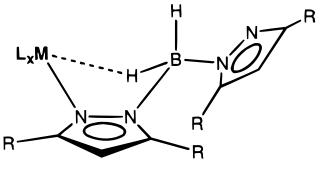
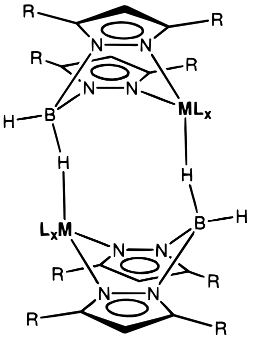


C



D

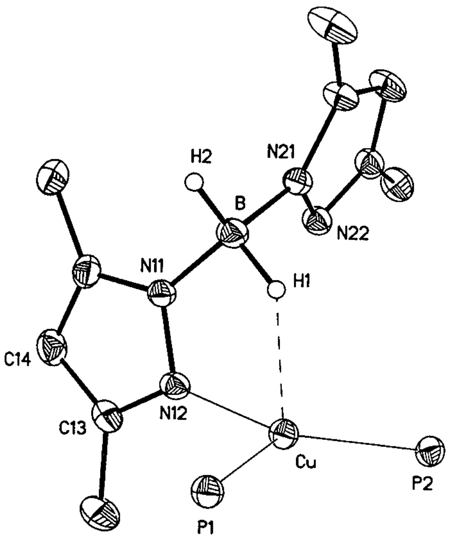


Figure 2. Structure of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ showing only a selected group of atoms.

The IR spectrum of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ in KBr shows two bands at 2505 and 2215 (broad) cm^{-1} assignable to ν_{B-H} and $\nu_{B-H\cdots Cu}$, respectively. The broad band at 2215 cm^{-1} is consistent with the Cu−H−B contact.[17] Corresponding B−H stretching frequencies of $\{[H_2B(3,5\text{-}(CF_3)_2Pz)_2]CuCNBu^t\}_2$ appear at 2568 cm^{-1} and 2303 and 2344 (shoulder) cm^{-1}.[16] The structurally characterized ruthenium adduct $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]RuH(COD)$ featuring type **B** coordination (Ru···HB = 1.97(3) Å) also shows similar infrared data for terminal and bridging B−H moieties (2555 cm^{-1} and 2128 and 2028 cm^{-1}).[12] The room-temperature NMR data of $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ suggest fluxional behavior in solution as ^{1}H, ^{13}C, and ^{19}F NMR spectra show resonances attributable to equivalent pyrazolyl moieties.

Overall, the results from this study demonstrate that it is possible to synthesize poly(pyrazolyl)boratometal complexes (where metal ≠ alkali metal) directly from metal tetrahydroborates. $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ shows an interesting solid-state structure which features a bis(pyrazolyl)borate primarily acting as a monodentate ligand. Infrared data and the Cu−H bond distance support the existence of a Cu−H−B interaction. However, the bond angle data clearly suggest this to be a very weak one. To our knowledge, $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PPh_3)_2$ represents the first structurally characterized bis(pyrazolyl)borate

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compound showing the type **C** coordination mode. On the basis of the spectroscopic data, very similar coordination behavior has been suggested for $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]RuH(H_2)(PCy_3)_2$ (ν_{B-H} 2514, 2149, 2007 cm^{-1}).[12] Very recently, a tris(pyrazolyl)borate adduct ($[HB(4\text{-}Cl\text{-}3,5\text{-}(CH_3)_2Pz)_3]Rh(CO)(PMePh_2)_2$) featuring rare κ^2 *N*,*H* coordination has also been reported.[18] The main reason for unusual modes of coordination in these poly(pyrazolyl)borate systems is believed to be steric in origin.[12,18,19]

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Supporting Information Available: X-ray crystallographic files in CIF format are available free of charge via the Internet at http://pubs.acs.org.

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