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# Copper(I) complexes supported by a heavily fluorinated bis(pyrazolyl)borate: syntheses and characterization of [H₂B(3,5-(CF₃)₂Pz)₂]CuL (where L = PPh₃, N≡CCH₃, HC≡CPh, H₂C=CHPh) and {[H₂B(3,5-(CF₃)₂Pz)₂]Cu}₂(1,5-COD)

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## Abstract

The fluorinated bis(pyrazolyl)borate $[H_2B(3,5-(CF_3)_2Pz)_2]^-$ allows the isolation of thermally stable copper(I) complexes containing phosphorus and nitrogen based donors, alkyne and alkene ligands. $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(PPh_3)$, $[H_2B(3,5-(CF_3)_2-Pz)_2]Cu(NCCH_3)$ and $\{[H_2B(3,5-(CF_3)_2Pz)_2]Cu\}_2(1,5-COD)$ were synthesized by using $[H_2B(3,5-(CF_3)_2Pz)_2]K$, $CF_3SO_3Cu$, and the appropriate ligand, $PPh_3$, $NCCH_3$ or 1,5-COD. $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(HC\equiv CPh)$ and $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(H_2C=CHPh)$ were obtained by treating $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(NCCH_3)$ with phenylacetylene and styrene, respectively. X-ray data show that $[H_2B(3,5-(CF_3)_2Pz)_2]CuL$ (where L = $PPh_3$, $HC\equiv CPh$, $H_2C=CHPh$) and $\{[H_2B(3,5-(CF_3)_2Pz)_2]Cu\}_2(1,5-COD)$ have three-coordinate, trigonal planar copper sites. The bis(pyrazolyl)borate moiety adopts the common boat conformation. The $\nu_{C\equiv C}$ stretching band of $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(PhC\equiv CH)$ was observed at 1927 cm$^{-1}$. Structural and spectroscopic data of the alkene and alkyne complexes indicate minimal back-bonding from the d$^{10}$ copper(I) center.
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*Keywords:* Copper; Bis(pyrazolyl)borate; Fluorinated; Alkene; Alkyne

## 1. Introduction

Poly(pyrazolyl)borates are widely used as auxiliary ligands in coordination, organometallic and bioinorganic chemistry [1–3]. These ligands are particularly attractive because it is possible to control the steric and electronic environment about a metal center by changing the number and nature of substituents on the pyrazolyl moieties.
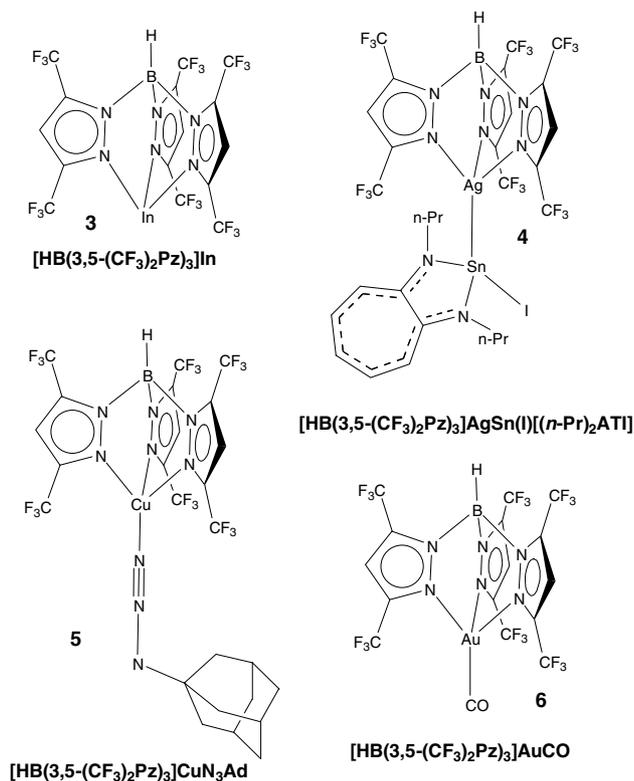
Over the past few years, we have focused our efforts on the development of weakly coordinating versions of poly(pyrazolyl)borate ligands by using inert, highly electron withdrawing, fluoroalkyl groups as substituents on the pyrazolyl rings [4–28]. For example, we have reported the synthesis of several tris(pyrazolyl)borates like $[HB(3-(CF_3),5-(Ph)Pz)_3]^-$ [27], $[HB(3-(CF_3)Pz)_3]^-$ [10], $[HB(3-(C_2F_5)Pz)_3]^-$ [7], $[HB(3-(C_3F_7)Pz)_3]^-$ [7], and $[HB(3,5-(CF_3)_2Pz)_3]^-$ (**1**) [6,10]. Fluoroalkylated tris(pyrazolyl)borates, $[HB(3-(CF_3),5-(Me)Pz)_3]^-$ and $[HB-(3-(CF_3),5-(thienyl)Pz)_3]^-$ have also been reported [29–31].

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**1**

**[HB(3,5-(CF₃)₂Pz)₃]⁻**

**2**

**[H₂B(3,5-(CF₃)₂Pz)₂]⁻**
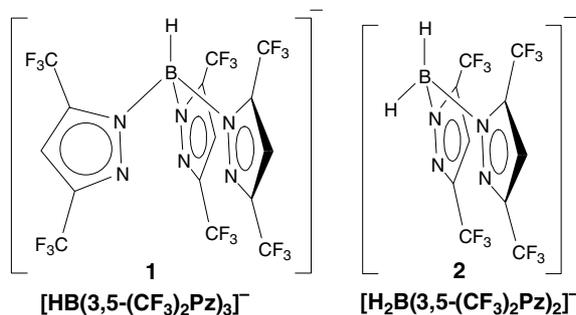
Although these fluorinated ligands are relatively new compared to the non-fluorinated tris(pyrazolyl)borates, they have already been used very successfully to investigate a wide range of topics [1–52] including catalytic C–H and C–Cl bond activation [26,28], oxidation chemistry, isolation of low valent gallium and indium compounds (e.g., **3**), [13,20] models for intermediates in silver halide metathesis (e.g., **4**) [16,21,22], and to stabilize labile or reactive species like metal-organoazide complexes (e.g., **5**) [17], silver and gold carbonyl (e.g., **6**) compounds [4,9,14], and copper and silver ethylene adducts [14,23].



**3**

**[HB(3,5-(CF₃)₂Pz)₃]In**

**4**

**[HB(3,5-(CF₃)₂Pz)₃]AgSn(I)[(*n*-Pr)₂ATI]**

**5**

**[HB(3,5-(CF₃)₂Pz)₃]CuN₃Ad**

**6**

**[HB(3,5-(CF₃)₂Pz)₃]AuCO**

Despite the interesting chemistry observed with fluorinated tris(pyrazolyl)borates, relatively little has been reported on the use of closely related bis(pyrazolyl)borates [11,12,19,24,34,38,45]. We described the

synthesis and properties of several copper(I) complexes involving the bis(pyrazolyl)borate bearing four trifluoromethyl substituents, [H₂B(3,5-(CF₃)₂Pz)₂]⁻ (**2**) [12]. These include [H₂B(3,5-(CF₃)₂Pz)₂]Cu(PPh₃)₂ [19], {[H₂B(3,5-(CF₃)₂Pz)₂]CuCNBu$^t$}₂ [11], [H₂B(3,5-(CF₃)₂-Pz)₂]Cu(2,4,6-collidine) [24] and [H₂B(3,5-(CF₃)₂Pz)₂]₂Cu [12]. The copper-collidine complex [H₂B(3,5-(CF₃)₂-Pz)₂]Cu(2,4,6-collidine) shows interesting blue luminescence [24]. [H₂B(3,5-(CF₃)₂Pz)₂]Cu(PPh₃)₂ [19] and {[H₂B(3,5-(CF₃)₂Pz)₂]CuCNBu$^t$}₂ [11] display unusual modes of coordination for bis(pyrazolyl)borate ligands.

Here, we describe the isolation of several new members of this [H₂B(3,5-(CF₃)₂Pz)₂]Cu family. In particular, we report the synthesis and characterization of [H₂B(3,5-(CF₃)₂Pz)₂]Cu complexes containing styrene, 1,5-cyclooctadiene (1,5-COD), phenylacetylene as well as the related copper(I) acetonitrile and triphenylphosphine adducts.

## 2. Experimental

### 2.1. General procedures

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques (unless noted otherwise). Solvents were purchased from commercial sources and distilled from conventional drying agents prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at room temperature on a JEOL Eclipse 500 (¹H, 500.16 MHz; ¹⁹F, 470.62 MHz; ³¹P, 202.46 MHz; ¹³C NMR, 125.78 MHz). Proton and carbon chemical shifts are reported in parts per million versus Me₄Si. ¹⁹F and ³¹P NMR chemical shifts were referenced relative to an external 85% H₃PO₄ and CFCl₃ standards, respectively. IR spectra were recorded on a JASCO FT-IR 410 spectrometer. Elemental analyses were performed at the University of Texas at Arlington using a Perkin–Elmer Model 2400 CHN analyzer. [H₂B(3,5-(CF₃)₂Pz)₂]K was prepared using the literature methods [12]. The copper(I) trifluoromethanesulfonate salt [CF₃SO₃Cu]₂ · C₆H₆ was purchased from commercial sources and used as received.

### 2.2. Synthesis of [H₂B(3,5-(CF₃)₂Pz)]Cu(PPh₃)

[H₂B(3,5-(CF₃)₂Pz)₂]K (0.50 g, 1.10 mmol) and bis(copper(I)trifluoromethanesulfonate)benzene (0.28 g, 0.56 mmol) were combined in toluene (12 mL) and stirred for 2 h at room temperature. Then, PPh₃ (0.29 g, 1.10 mmol) in toluene (10 mL) was added and the resulting mixture was stirred overnight. The solvents were removed under reduced pressure, and the resulting colorless solid was extracted into hexane, filtered over Celite, and the filtrate was collected. It was

concentrated and cooled to 25 °C to obtain crystals of [H$_2$B(3,5-(CF$_3$)$_2$Pz)]Cu(PPh$_3$) (0.75 g, 92% yield). M.p.: 124–126 °C. $^1$H NMR (C$_6$D$_6$): $\delta$ 6.28 (s, pyr-CH, 2 H); 6.97 (m, Ph, 9H); 7.48 (m, Ph, 6H); $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 106.0 (s, pyr-CH); 119.7 (q, $^1J_{CF}$ = 271 Hz, CF$_3$); 120.5 (q, $^1J_{CF}$ = 269 Hz, CF$_3$); 129.0 (d, $^3J_{CP}$ = 10 Hz, C$_m$); 130.6 (s, C$_p$); 131.3 (d, $^1J_{CP}$ = 42 Hz, C$_i$); 133.6 (d, $^2J_{CP}$ = 15 Hz, C$_o$);139.0 (q, $^2J_{CF}$ = 41 Hz, CCF$_3$); 141.6 (q, $^2J_{CF}$ = 38 Hz, CCF$_3$); $^{19}$F NMR (C$_6$D$_6$): $\delta$ −60.5, −58.7; $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 3.37 (s); IR (Nujol), cm$^{-1}$: 3162, 2547, 2381, 1547, 1498, 1462, 1377, 1264, 1044, 995, 895, 824, 769, 741, 721, 692, 666. Anal. Calc. for C$_{28}$H$_{19}$BF$_{12}$N$_4$PCu: C, 45.16; H, 2.57; N, 7.52. Found: C, 45.56; H, 2.61; N, 7.41%.

## 2.3. Synthesis of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(NCCH$_3$)

Bis(copper(I) trifluoromethanesulfonate) benzene (0.56 g, 1.11 mmol) and [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]K (1.01 g, 2.20 mmol) were combined in toluene (25 mL) and stirred for 15 min. Dry acetonitrile (0.47 g, 11.4 mmol) was added to this mixture and the solution was heated to 80 °C. This temperature was maintained for 1 h. The mixture was filtered through Celite and the toluene removed under reduced pressure to obtain [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(NCCH$_3$) as a pale yellow solid, 1.05 g, 91% yield. M.p.: 109–115 °C. $^1$H NMR (C$_6$D$_6$): $\delta$ 0.33 (s, CH$_3$, 3H), 6.37 (s, pyr-CH, 2H). $^{13}$C{$^1$H}NMR (C$_6$D$_6$): $\delta$ 1.54 (s, CH$_3$), 106.1 (s, pyr-CH), 116.8 (s, CN), 120.2 (q, $^1J_{CF}$ = 270 Hz, CF$_3$), 121.2 (q, $^1J_{CF}$ = 269 Hz, CF$_3$), 139.4 (q, $^2J_{CF}$ = 42 Hz, CCF$_3$), 141.8 (q, $^2J_{CF}$ = 39 Hz, CCF$_3$). $^{19}$F NMR (C$_6$D$_6$): $\delta$ −59.3, −61.2. IR (Nujol, cm$^{-1}$): 3160, 2528, 2411, 2356, 2324, 2195, 1645, 1555, 1500, 1266, 1044, 997, 889, 830, 768, 738, 719, 661, 615. Anal. Calc. for C$_{12}$H$_7$BF$_{12}$N$_5$Cu: C, 27.53; H, 1.35; N, 13.38. Found: C, 27.40; H, 0.95; N, 13.25%.

## 2.4. Synthesis of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhC≡CH)

Phenylacetylene (0.10 g, 0.98 mmol) in methylene chloride (30 mL) was added to [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(NCCH$_3$) (0.20 g, 0.38 mmol) in dichloromethane (30 mL) and stirred for 30 min at room temperature. The solvent was removed under reduced pressure to obtain [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhC≡CH) as a pale yellow solid. It was recrystallized from toluene/hexane mixture at −25 °C to obtain colorless crystals. 77% yield. M.p.: 62–66 °C. $^1$H NMR (C$_6$D$_6$): $\delta$ 4.60 (s, C≡CH, 1H), 6.19 (s, pyr-CH, 2H), 6.8–7.2 (m, Ph-H, 5H). $^{13}$C{$^1$H}NMR (C$_6$D$_6$): $\delta$ 79.2 (s, C≡CH), 95.4 (s, C≡CH), 106.5 (s, pyr-CH), 119.8 (q, $^1J_{CF}$ = 271 Hz, CF$_3$), 120.2 (q, $^1J_{CF}$ = 270 Hz, CF$_3$), 121.8 (s, C–C≡C), 128.8 (s, Ph), 130.2 (s, Ph), 131.6 (s, Ph), 139.8 (q, $^2J_{CF}$ = 42 Hz, CCF$_3$), 141.9

(q, $^2J_{CF}$ = 42 Hz, CCF$_3$). $^{19}$F NMR (C$_6$D$_6$): $\delta$−59.5, −61.3. IR (Nujol, cm$^{-1}$): 3218, 2558, 2401, 1927 ($\nu_{C≡C}$), 1550, 1498, 1397, 1265, 1154, 1100, 1047, 999, 925, 909, 894, 832, 803, 768, 756, 736, 720, 691, 669, 651, 627, 551, 526. Anal. Calc. for C$_{18}$H$_{10}$BF$_{12}$N$_4$Cu: C, 36.98; H, 1.72; N, 9.58. Found: C, 37.30; H, 1.59; N, 8.98%.

## 2.5. Synthesis of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu-(PhCH= CH$_2$)]

[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(NCCH$_3$)] (1.26 g, 2.40 mmol) and styrene (1.25 g, 12.0 mmol) were dissolved in diethyl ether (20 mL) and stirred for 9 h at room temperature. The solvent was removed under vacuum, to obtain the product as a white powder. X-ray quality crystals were grown from hexane at −25 °C. 84% yield. M.p.: 78.79 °C. $^1$H NMR (C$_6$D$_6$): $\delta$ 4.25 (d, H$_A$, $^3J_{HH}$ = 10 Hz, 1H), 4.58 (d, H$_B$, $^3J_{HH}$ = 16 Hz, 1H), 5.98 (dd, H$_X$, $^3J_{HH}$ = 16 Hz, $^3J_{HH}$ = 10 Hz, 1H), 6.15 (s, pyr-CH, 2H); 6.86 (m, Ph-H, 1H), 6.92 (m, Ph-H, 2H), 7.09 (m, Ph-H, 2H). $^1$H NMR (CDCl$_3$): $\delta$ 4.61 (d, H$_A$, $^3J_{HH}$ = 10 Hz, 1H), 4.98 (d, H$_B$, $^3J_{HH}$ = 16 Hz, 1H), 6.33 (dd, H$_X$, $^3J_{HH}$ = 16 Hz, $^3J_{HH}$ = 10 Hz, 1H), 6.83 (s, pyr-CH, 2H); 7.27 (m, Ph-H, 3H), 7.38 (m, Ph-H, 2H). $^{13}$C{$^1$H}NMR (CDCl$_3$): $\delta$ 76 (br), 105 (br), 106.1 (s, pyr-CH), 119.0 (q, $^1J_{CF}$ = 270 Hz, CF$_3$), 120.1 (q, $^1J_{CF}$ = 269 Hz, CF$_3$), 126.4, 129.0, 129.2, 135.2, 139.4 (q, $^2J_{CF}$ = 41 Hz, CCF$_3$), 141.8 (q, $^2J_{CF}$ = 39 Hz, CCF$_3$). $^{19}$F NMR (C$_6$D$_6$): $\delta$−59.1, −60.2. $^{19}$F NMR (CDCl$_3$): $\delta$−59.5, −60.5. $^{11}$B NMR (CDCl$_3$): $\delta$−9.3. IR (Nujol, cm$^{-1}$): 2539, 2424, 1655, 1631, 1545, 1488, 1396, 1277, 1137, 1087, 1054, 986, 887, 825, 773. Anal. Calc. for C$_{18}$H$_{12}$BF$_{12}$N$_4$Cu: C, 36.85; H, 2.06; N, 9.55. Found: C, 37.31; H, 2.42; N, 9.41%.

## 2.6. Synthesis of {[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu}$_2$-(1,5-COD)

[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]K (0.10 g, 0.218 mmol) and bis(copper(I) trifluoromethanesulfonate)benzene (0.11 g, 0.11 mmol) were combined in tetrahydrofuran. 1,5-cyclooctadiene (0.02 g, 0.22 mmol) was added drop-wise to this solution and the resulting mixture was stirred overnight. Solvents were removed under reduced pressure and the product was extracted into toluene. After filtration through Celite, the toluene was removed to obtain a light yellow solid (0.11 g, 85%). X-ray quality crystals were grown from toluene at −25 °C. 85% yield. M.p.: 150–155 °C. $^1$H NMR (C$_6$D$_6$): $\delta$ 1.69 (br s, CH$_2$, 8H), 5.01 (br s, CH=CH, 4H), 6.25 (s, pyr-CH, 4H). IR (Nujol, cm$^{-1}$): 3159, 2925, 2544, 2419, 1662, 1643, 1553, 1498, 1459, 1401, 1376, 1267, 1140, 1097, 1046, 998, 892, 830, 820, 768. Anal. Calc. for C$_{28}$H$_{20}$B$_2$F$_{24}$N$_8$Cu$_2$·C$_7$H$_8$: C, 36.07; H, 2.42; N, 9.62. Found: C, 35.01; H, 2.19; N, 9.74%.

## 2.7. X-ray structure determination

The X-ray intensity data for [$H_2B$ (3,5-($CF_3$)$_2$Pz)$_2$]Cu(PPh$_3$) and [$H_2B$(3,5-($CF_3$)$_2$Pz)$_2$] Cu(PhCH=CH$_2$) · 0.5 hexane were measured on a Bruker SMART APEX CCD area detector system equipped with an Oxford Cryosystems 700 Series Cryostream cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube ($\lambda = 0.710\ 73$ Å). The detector was placed at a distance of 5.995 cm from the crystal. The data frames were integrated with the Bruker SAINT-PLUS software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Data collections for [$H_2B$(3,5-($CF_3$)$_2$Pz)$_2$]Cu(PhC≡CH) and {[$H_2B$(3,5-($CF_3$)$_2$Pz)$_2$]Cu}$_2$(1,5-COD) · $C_7H_8$ were carried out on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). All the structures were solved and refined using the Bruker SHELXTL software package. Some details of data collection and refinements are given in Table 1. Selected bond distances and angles are given in Tables 2–5.

## 3. Results and discussion

The copper(I) phosphine complex [$H_2B$(3,5-($CF_3$)$_2$Pz)$_2$]Cu(PPh$_3$) **7** was synthesized by treating the product obtained from a mixture of [$H_2B$(3,5-($CF_3$)$_2$Pz)$_2$]K and $CF_3SO_3$Cu with PPh$_3$. It was isolated as an air stable, colorless solid. Elemental analysis data indicate the formation of a monophosphine adduct. The $^{31}$P{$^1$H} NMR spectrum shows a singlet at δ 3.37. We

previously reported the synthesis of a copper phosphine complex [$H_2B$(3,5-($CF_3$)$_2$Pz)$_2$]Cu(PPh$_3$)$_2$ **8** using (PPh$_3$)$_2$-CuBH$_4$ and 3,5-($CF_3$)$_2$PzH [19]. It has two PPh$_3$ ligands on the copper center, which is the type of product more

Table 2

Selected bond distances (Å) and bond angles (deg) for [$H_2B$(3,5-($CF_3$)$_2$Pz)$_2$]Cu(PPh$_3$)

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| Cu(1)–N(2) | 2.026(2) | Cu(2)–N(6) | 2.021(2) |
| Cu(1)–N(4) | 2.031(2) | Cu(2)–N(8) | 2.025(2) |
| Cu(1)–P(1) | 2.1754(8) | Cu(2)–P(2) | 2.1751(8) |
| P(1)–C(23) | 1.821(3) | P(2)–C(44) | 1.820(3) |
| P(1)–C(17) | 1.829(3) | P(2)–C(50) | 1.827(3) |
| P(1)–C(11) | 1.831(3) | P(2)–C(38) | 1.831(3) |
| N(2)–C(1) | 1.340(4) | N(6)–C(29) | 1.340(4) |
| N(2)–N(1) | 1.359(3) | N(6)–N(5) | 1.359(3) |
| N(4)–C(6) | 1.333(4) | N(8)–C(33) | 1.341(4) |
| N(4)–N(3) | 1.364(3) | N(8)–N(7) | 1.351(3) |
| N(1)–B(1) | 1.562(4) | B(2)–N(5) | 1.568(4) |
| N(3)–B(1) | 1.568(4) | B(2)–N(7) | 1.570(4) |
| | | | |
| N(2)–Cu(1)–N(4) | 94.27(9) | N(6)–Cu(2)–N(8) | 93.56(9) |
| N(2)–Cu(1)–P(1) | 129.47(7) | N(6)–Cu(2)–P(2) | 135.89(7) |
| N(4)–Cu(1)–P(1) | 135.46(7) | N(8)–Cu(2)–P(2) | 129.86(7) |
| C(23)–P(1)–C(17) | 105.33(13) | C(44)–P(2)–C(50) | 105.10(13) |
| C(23)–P(1)–C(11) | 101.31(13) | C(44)–P(2)–C(38) | 104.25(13) |
| C(17)–P(1)–C(11) | 104.50(13) | C(50)–P(2)–C(38) | 101.13(13) |
| C(23)–P(1)–Cu(1) | 113.88(10) | C(44)–P(2)–Cu(2) | 115.68(9) |
| C(17)–P(1)–Cu(1) | 115.47(9) | C(50)–P(2)–Cu(2) | 114.05(10) |
| C(11)–P(1)–Cu(1) | 114.83(10) | C(38)–P(2)–Cu(2) | 115.02(9) |
| C(1)–N(2)–Cu(1) | 138.1(2) | C(29)–N(6)–Cu(2) | 138.2(2) |
| N(1)–N(2)–Cu(1) | 114.43(17) | N(5)–N(6)–Cu(2) | 115.31(17) |
| C(6)–N(4)–Cu(1) | 138.9(2) | C(33)–N(8)–Cu(2) | 136.9(2) |
| N(3)–N(4)–Cu(1) | 114.45(17) | N(7)–N(8)–Cu(2) | 115.48(17) |
| N(2)–N(1)–B(1) | 118.2(2) | N(8)–N(7)–B(2) | 117.8(2) |
| N(4)–N(3)–B(1) | 118.4(2) | N(6)–N(5)–B(2) | 118.5(2) |

Table 1

X-ray crystallographic data and structure refinement for LCu(PPh$_3$), LCu(PhC≡CH), LCu(PhCH=CH$_2$) · 0.5 hexane, and {LCu}$_2$(1,5-COD) · $C_7H_8$ (where L = [$H_2B$(3,5-($CF_3$)$_2$Pz)$_2$])

| | LCu(PPh$_3$) | LCu(PhCH=CH$_2$) · 0.5 hexane | {LCu}$_2$(1,5-COD) · $C_7H_8$ | LCu(PhC≡CH) |
|---|---|---|---|---|
| Empirical formula | $C_{28}H_{19}BCuF_{12}N_4P$ | $C_{21}H_{19}BCuF_{12}N_4$ | $C_{35}H_{28}B_2Cu_2F_{24}N_8$ | $C_{18}H_{10}BCuF_{12}N_4$ |
| Formula weight | 744.79 | 629.75 | 1165.35 | 584.65 |
| Temperature (K) | 100(2) | 100(2) | 187(2) | 298(2) |
| Crystal system | Triclinic | Triclinic | Triclinic | Monocinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2(1)/c$ |
| *Unit cell dimensions* | | | | |
| *a* (Å) | 9.8842(14) | 9.171(6) | 9.6634(13) | 8.7233(17) |
| *b* (Å) | 9.9086(14) | 10.739(7) | 13.8053(18) | 30.443(8) |
| *c* (Å) | 30.695(5) | 13.737(9) | 18.169(3) | 9.225(2) |
| α (°) | 80.922(2) | 84.602(7) | 91.405(11) | 90 |
| β (°) | 85.514(2) | 83.473(7) | 100.899(11) | 113.594(15) |
| γ (°) | 89.743(2) | 67.565(6) | 106.598(10) | 90 |
| *V* (Å$^3$) | 2959.4(7) | 1240.5(13) | 2273.0(6) | 2245.1(9) |
| *Z* | 4 | 2 | 2 | 4 |
| $D_{calc}$ (mg/m$^3$) | 1.672 | 1.686 | 1.703 | 1.730 |
| Absorption coefficient (mm$^{-1}$) | 0.896 | 0.989 | 1.072 | 1.086 |
| Goodness-of-fit on $F_2$ | 1.003 | 1.014 | 1.046 | 1.034 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0439, 0.0955 | 0.0473, 0.1291 | 0.0326, 0.0766 | 0.0334, 0.0761 |
| $R_1$, $wR_2$ (all data) | 0.0623, 0.1054 | 0.0564, 0.1368 | 0.0413, 0.0808 | 0.0497, 0.0839 |

Table 3
Selected bond distances (Å) and bond angles (°) for [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhC≡CH)

| | | | |
|---|---|---|---|
| Cu–C(1) | 1.936(4) | C(1)–Cu–N(22) | 112.12(18) |
| Cu–N(22) | 1.989(3) | C(1)–Cu–N(12) | 153.37(18) |
| Cu–N(12) | 1.991(3) | N(22)–Cu–N(12) | 94.16(11) |
| Cu–C(2) | 2.003(4) | C(1)–Cu–C(2) | 35.56(18) |
| N(11)–N(12) | 1.350(4) | N(22)–Cu–C(2) | 147.53(14) |
| N(11)–C(15) | 1.353(4) | N(12)–Cu–C(2) | 117.89(14) |
| N(11)–B | 1.575(5) | N(11)–N(12)–Cu | 114.84(19) |
| N(12)–C(13) | 1.338(4) | N(21)–N(22)–Cu | 115.18(19) |
| N(21)–C(25) | 1.344(4) | C(2)–C(1)–Cu | 75.2(3) |
| N(21)–N(22) | 1.355(4) | C(2)–C(1)–H(1) | 165(3) |
| N(21)–B | 1.582(5) | Cu–C(1)–H(1) | 120(3) |
| N(22)–C(23) | 1.338(4) | C(1)–C(2)–C(3) | 163.5(4) |
| C(1)–C(2) | 1.205(6) | C(1)–C(2)–Cu | 69.2(3) |
| C(1)–H(1) | 0.84(4) | C(3)–C(2)–Cu | 127.3(3) |
| C(2)–C(3) | 1.444(6) | | |

Table 4
Selected bond distances (Å) and bond angles (°) for [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhCH=CH$_2$)

| | | | |
|---|---|---|---|
| Cu–N(4) | 1.993(3) | N(4)–Cu–N(2) | 93.14(11) |
| Cu–N(2) | 2.000(3) | N(4)–Cu–C(11) | 111.08(13) |
| Cu–C(11) | 2.020(3) | N(2)–Cu–C(12) | 116.39(12) |
| Cu–C(12) | 2.055(3) | C(11)–Cu–C(12) | 39.21(13) |
| N(1)–N(2) | 1.356(4) | N(1)–N(2)–Cu | 115.49(18) |
| N(2)–C(1) | 1.339(4) | N(3)–N(4)–Cu | 116.47(19) |
| N(3)–N(4) | 1.352(4) | C(11)–C(12)–Cu | 69.04(19) |
| N(4)–C(6) | 1.339(4) | C(13)–C(12)–Cu | 109.4(2) |
| C(13)–C(12) | 1.484(5) | C(13)–C(12)–H(3) | 113(2) |
| C(12)–C(11) | 1.368(5) | Cu–C(12)–H(3) | 104(2) |
| C(12)–H(3) | 0.94(3) | C(12)–C(11)–Cu | 71.75(19) |
| C(11)–H(4) | 0.96(4) | Cu–C(11)–H(4) | 107(2) |
| C(11)–H(5) | 0.96(4) | Cu–C(11)–H(5) | 100(2) |
| | | H(4)–C(11)–H(5) | 117(3) |

Table 5
Selected bond distances (Å) and bond angles (°) for {[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu}$_2$(1,5-COD)

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| Cu(1)–N(22) | 1.989(3) | Cu(2)–N(32) | 1.985(2) |
| Cu(1)–N(12) | 1.994(3) | Cu(2)–N(42) | 1.989(3) |
| Cu(1)–C(3) | 2.021(3) | Cu(2)–C(2′) | 2.023(3) |
| Cu(1)–C(2) | 2.030(3) | Cu(2)–C(3′) | 2.025(3) |
| N(11)–N(12) | 1.355(4) | N(31)–N(32) | 1.355(3) |
| N(11)–B(1) | 1.566(5) | N(31)–B(2) | 1.578(5) |
| N(21)–C(25) | 1.351(4) | N(41)–C(45) | 1.351(4) |
| N(21)–N(22) | 1.357(4) | N(41)–N(42) | 1.576(5) |
| N(21)–B(1) | 1.580(5) | N(41)–B(2) | 1.576(5) |
| N(22)–C(23) | 1.331(4) | N(42)–C(43) | 1.329(4) |
| C(1)–C(2) | 1.515(5) | C(1′)–C(2′) | 1.509(4) |
| C(1)–C(4A) | 1.552(5) | C(1′)–C(4′B) | 1.544(4) |
| C(2)–C(3) | 1.370(4) | C(2′)–C(3′) | 1.374(4) |
| C(3)–C(4) | 1.516(5) | C(3′)–C(4′) | 1.510(4) |
| C(4)–C(1A) | 1.552(5) | C(4′)–C(1′B) | 1.544(4) |
| | | | |
| N(22)–Cu(1)–N(12) | 94.50(11) | N(32)–Cu(2)–N(42) | 94.47(10) |
| N(22)–Cu(1)–C(3) | 153.19(12) | N(32)–Cu(2)–C(2′) | 113.14(12) |
| N(12)–Cu(1)–C(3) | 111.98(12) | N(42)–Cu(2)–C(2′) | 151.20(11) |
| N(22)–Cu(1)–C(2) | 113.76(12) | N(32)–Cu(2)–C(3′) | 152.72(12) |
| N(12)–Cu(1)–C(2) | 151.42(12) | N(42)–Cu(2)–C(3′) | 112.11(11) |
| C(3)–Cu(1)–C(2) | 39.54(13) | C(2′)–Cu(2)–C(3′) | 39.69(12) |
| N(12)–N(11)–C(15) | 108.5(3) | N(32)–N(31)–C(35) | 108.6(2) |
| N(12)–N(11)–B(1) | 118.0(3) | N(32)–N(31)–B(2) | 118.2(2) |
| N(11)–N(12)–Cu(1) | 115.79(19) | N(31)–N(32)–Cu(2) | 115.88(18) |
| C(3)–C(2)–C(1) | 126.0(3) | C(3′)–C(2′)–C(1′) | 125.4(3) |
| C(3)–C(2)–Cu(1) | 69.87(19) | C(3′)–C(2′)–Cu(2) | 70.22(17) |
| C(1)–C(2)–Cu(1) | 113.1(2) | C(1′)–C(2′)–Cu(2) | 111.1(2) |
| C(2)–C(3)–C(4) | 125.5(3) | C(2′)–C(3′)–C(4′) | 125.6(3) |
| C(2)–C(3)–Cu(1) | 70.59(18) | C(2′)–C(3′)–Cu(2) | 70.08(17) |
| C(4)–C(3)–Cu(1) | 112.3(2) | C(4′)–C(3′)–Cu(2) | 111.1(2) |

commonly observed (rather than 1:1 Cu:PPh$_3$ as in **7**) when bis(pyrazolyl)boratocopper moieties react with PPh$_3$ ligands, e.g. [H$_2$B(Pz)$_2$]Cu(PPh$_3$)$_2$ **9** [53].
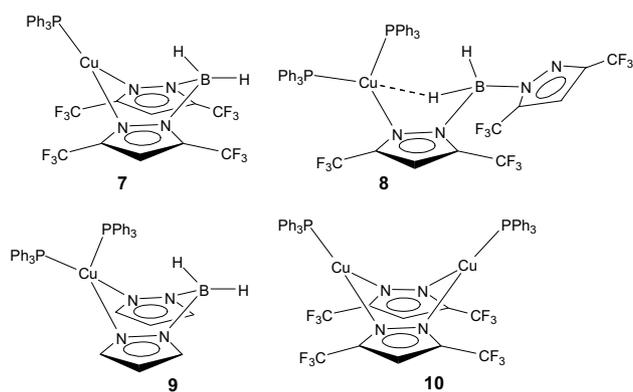


Fig. 1 depicts the X-ray crystal structure of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PPh$_3$). It crystallizes in the $P\bar{1}$ space group with two chemically similar but crystallographically different molecules in the asymmetric unit. The copper centers adopt a distorted trigonal planar geometry. The average Cu–P distance of 2.1753(8) Å observed for [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PPh$_3$) is shorter than the corresponding bond lengths observed for the three-coordinate bis(phosphine) adduct [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]-Cu(PPh$_3$)$_2$ (2.2388(7), 2.2690(7) Å) [19], but similar to those found in the copper(I) pyrazolate {[μ-{3,5-(CF$_3$)$_2$Pz}]Cu(PPh$_3$)}$_2$ (**10**) (Cu–P = 2.181(1), 2.175(1) Å) [54]. Both [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PPh$_3$) (**7**) and {[μ-{3,5-(CF$_3$)$_2$Pz}]Cu(PPh$_3$)}$_2$(**10**) have copper centers bonded to N,N,P-donors. Therefore, the similarity is not surprising. The longer Cu–P distance in [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PPh$_3$)$_2$ may be a result of steric effects. It features P,P,N-donors at copper (see **8**). X-ray crystallographic data of the non-fluorinated system [H$_2$B(Pz)$_2$]Cu(PMePh$_2$)$_2$ have been reported (Cu–P = 2.2480(5), 2.2730(5) Å). It is a four coordinate copper complex and has a tetrahedral copper site [53,55].

The related copper acetonitrile adduct [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(NCCH$_3$) could be prepared from [H$_2$B-(3,5-(CF$_3$)$_2$Pz)$_2$]K, CF$_3$SO$_3$Cu and CH$_3$CN. Elemental analysis data and the $^1$H NMR spectrum indicate the formation of 1:1 Cu/NCCH$_3$ adduct. The signal corresponding to the nitrile carbon appears at 116.8 ppm in
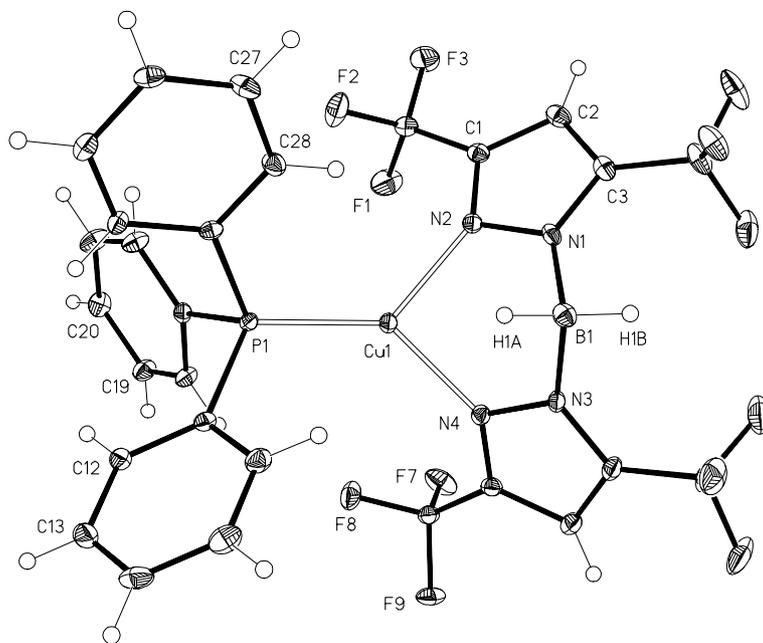
Fig. 1. Molecular structure of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PPh$_3$).

the $^{13}$C{$^1$H} NMR spectrum. This value is very close to those observed for the fluorinated tris(pyrazolyl)borate complex [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Cu(NCCH$_3$) (114.9 ppm) [56] and free acetonitrile (116.9 ppm). Thus far, we have not been able to obtain X-ray quality crystals of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(NCCH$_3$). It serves as a good precursor for the synthesis of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu adducts like [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhC≡CH) and [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhCH=CH$_2$) (vide infra).

The copper(I) alkyne complex [H$_2$B(3,5-(CF$_3$)$_2$-Pz)$_2$]Cu(PhC≡CH) was obtained by the treatment of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(NCCH$_3$) with phenylacetylene. Such compounds are of interest, because they serve as models for intermediates in copper mediated activation of C$_{sp}$–H bonds of terminal alkynes and for other processes involving copper catalysts and alkynes [57–64]. Structurally characterized copper complexes of terminal alkynes are also rare [65–69].

The $^1$H NMR spectrum of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]-Cu(PhC≡CH) displayed a resonance at δ 4.60 due to alkyne proton of the coordinated phenylacetylene (cf. free ligand at 3.05 ppm) [70]. The $^{13}$C NMR spectrum exhibited resonances at δ 79.2 and 95.4 which correspond to the H–*C* and *C*–Ph carbons of the alkyne unit. The corresponding resonances of the free ligand were observed at δ 77.6 and 83.9, respectively [70]. For comparison, the $^{13}$C signal for H–*C* in [(phen)Cu(HC≡CPh)]ClO$_4$ (phen = 1,10-phenanthroline) appears at δ 79.7 [66]. The IR data provide very useful information about the metal–alkyne interaction. The $v_{C≡C}$ stretching band of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhC≡CH) was observed at 1927 cm$^{-1}$. This value is about 183 cm$^{-1}$ lower than the $v_{C≡C}$ band for free HC≡CPh ligand (2110 cm$^{-1}$).

Compounds [(phen)Cu(HC≡CPh)]ClO$_4$ and ClCu-(HC≡CPh) represent two structurally characterized Cu(I) phenylacetylene complexes [65,66]. They show $v_{C≡C}$ bands at 1921 and 1977 cm$^{-1}$, respectively. These values are consistent with the $v_{C≡C}$ observed for the [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhC≡CH).

The X-ray crystal structure of [H$_2$B(3,5-(CF$_3$)$_2$-Pz)$_2$]Cu(PhC≡CH) is depicted in Fig. 2. The hydrogen atom on the alkyne was located from the difference map during refinement. The copper center adopts a trigonal planar geometry. The phenylacetylene coordinates to the cooper in an η$^2$-fashion with slightly different Cu–C distances of 1.936(4) and 2.003(4) Å. Similar asymmetric bonding of HC≡CPh to Cu(I) has been observed in other copper(I) systems. For example, the Cu–C separations in ClCu(HC≡CPh) and [(phen)Cu(HC≡CPh)]ClO$_4$ are 1.999(4), 2.066(3) Å, and 1.922(12), 1.995(10) Å, respectively [65,66]. The C≡C–C angle of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhC≡CH) is 163.5(4)°. This corresponds to only about 16.5(4)° bending-back angle (i.e., deviation from 180°).

There is a good linear relationship between Δ$v_{C≡C}$ (Δ$v = v_{free} - v_{complex}$) and the bending-back angle of transition metal–alkyne complexes [66,71]. Smaller Δ$v_{C≡C}$ values generally correspond to smaller bending-back angles. For example, Δ$v_{C≡C}$ of 69 cm$^{-1}$ observed for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh) is in excellent agreement with the relatively small bending-back angle of 6.7° [14]. Copper adducts like ClCu(HC≡CPh) (Δ$v_{C≡C}$ = 133 cm$^{-1}$, bending-back angle = 17.1(3)°) and [(phen)Cu(HC≡CPh)]ClO$_4$ (Δ$v_{C≡C}$ = 195 cm$^{-1}$, bending-back angle = 17.2(12)°) show Δ$v_{C≡C}$ and bending-back angle values similar to that seen for [H$_2$B(3,5-

Fig. 2. Molecular structure of [H₂B(3,5(CF₃)₂Pz)₂]Cu(PhC≡CH).

$[H_2B(3,5-(CF_3)_2Pz)_2]Cu(PhCH=CH_2)$ are also consistent with the other structurally characterized Cu(I) styrene adducts. The reported Cu–C and C=C bond distances of copper(I) styrene complexes are in the range 1.966–2.054 and 1.342–1.386 Å, respectively [73,74]. The alkene bond distance of the free styrene for comparison is 1.3245(16) Å [81]. The dihedral angle between the Cu, C11, C12, plane and C11, C12, C13 plane is 80.9°, which indicates that relative to the ideal orthogonal arrangement, the phenyl group bends back about 9.1°.

The room temperature $^1H$ NMR spectrum of $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(PhCH=CH_2)$ in CDCl₃ shows that signals due to CH₂=CH-protons appear at 4.61, 4.98, and 6.33 ppm (same signals in $C_6D_6$ appear at 4.25, 4.58, 5.98 ppm). Comparison to the corresponding resonances of the free ligand (room temperature data of $CH_2=CHPh$ in CDCl₃: 5.26, 5.77, and 6.74 ppm) shows that these signals have been shifted to a lower frequency (shows an upfield shift) upon coordination to copper(I).
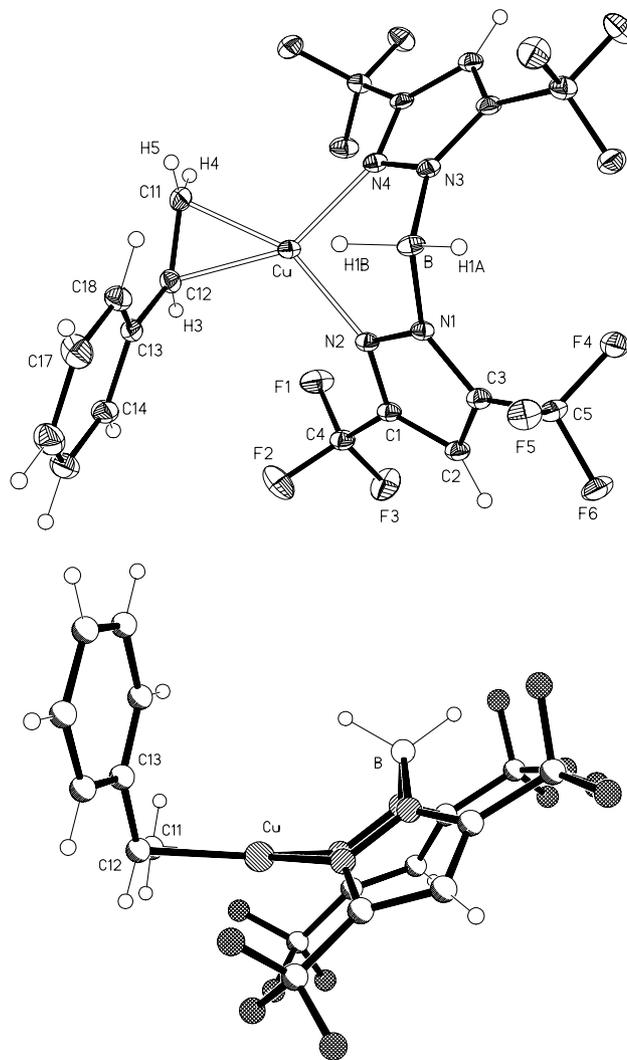
(CF₃)₂Pz)₂]Cu(PhC≡CH) [65,66]. On the other hand, alkyne complexes of low valent metals like Pt, Ni, Ir, and W generally show large $\Delta v_{C\equiv C}$ (410–540 cm$^{-1}$) and large bending-back angles (30–40° range) [66,71]. The $\Delta v_{C\equiv C}$ and bending-back angle provides valuable information about the extent of metal-to-alkyne backbonding in these molecules.

Copper(I) olefin complexes are also of interest for a variety of reasons [23,72–78]. For example, they serve as models for copper(I) based ethylene receptor sites in plants [79,80] and resting state of the catalyst in copper catalyzed cyclopropanation reactions of olefins [72]. Most alkene (in particular ethylene) complexes of copper are quite labile [23]. Considering the successes we had with fluorinated tris(pyrazolyl)borates like $[HB(3,5-(CF_3)_2Pz)_3]^-$ and $[HB(3-(CF_3)Pz)_3]^-$ in copper(I) olefin chemistry (e.g., $[HB(3,5-(CF_3)_2Pz)_3]Cu-(CH_2=CH_2)$ is a thermally stable solid) [23], we set out to explore the use of the fluorinated bis(pyrazolyl)borate analogs in this field.

$[H_2B(3,5-(CF_3)_2Pz)_2]Cu(PhCH=CH_2)$ could be synthesized by treating $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(NCCH_3)$ with styrene. It was isolated as colorless crystals from hexane. Crystal structure of $[H_2B(3,5-(CF_3)_2Pz)_2]Cu-(PhCH=CH_2)$ is shown in Fig. 3. It crystallizes with half a molecule of hexane in the asymmetric unit. The copper center has a trigonal planar geometry. The styrene coordinates to the copper center in an $\eta^2$-fashion. The Cu–C distances of 2.020(3) and 2.055(3) Å are slightly longer than the Cu–C distances of the phenylacetylene analog $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(PhC\equiv CH)$ (1.936(4), 2.003(4) Å). The C=C and C≡C distances of the two adducts are 1.368(5) and 1.205(6) Å, respectively. These bond lengths follow the expected trends. The X-ray data of



Fig. 3. Two views of the molecular structure of [H₂B(3,5-(CF₃)₂Pz)₂]-Cu(PhCH=CH₂).

Copper(I)–styrene complexes bearing relatively electron-rich ligands (e.g., [HC{MeC(2,6-Me$_2$C$_6$H$_3$)N}$_2$]Cu-(PhCH=CH$_2$)) exhibit a much greater shift towards lower frequency (e.g., 3.00, 3.30, 4.47 ppm in C$_6$D$_6$) [74].

We could not observe the peaks corresponding to the olefin moiety in the proton coupled $^{13}$C NMR spectrum of [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(PhCH=CH$_2$) taken at room temperature. However, the $^{13}$C{$^1$H} NMR spectrum displayed two broad peaks at 105 and 76 ppm (all the other signals were sharp). These could be the signals resulting from olefin carbons. For comparison, Ph*CH*=*C*H$_2$ resonances of the free ligand and [HC{MeC(2,6-Me$_2$C$_6$H$_3$)N}$_2$]Cu(PhCH=CH$_2$) appear at 137.0, 113.2 ppm and 92.39, 67.08 ppm, respectively [74,82]. Overall, only a small change in C=C bond length and the relatively small shift of $^1$H NMR signals upon coordination to Cu(I) indicate minimal back-bonding between the d$^{10}$ copper(I) center and styrene.

The 1,5-cyclooctadiene (1,5-COD) adduct of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Cu was prepared by using [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]K, CF$_3$SO$_3$Cu, and 1,5-COD. Interestingly, 1,5-COD forms a product in which the cyclooctadiene ligand acts as a bridge between two [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu units. The room temperature $^1$H NMR spectrum of {[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu}$_2$(1,5-COD) shows broad peaks for 1,5-COD protons. This suggests the presence of a fairly labile Cu–COD interaction or the existence of copper complexes with different and interconverting COD conformations in solution at room temperature. Broad peaks for the COD moiety have been observed in several Cu(I)-(1,5-COD) systems, e.g., (CF$_3$CO$_2$Cu)$_2$(1,5-COD) and (hexafluoroacetylacetonate)Cu(1,5-COD) [83,84].

{[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu}$_2$(1,5-COD) crystallizes in the P$\bar{1}$ space group (Fig. 4). The copper adduct lies on an inversion center. The olefin moieties of the 1,5-COD coordinate to copper atoms in an η$^2$-fashion. The average C=C distance of 1.372(4) Å is essentially identical to the corresponding bond length in the styrene adduct. The COD ring in {[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu}$_2$-
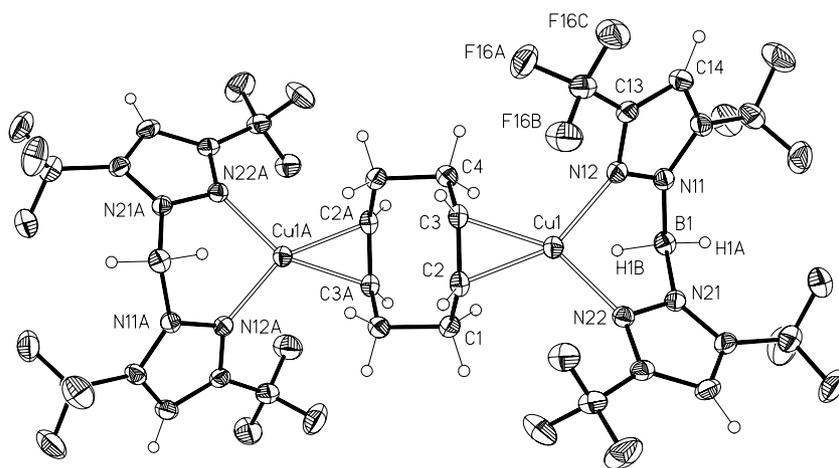


Fig. 4. Molecular structure of {[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu}$_2$(1,5-COD).
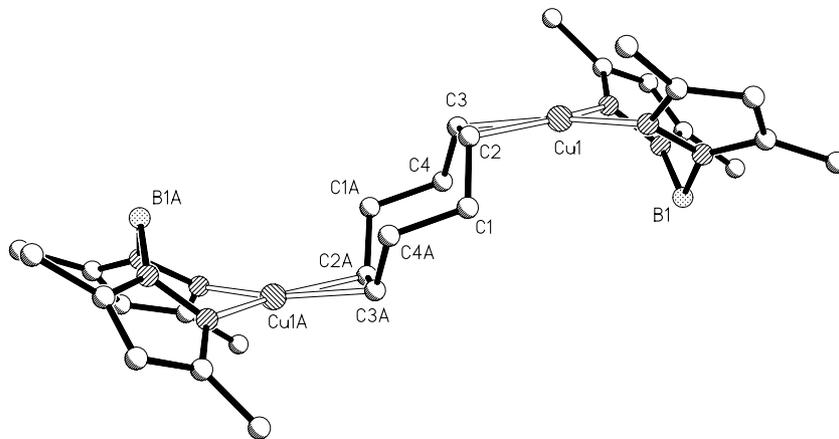


Fig. 5. Molecular structure of {[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu}$_2$(1,5-COD) showing the 1,5-COD ring chair conformation and the bis(pyrazolyl)borate ligand boat conformation; hydrogen and fluorine atoms have been omitted for clarity.

(1,5-COD) adopts a chair conformation (Fig. 5). In contrast, chelating COD ligands and boat conformations are more common in copper(I)-1,5-COD chemistry [84–86].

Overall, here, we describe the successful utility of a highly fluorinated bis(pyrazolyl)borate in copper(I) coordination chemistry. $[H_2B(3,5-(CF_3)_2Pz)_2]^-$ allows the isolation of thermally stable Cu(I) complexes of P, N, alkyne, and alkene donors. $[H_2B(3,5-(CF_3)_2Pz)_2]$-CuL (where L = $PPh_3$, $HC{\equiv}CPh$, $H_2C{=}CHPh$) and $\{[H_2B(3,5-(CF_3)_2Pz)_2]Cu\}_2(1,5-COD)$ feature three-coordinate, trigonal planar copper sites. The bis(pyrazolyl)-borate ligand adopts the common boat conformation. The related tris(pyrazolyl)boratocopper complexes are useful cyclopropanation and aziridination catalysts. We are currently exploring the catalytic as well as other chemical and physical properties of the title compounds.

## 4. Supplementary material

Crystallographic data for $[H_2B(3,5-(CF_3)_2Pz)_2]$-$Cu(PPh_3)$, $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(PhC{\equiv}CH)$, $[H_2B-(3,5-(CF_3)_2Pz)_2]Cu(PhCH{=}CH_2) \cdot 0.5$ hexane, and $\{[H_2B(3,5-(CF_3)_2Pz)_2]Cu\}_2(1,5-COD) \cdot C_7H_8$ have been deposited with the Cambridge Crystallographic Data Center, CCDS Nos. 250203–250206. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

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