DOI: 10.1002/ejic.200900420

Copper(I) Isocyanide and Phosphane Complexes of Fluorinated Mono- and Bis(pyrazolyl)borates

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Keywords: Copper / Phosphanes / Scorpionate ligands / Isocyanide ligands / Structure elucidation

New copper(I) complexes have been synthesized from the reaction between $[Cu(CH_3CN)_4]PF_6$ or CuI, triphenylphosphane, *tert*-butyl isocyanide or cyclohexyl isocyanide co-ligands, and the fluorinated pyrazolylborate ligands sodium trihydro[5-(trifluoromethyl)pyrazol-1-yl]borate and potassium dihydrobis[3-(trifluoromethyl)pyrazol-1-yl]borate. These compounds have been characterized by elemental analysis, FT-IR and multinuclear (^1H, ^{13}C, ^{19}F and ^{31}P) NMR spectroscopy, and ESI mass spectrometry. The solid-state structure of $[\{H_3B[5\text{-}(CF_3)pz]\}Cu(PPh_3)_2]$ is also reported. This complex features a κ^2N,H-bonded trihydro(pyrazolyl)-borate ligand, a rare Cu–HB bond, and a distorted, pseudo-tetrahedral copper atom with a large P–Cu–P angle. The solid state structures of $[\{H_2B[3\text{-}(CF_3)pz]_2\}Cu(CNtBu)_2]$ and $[\{H_2B[3\text{-}(CF_3)pz]_2\}Cu(CNCy)_2]$, which have pseudo-tetrahedral copper sites, are also reported. The bis(pyrazolyl)-borate ligand in these complexes acts as a κ^2N,N' donor and adopts a flattened boat conformation.
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Introduction

Pyrazolylborate auxiliary ligands have played an important role in several key areas of coinage metal (Cu, Ag, Au) chemistry[1–5] and they have also proved immensely useful for the stabilization of group 11 metal complexes of small carbon-based ligands,[6,7] the synthesis of metalloenzyme models relevant to biochemistry,[8–11] the development of homogeneous catalysts[12–16] and in the MOCVD of copper films.[17] An area of particular interest to us has been the effects of electron-withdrawing substituents on scorpionates and their metal adducts.[1,4,18,19] Accordingly, we have developed and isolated a variety of fluorinated tris- and bis(pyrazolyl)borate ligands, as well as rare mono(pyrazolyl)-borates. For example, we recently reported the first successful synthesis of the 5-substituted pyrazolylborate anion $[H_3B\{5\text{-}(CF_3)pz\}]^-$ under nonthermolytic conditions.[20] Herein we report the isolation of copper(I) phosphane and isocyanide complexes supported by $[H_3B\{5\text{-}(CF_3)pz\}]^-$. To supplement the investigation of electron-withdrawing systems, we also included the analogous copper adducts of the dihydrobis[3-(trifluoromethyl)pyrazolyl]borate ligand $[H_2B\{3\text{-}(CF_3)pz\}_2]^-$.[19]

Exploring the chemistry of metal isonitriles has led to new advances in both science and technology.[21,22] For example, Cardiolite®, which has been approved for use in cardiac imaging, is an isocyanide complex.[23] Copper-64 isocyanide or phosphane complexes offer an attractive option for the development of innovative radiopharmaceuticals useful in both positron emission tomography (PET) and targeted radiotherapy.[24,25] The synthetic value of copper–isocyanide complexes has also been amply demonstrated in the literature. Thus, cyclopentane- and cyclohexanecarboxylates have been prepared[26] by the stepwise cycloaddition of 1,ω-diiodo-propanes and -butanes, respectively, with dialkyl fumarate and maleate in the presence of cyclohexyl isocyanide and metallic copper. Other synthetic uses of copper–isocyanide complexes include conjugate additions[27] of activated methylene species, cyclopropanations,[28,29] allene synthesis[30] from *gem*-dibromocyclopropanes, dimerization of alkyl halides,[31] and hydrosilylations of acrylonitriles.[32]

Despite the large number of papers describing group 11 metal complexes of pyrazolylborate, in particular those involving poly(pyrazolyl)borates,[3,4,33] relatively little attention has been devoted to systems containing copper–isocyanide species. $[\{H_2B[3,5\text{-}(CF_3)_2pz]_2\}Cu(CNtBu)_2]_2$ and $[\{HB[3,5\text{-}(CF_3)_2pz]_3\}Cu(CNtBu)]$[34] [see parts (a) and (b) of Figure 1] were the first structurally characterized copper–isocyanide adducts involving poly(pyrazolyl)borate ligands. They also exemplify the use of two highly fluorinated ligands in copper chemistry. The synthesis and properties of several phosphane copper(I) complexes of poly(pyrazolyl)borates bearing trifluoromethyl substituents have

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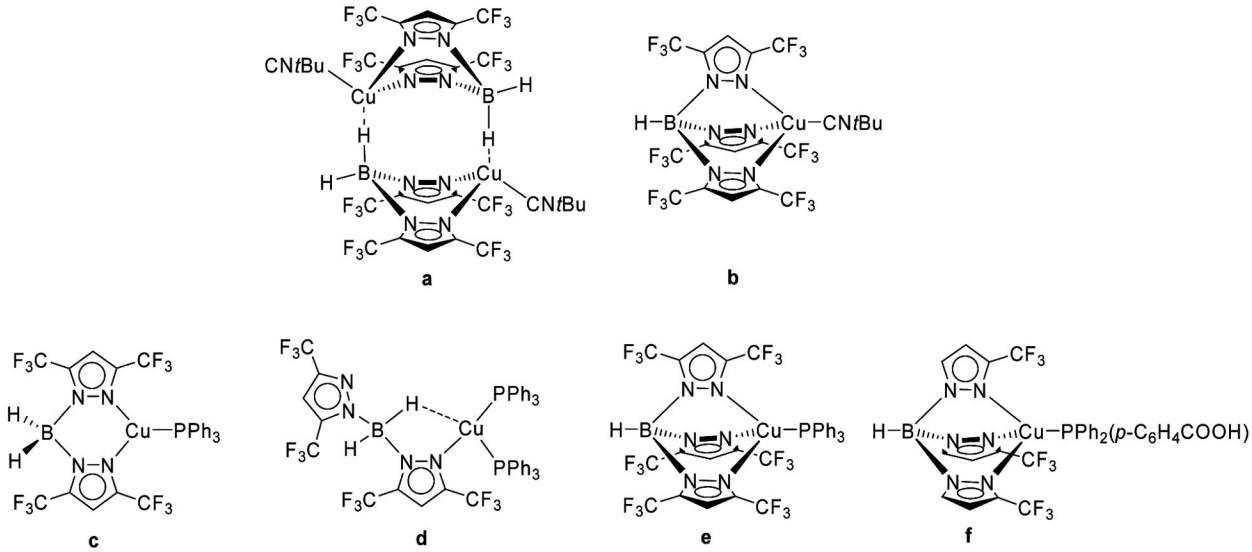
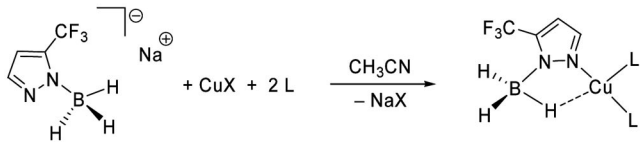


Figure 1. Copper(I) isocyanide and phosphane complexes supported by fluorinated poly(pyrazolyl)borates.

been described; these include [{H_2B[3,5-$(CF_3)_2$pz]$_2$}Cu(PPh$_3$)][35] [Figure 1 (c)], [{H_2B[3,5-$(CF_3)_2$pz]$_2$}Cu(PPh$_3$)$_2$][36] [Figure 1 (d)], [{HB[3,5-$(CF_3)_2$pz]$_3$}Cu(PPh$_3$)][37] [Figure 1 (e)] and [{HB[3-(CF_3)pz]$_3$}Cu{PPh_2(p-C_6H_4COOH)}][38] [Figure 1 (f)].

Results and Discussion

The sodium salt of the trihydro[5-(trifluoromethyl)pyrazol-1-yl]borate ligand, Na[H_3B{5-(CF_3)pz}], was synthesized by treating a thf solution of 3-(trifluoromethyl)-1*H*-pyrazole with $NaBH_4$ in a 1:1 molar ratio, in accordance with the literature.[20] Na[H_3B{5-(CF_3)pz}] was used in the preparation of the copper(I) complexes [{H_3B[5-(CF_3)-pz]}Cu(PPh$_3$)$_2$] and [{H_3B[5-(CF_3)pz]}Cu(CNR)$_2$] (R = *t*Bu or Cy). The treatment of Na[H_3B{5-(CF_3)pz}] with an acetonitrile solution of [Cu$(CH_3CN)_4$]PF_6 in the presence of two equivalents of triphenylphosphane led to compound **1** in good yield (Scheme 1). The stoichiometry of the compound was not affected by increasing (>2 equiv.) or reducing the amount of phosphane used. Compounds **2** and **3** were obtained from the reaction between sodium trihydro[5-(trifluoromethyl)pyrazol-1-yl]borate and CuI in an acetonitrile solution of *tert*-butyl isocyanide or cyclohexyl isocyanide, respectively (Scheme 1).



1, CuX = [Cu$(CH_3CN)_4$]PF_6; L = PPh$_3$
2, CuX = CuI; L = CN*t*Bu
3, CuX = CuI; L = CNCy

Scheme 1.

Compounds **1**–**3** are soluble in methanol, acetone, diethyl ether, DMSO, and chlorinated solvents and insoluble in water and aliphatic or aromatic hydrocarbon solvents. The IR spectra of complexes **1**–**3** show all the bands required by the presence of the trihydro[5-(trifluoromethyl)pyrazol-1-yl]borate and phosphane or isocyanide co-ligands, with weak absorptions in the range 2937–3100 cm^{-1} due to the pz ring C–H stretches and medium absorptions at about 1520 cm^{-1} related to ring "breathing" vibrations. Furthermore, the IR spectra allowed us to detect an agostic M–H–B interaction.[39] Thus, free B–H bands in our complexes were observed in the range 2317–2395 cm^{-1}, whereas the agostic Cu–H–B bands are shifted to lower energies of between 2068 and 2290 cm^{-1}; these shifts are in accordance with a κ^2N,H chelating coordination of the ligand, as depicted in Figure 2.

The IR stretching bands corresponding to the CN moieties of **2** and **3** appear as strong peaks at 2179 and 2176 cm^{-1}, respectively. They are significantly higher than the $\tilde{\nu}_{CN}$ values observed for free *tert*-butyl isocyanide ($\tilde{\nu}_{CN}$ = 2135 cm^{-1}) or cyclohexyl isocyanide ($\tilde{\nu}_{CN}$ = 2137 cm^{-1}). They are also higher than the corresponding values for [{B$(pz)_4$}Cu(CN*t*Bu)] ($\tilde{\nu}_{CN}$ = 2140 cm^{-1}) and [{HB(pz)$_3$}Cu(CN*t*Bu)] ($\tilde{\nu}_{CN}$ = 2155 cm^{-1});[40] the relatively high C–N stretching frequency for complexes **2** and **3** may be a direct result of the increased Lewis acidity of the copper center due to the presence of the highly electron-deficient pyrazolylborate ligand. Indeed, [{HB[3,5-$(CF_3)_2$pz]$_3$}Cu(CN*t*Bu)], which has an even more highly fluorinated supporting ligand, has an $\tilde{\nu}_{CN}$ value of 2196 cm^{-1}.[34]

The room-temperature ^{1}H NMR spectra of complexes **1**–**3** in [D_6]DMSO or $CDCl_3$ solution show only one set of resonances for H(4) and H(3) protons in the range δ = 6.36–7.45 ppm. The phosphane co-ligands show a characteristic series of resonances in the aromatic region, while the *tert*-butyl or cyclohexyl isocyanide co-ligands show a character-

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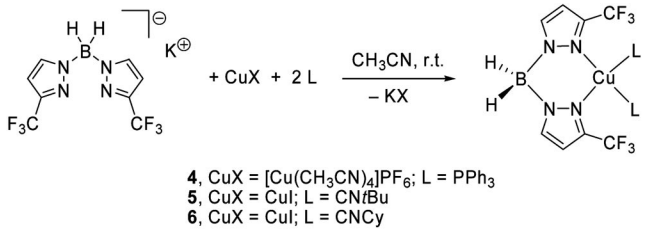
istic pattern of signals in the aliphatic region. The absence of distinct resonances for the terminal B–H and bridging B–H–M hydrides clearly implies a fluxional process in solution, as often observed for complexes bound to borohydrides.[20,41] The ^{19}F NMR signals in the range δ = –57.83 to –59.40 ppm for compounds **1**–**3** in [D$_6$]DMSO or $CDCl_3$ solution were assigned to the trifluoromethyl group at the 5-position of the pyrazole ring. The ^{31}P NMR spectrum of [{H_3B[5-(CF_3)pz]}Cu(PPh_3)$_2$] (**1**) in [D$_6$]DMSO solution shows a single broad signal at δ = –0.85 ppm at 293 K in the range typical for bis(phosphane) species,[20,42,43] in accordance with the crystallographic data. The ^{13}C chemical shifts of the 4-*C*H and 3-*C*H carbons in compounds **1**–**3** (in $CDCl_3$ solution) are in the ranges δ = 104.75–106.60 and 136.17–139.05 ppm, respectively; the ^{13}C chemical shift of the *C*F_3 carbons (δ = 121.28–121.97 ppm) and the $^1J_{C,F}$ coupling constant of 267.0 Hz are in accordance with the values reported for other polyfluorinated scorpionate ligands.[19,37] The broad resonances observed in the range δ = 139.90–140.30 ppm in the ^{13}C NMR spectra of **2** and **3** can be assigned to the isocyanide carbons. These values can be compared to the ^{13}C isocyanide carbon resonances at δ = 153.40 and 154.02 ppm in free CN*t*Bu and CNCy, respectively.

The potassium salt of dihydrobis[3-(trifluoromethyl)pyrazol-1-yl]borate, K[H_2B{3-(CF_3)pz}$_2$], was synthesized by treating KBH_4 with 3-(trifluoromethyl)-1*H*-pyrazole at 110 °C for 8 h, in accordance with the literature.[19] The N-donor/copper ion/C- or P-based co-ligand (1:1:2) complexes **4**–**6** were obtained in high yield from the reaction between one equivalent of the potassium salt K[H_2B{3-(CF_3)pz}$_2$], an equimolar quantity of [Cu(CH_3CN)$_4$]PF_6 or CuI, and two equivalents of triphenylphosphane, *tert*-butyl isocyanide, or cyclohexyl isocyanide (Scheme 2), in acetonitrile solution, at room temperature. The stoichiometry of the compounds was not affected by reducing (1 equiv.) or increasing (>2 equiv.) the amount of co-ligand.



Scheme 2.

Compounds **4**–**6** are soluble in methanol, acetone, diethyl ether, DMSO, and chlorinated solvents and are insoluble in water and aliphatic or aromatic hydrocarbon solvents. The IR spectra of complexes **4**–**6** show the bands required by the presence of the dihydridobis[3-(trifluoromethyl)pyrazol-1-yl]borate and phosphane or isocyanide co-ligands, with weak absorptions in the range 2942–3157 cm^{-1} due to the pz ring C–H stretching and medium absorptions in the range 1509–1516 cm^{-1} related to ring "breathing" vibrations. Complexes **4**–**6** exhibit B–H stretching vibrations in the range 2325–2460 cm^{-1}, in accordance with a κ^2N,N' chelating coordination of the ligand, and consistent with the solid-state structures depicted in Figures 3 and 4. The IR stretching bands corresponding to the CN moieties of derivatives **5** and **6** appear as strong peaks at 2161 and 2170 cm^{-1}, respectively. These values are higher than those for analogous electron rich poly(pyrazolyl)borate copper complexes such as [{HB[3,5-(CH_3)$_2$pz]$_3$}Cu($CNCH_2NC$)-Mn(CO)$_2$Cp] ($\tilde{\nu}_{CN}$ = 2145 cm^{-1}).[44]

The room-temperature ^1H NMR spectra of complexes **4**–**6** in $CDCl_3$ solution show only one set of resonances for the H(4) and H(5) protons in the range δ = 6.45–7.76 ppm. The phosphane co-ligands show a characteristic series of resonances in the aromatic region, while the *tert*-butyl or cyclohexyl isocyanide co-ligands show a characteristic pattern of resonances in the aliphatic region. The B–H protons appear as broad signals in the range δ = 3.00–3.20 ppm. The ^{19}F NMR signals in $CDCl_3$ solution appear in the range δ = –60.19 to –62.27 ppm and were assigned to the trifluoromethyl groups at the 3-position of the pyrazole ring. A single broad signal is observed at δ = –2.21 ppm in the ^{31}P NMR spectrum of [{H_2B[3-(CF_3)pz]$_2$}-Cu(PPh_3)$_2$] (**4**) in $CDCl_3$ solution at 293 K; this value is within the range typical of bis(phosphane) species. The resonances observed in the range δ = 139.58–140.90 ppm in the ^{13}C NMR spectra of **5** and **6** can be assigned to the isocyanide carbons.

Electrospray ionization mass spectrometry was used to probe the existence of aggregates of the scorpionate ligands with Cu^I and phosphane or isocyanide co-ligand in solution. Both positive- and negative-ion spectra of complexes **1**–**6** in methanol were recorded at low voltage (3.5–4.0 kV); under these experimental conditions, the dissociation is minimal and most of the analyte is transported to the mass spectrometer as the intact molecular species.[45] The negative-ion spectra of compounds **1**–**3** in methanol solution are dominated by the fragment at *m*/*z* 149 (100%) due to the free scorpionate ligand [H_3B{5-(CF_3)pz}]$^-$. Likewise, the negative-ion spectra of compounds **4**–**6** are dominated by the fragment at *m*/*z* 283 (100%) due to the free scorpionate ligand [H_2B{3-(CF_3)pz}$_2$]$^-$. The positive-ion spectra of the triphenylphosphane derivatives **1** and **4** are dominated by the fragment at *m*/*z* 588 (100%) [Cu(PPh_3)$_2$]$^+$, thus indicating the presence of individual species with a metal-to-ligand ratio of 1:2 in solution. The positive-ion spectra of the *tert*-butyl isocyanide derivatives **2** and **5** are dominated by the fragment at *m*/*z* 230 (100%) [Cu(CN*t*Bu)$_2$]$^+$, and the positive-ion spectra of the cyclohexyl isocyanide derivatives **3** and **6** are dominated by the fragments at *m*/*z* 282 [Cu(CNCy)$_2$]$^+$ and 391 [Cu(CNCy)$_3$]$^+$.

X-ray quality crystals of **1** were obtained from a $CHCl_3$/diethyl ether solution and X-ray quality crystals of **5** and **6** were obtained from a diethyl ether/*n*-hexane solution. The solid-state structure of [{H_3B[5-(CF_3)pz]}Cu(PPh_3)$_2$] (**1**) is shown in Figure 2.

Complex **1** is a monomeric species containing a κ^2N,H-bonded [H_3B{5-(CF_3)pz}]$^-$ ligand. The copper atom in **1** coordinates to one of the hydrogen atoms on boron, two P

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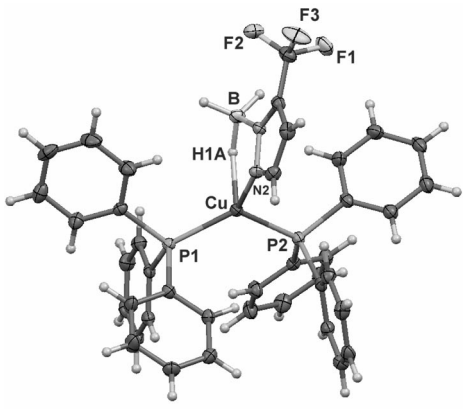

Figure 2. Thermal ellipsoid plot (50% probability) for [{H_3B[5-(CF_3)pz]}Cu(PPh_3)$_2$]. Selected bond lengths [Å] and angles [°]: Cu–N(2) 2.0422(14), Cu–P(1) 2.2450(5), Cu–P(2) 2.2664(5), Cu–H(1A) 1.88(2), B–H(1A) 1.21(2), B–H(1B) 1.09(2), B–H(1C) 1.10(2), N(1)–B 1.572(2), Cu···B 2.781; N(2)–Cu–P(1) 117.24(4), N(2)–Cu–P(2) 109.08(4), P(1)–Cu–P(2) 125.730(17), N(2)–Cu–H(1A) 80.2(6), P(1)–Cu–H(1A) 112.4(6), P(2)–Cu–H(1A) 101.6(6).

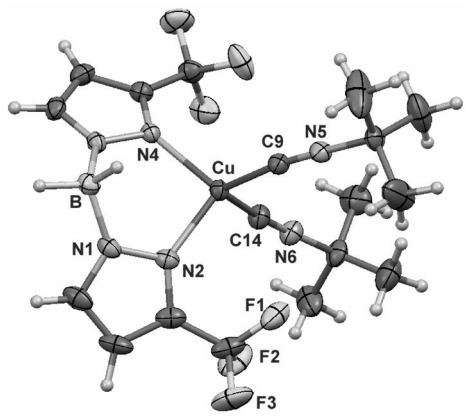

Figure 3. Thermal ellipsoid plot (50% probability) for **5**. Selected bond lengths [Å] and angles [°]: Cu–C(9) 1.914(2), Cu–C(14) 1.9308(19), Cu–N(4) 2.0606(16), Cu–N(2) 2.0840(17), N(1)–B 1.560(3), N(3)–B 1.556(3), N6–C14 1.145(3), Cu···B 3.256, C(9)–Cu–C(14) 107.29(8), C(9)–Cu–N(4) 117.05(7), C(14)–Cu–N(4) 112.98(7), C(9)–Cu–N(2) 114.14(7), C(14)–Cu–N(2) 108.21(8), N(4)–Cu–N(2) 96.77(6), N(3)–B–N(1) 109.81(16).

atoms, and the pyrazolyl ring nitrogen, and adopts a distorted pseudo-tetrahedral structure. The sum of the angles containing Cu, two P and N is 352.0°, thus indicating a small deviation from the trigonal planar arrangement (ideal 360°) as a result of the Cu–HB bond. The P–Cu–P angle is relatively large at 125.730(17)°, which is perhaps a result of steric effects due to the bulky phosphanes; this value is comparable with that observed in the analogous trihydro(pyrazolyl)borate silver(I) complex [{H_3B[5-(CF_3)pz]}Ag(PPh_3)$_2$] [P(1)–Ag(1)–P(2) 125.26(3)°].[20] The Cu–P distances [Cu–P(1) 2.2450(5), Cu–P(2) 2.2664(5) Å] are shorter than the corresponding Ag–P distances [Ag(1)–P(1) 2.4285(10), Ag(1)–P(2) 2.4736(10) Å] in [{H_3B[5-(CF_3)pz]}Ag(PPh_3)$_2$],[20] which is not surprising since copper has a smaller covalent radius than silver.

The bis(pyrazolyl)borate adduct [{H_2B[3,5-(CF_3)$_2$pz]$_2$}Cu(PPh_3)$_2$][36] also features κ^2N,H bonding (Figure 1, d). However, the Cu···B separation (2.891 Å) and the sum of the angles involving Cu, N and two P atoms (358.8°) in [{H_2B[3,5-(CF_3)$_2$pz]$_2$}Cu(PPh_3)$_2$] and the corresponding metric parameters in **1** (Figure 2; Cu···B separation of 2.781 Å, and sum of the angles involving Cu, N and two P atoms of 352.0°) suggest that the latter has a stronger Cu–H contact. For comparison, the Cu–P distances of [{H_2B[3,5-(CF_3)$_2$pz]$_2$}Cu(PPh_3)$_2$] are 2.2388(7) and 2.2690(7) Å.

The crystal structures of [{H_2B[3-(CF_3)pz]$_2$}Cu(CN*t*Bu)$_2$] (**5**) and [{H_2B[3-(CF_3)pz]$_2$}Cu(CNCy)$_2$] (**6**) are illustrated in Figures 3 and 4, respectively.

These complexes feature pseudo-tetrahedral copper sites, with the fluorinated bis(pyrazolyl)borate ligand coordination to copper in the more common κ^2N,N' fashion. The [H_2B{3-(CF_3)pz}$_2$]$^-$ moiety displays a flattened boat conformation. The Cu–C distances in **5** [Cu–C(9) 1.914(2), Cu–C(14) 1.9308(19) Å] and **6** [Cu–C(16) 1.9131(18), Cu–C(9) 1.9164(18) Å] are very similar in the two adducts. These Cu–C distances are longer than the corresponding bond lengths observed for the closely related *tert*-butyl isocyanide

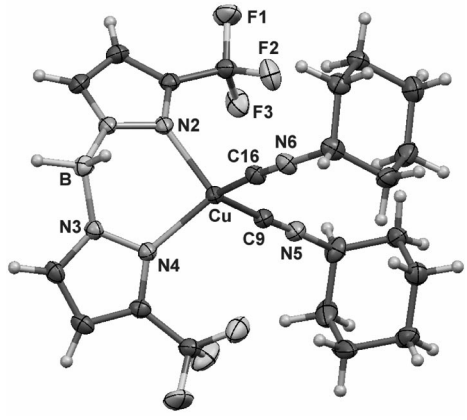

Figure 4. Thermal ellipsoid plot (50% probability) for **6**. Selected bond lengths [Å] and angles [°]: Cu–C(16) 1.9131(18), Cu–C(9) 1.9164(18), Cu–N(4) 2.0803(14), Cu–N(2) 2.0860(14), N(1)–B 1.556(2), N(3)–B 1.560(2), Cu···B 3.246; C(16)–Cu–C(9) 113.62(7), C(16)–Cu–N(4) 113.05(6), C(9)–Cu–N(4) 112.78(6), C(16)–Cu–N(2) 108.83(6), C(9)–Cu–N(2) 110.71(6), N(4)–Cu–N(2) 96.49(5), N(1)–B–N(3) 110.23(14).

complexes [{HB(3,5-(CF_3)$_2$pz]$_3$}Cu(CN*t*Bu)] [1.827(6) Å] and [{H_2B[3,5-(CF_3)$_2$pz]$_2$}Cu(CN*t*Bu)]$_2$ [1.855(3) Å].[34] For comparison, the Cu–C distance observed in the electron-rich copper isocyanide scorpionate complex [{HB(3,5-(CH_3)$_2$pz]$_3$}Cu(CNCH_2NC)Mn(CO)$_2$Cp] is 1.824(3) Å.[44]

Conclusions

We have described the isolation of the first copper adducts of the 5-CF_3-substituted trihydro(pyrazolyl)borate ligand [H_3B{5-(CF_3)pz}]$^-$. The copper(I) complexes bearing two phosphanes or isocyanides have been isolated in good yield. The X-ray structure of [{H_3B[5-(CF_3)pz]}Cu(PPh_3)$_2$] reveals the presence of a Cu–HB bond and a κ^2N,H-bonded [H_3B{5-(CF_3)pz}]$^-$ ligand. Copper(I) complexes of [H_2B{3-

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$(CF_3)pz\}_2]^-$ containing two phosphane or isocyanide co-ligands have also been isolated. The X-ray data of $[\{H_2B$-$[3$-$(CF_3)pz]_2\}Cu(CNtBu)_2]$ and $[\{H_2B[3$-$(CF_3)pz]_2\}Cu$-$(CNCy)_2]$ show the presence of κ^2N,N'-bonded bis(pyrazolyl)borates ligands. These copper(I) isocyanide complexes display relatively high CN stretching frequencies for the isocyanide moieties, perhaps indicating the presence of acidic metal sites due to the presence of fluorinated pyrazolylborate supporting ligands. These isocyanide and phosphane copper complexes offer an attractive option for the development of innovative radiopharmaceuticals and catalysts.

Experimental Section

Materials and General Methods: All syntheses and handling were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques or a glove box. All solvents were dried, degassed, and distilled prior to use. Elemental analyses (C,H,N,S) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were measured on an SMP3 Stuart Scientific Instrument. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer SPECTRUM ONE System FT-IR instrument. ^1H, ^{19}F, and ^{31}P NMR spectra were recorded with an Oxford-400 Varian spectrometer (400.4 MHz for ^1H, 100.1 MHz for ^{13}C, 376.8 MHz for ^{19}F and 162.1 MHz for ^{31}P). Chemical shifts, in ppm, for ^1H NMR spectra are quoted relative to internal Me_4Si. ^{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. Electrospray mass spectra (ESI-MS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using an acetone mobile phase. The compounds were added to reagent grade methanol to give solutions of approximate concentration 0.1 mM. These solutions were injected (1 μL) into the spectrometer via a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 μL min^{-1}; nitrogen was employed as both drying and nebulizing gas. Capillary voltages were typically 4000 and 3500 V for the positive- and negative-ion modes, respectively. Confirmation of all major species in this ESI-MS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter of which were calculated using the IsoPro 3.0 computer program.

Synthesis of the Ligands: The ligands sodium trihydro[5-(trifluoromethyl)pyrazol-1-yl]borate, $Na[H_3B\{5$-$(CF_3)pz\}]$[20] and potassium dihydrobis[3-(trifluoromethyl)pyrazol-1-yl]borate, $K[H_2B\{3$-(CF_3)-$pz\}_2]$[19] were prepared according to literature methods.

Syntheses of Copper Complexes

$[\{H_3B[5$-$(CF_3)pz]\}Cu(PPh_3)_2]$ (1): Triphenylphosphane (0.525 g, 2.0 mmol) was added to an acetonitrile solution (25 mL) of $[Cu(CH_3CN)_4]PF_6$ (0.373 g, 1.0 mmol) at room temperature and stirred for 4 h to give a colorless solution. Sodium trihydro[5-(trifluoromethyl)pyrazol-1-yl]borate, $Na[H_3B\{5$-$(CF_3)pz\}]$, (0.172 g, 1.0 mmol) was then added and the reaction mixture stirred for 12 h. The resulting white solid was filtered off and re-crystallized from $CHCl_3$/diethyl ether (1:2) to give complex **1** (0.457 g) in 62% yield. Crude **1** was dissolved in $CHCl_3$/diethyl ether solution to give a single crystal suitable for X-ray diffraction analysis; m.p. 135–137 °C. ^1H NMR ($[D_6]$DMSO, 293 K): δ = 2.70 (br., 3 H, BH_3), 6.61 (d, 1 H, 4-C*H*), 7.17–7.45 (m, 31 H, C_6H_5 and 3-C*H*) ppm. $^{13}C\{^1H\}$NMR ($CDCl_3$, 293 K): δ = 106.60 (4-*C*H), 121.28 (q, $^1J_{C,F}$ = 267.0 Hz, *C*F_3), 128.76, 129.95, 132.98, 133.83 (C_6H_5), 136.17 (3-*C*H) ppm. ^{19}F NMR ($[D_6]$DMSO, 293 K): δ = –59.40 (s) ppm. ^{31}P NMR ($[D_6]$DMSO, 293 K): δ = –0.85 (s) ppm. IR: $\tilde{\nu}$ = 3058 (w), 3000 (w, CH), 2395 (m br.), 2317 (m), 2187 (w), 2068 (m, BH), 1523 (w, C=C + C=N) cm^{-1}. ESI-MS (major negative-ions, CH_3OH): *m*/*z* (%) 149 (100) $[H_3B\{5$-$(CF_3)pz\}]^-$. ESI-MS (major positive-ions, CH_3OH): *m*/*z* (%) 588 (100) $[Cu(PPh_3)_2]^+$. $C_{40}H_{35}BCuF_3N_2P_2$ (737.03): calcd. C 65.19, H 4.79, N 3.80; found C 65.28, H 4.64, N 3.63.

$[\{H_3B[5$-$(CF_3)pz]\}Cu(CNtBu)_2]$ (2): CuI (0.190 g, 1.0 mmol) was added to an acetonitrile solution (5 mL) of *tert*-butyl isocyanide (0.333 g, 4.0 mmol) at room temperature and the mixture stirred for 4 h to give a colorless solution. Sodium trihydro[5-(trifluoromethyl)pyrazol-1-yl]borate, $Na[H_3B\{5$-$(CF_3)pz\}]$, (0.172 g, 1.0 mmol) was then added and the reaction mixture stirred for 12 h and concentrated under vacuum. The resulting solid was recrystallized from diethyl ether/*n*-hexane (1:2), to give complex **2** (0.200 g) in 53% yield; m.p. 47 °C (dec.). ^1H NMR ($CDCl_3$, 293 K): δ = 1.48 (s, 18 H, CCH_3), 2.50 (br., 3 H, BH_3), 6.42 (d, 1 H, 4-C*H*), 7.35 (d, 1 H, 3-C*H*) ppm. ^1H NMR ($[D_6]$DMSO, 293 K): δ = 1.46 (s, 18 H, CCH_3), 2.10 (br., 3 H, BH_3), 6.36 (d, 1 H, 4-C*H*), 7.23 (d, 1 H, 3-C*H*) ppm. $^{13}C\{^1H\}$NMR ($CDCl_3$, 293 K): δ = 30.35 (C*C*H_3), 56.55 (*C*CH_3), 105.08 (4-*C*H), 121.95 (q, $^1J_{C,F}$ = 267.0 Hz, *C*F_3), 136.73 (3-*C*H), 139.90 (*C*N) ppm. ^{19}F NMR ($[D_6]$DMSO, 293 K): δ = –57.83 (s) ppm. IR: $\tilde{\nu}$ = 3100 (br), 2988 (w, CH), 2369 (br), 2337 (sh), 2290 (m, BH), 2179 (s, νCN), 1522 (w, C=C + C=N) cm^{-1}. ESI-MS (major negative-ions, CH_3OH): *m*/*z* (%) 149 (100) $[H_3B\{5$-$(CF_3)pz\}]^-$. ESI-MS (major positive-ions, CH_3OH): *m*/*z* (%) 230 (100) $[Cu(CNtBu)_2]^+$. $C_{14}H_{23}BCuF_3N_4$ (378.71): calcd. C 44.40, H 6.12, N 14.79; found C 44.21, H 5.99, N 14.65.

$[\{H_3B[5$-$(CF_3)pz]\}Cu(CNCy)_2]$ (3): Complex **3** was prepared in a similar manner to compound **2** from cyclohexyl isocyanide (0.437 g, 4 mmol), CuI (0.190 g, 1.0 mmol), and $Na[H_3B\{5$-$(CF_3)pz\}]$ (0.172 g, 1.0 mmol). The product was purified from diethyl ether/*n*-hexane (1:2) to afford **3** (oil, 0.244 g) in 57% yield. ^1H NMR ($CDCl_3$, 293 K): δ = 1.36–1.93 (m, 20 H, Cy) 3.75 (m, 2 H, Cy), 6.41 (d, 1 H, 4-C*H*), 7.38 (d, 1 H, 3-C*H*) ppm. $^{13}C\{^1H\}$NMR ($CDCl_3$, 293 K): δ = 22.68, 24.78, 32.02, 53.34 (Cy), 104.75 (4-*C*H), 121.97 (q, $^1J_{C,F}$ = 267.0 Hz, *C*F_3), 139.05 (3-*C*H), 140.30 (*C*N) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –59.37 (s) ppm. IR: $\tilde{\nu}$ = 2937 (m, CH), 2340 (sh), 2286 (m), 2254 (m, BH), 2176 (s, νNC), 1522 (w, C=C + C=N) cm^{-1}. ESI-MS (major negative-ions, CH_3OH): *m*/*z* (%) 149 (100) $[H_3B\{5$-$(CF_3)pz\}]^-$, 321 (80) $[2\{H_3B[5$-$(CF_3)pz]\}$ + $Na^+]^-$. ESI-MS (major positive-ions, CH_3OH): *m*/*z* (%) 282 (20) $[Cu(CNCy)_2]^+$, 391 (100) $[Cu(CNCy)_3]^+$. $C_{18}H_{24}BCuF_3N_4$ (427.77): calcd. C 50.19, H 6.32, N 13.01; found C 50.32, H 6.50, N 12.95.

$[\{H_2B[3$-$(CF_3)pz]_2\}Cu(PPh_3)_2]$ (4): Triphenylphosphane (0.525 g, 2.0 mmol) was added to an acetonitrile solution (25 mL) of $[Cu(CH_3CN)_4]PF_6$ (0.373 g, 1.0 mmol) at room temperature and stirred for 4 h to give a colorless solution. Potassium dihydrobis[3-(trifluoromethyl)pyrazol-1-yl]borate, $K[H_2B\{3$-$(CF_3)pz\}_2]$, (0.322 g, 1.0 mmol) was then added and the reaction mixture stirred for 12 h. The solution was then concentrated under vacuum and diethyl ether added (30 mL). The resulting mixture was filtered, the filtrate concentrated under vacuum, and the resulting white solid recrystallized from diethyl ether/*n*-hexane (1:2) to give **4** (0.505 g) in 58% yield; m.p. 94–96 °C. ^1H NMR ($CDCl_3$, 293 K): δ = 3.20 (br., 2 H, B*H*), 6.70 (br., 2 H, 4-C*H*), 7.20–7.40 (m, 30 H, C_6H_5), 7.76 (br., 2 H, 5-C*H*) ppm. $^{13}C\{^1H\}$NMR ($CDCl_3$, 293 K): δ = 104.13 (4-*C*H), 121.37 (q, $^1J_{C,F}$ = 267.0 Hz, *C*F_3), 128.84, 129.88, 134.00, 136.17 (C_6H_5), 136.74 (5-*C*H), 142.11 (q, $^2J_{C,F}$ = 36.4 Hz, 3-*C*CF_3) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –62.27 (s)

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ppm. ^{31}P NMR ($CDCl_3$, 293 K): δ = –2.21 (br. s) ppm. IR: $\tilde{\nu}$ = 3144 (w), 3057 (w, CH), 2402 (br. m, BH), 1516 (m, C=C + C=N) cm^{-1}. ESI-MS (major negative-ions, CH_3OH): *m*/*z* (%) 283 (100) $[H_2B\{3\text{-}(CF_3)pz\}_2]^-$, 589 (20) $[2H_2B\{3\text{-}(CF_3)pz\}_2 + Na]^-$, 629 (15) $[2H_2B\{3\text{-}(CF_3)pz\}_2 + Cu]^-$. ESI-MS (major positive-ions, CH_3OH): *m*/*z* (%) 588 (100) $[Cu(PPh_3)_2]^+$, 632 (20) $[H_2B[3\text{-}(CF_3)pz]_2CuP(C_6H_5)_3 + Na]^+$. $C_{44}H_{36}BCuF_6N_4P_2$ (871.09): calcd. C 60.67, H 4.17, N 6.43; found C 60.54, H 4.02, N 6.55.

[{H$_2$B[3-(CF$_3$)pz]$_2$}Cu(CN*t*Bu)$_2$] (5): CuI (0.190 g, 1.0 mmol) was added to an acetonitrile solution (10 mL) of *tert*-butyl isocyanide (0.166 g, 2.0 mmol) at room temperature and stirred for 4 h to give a colorless solution. Potassium dihydrobis[3-(trifluoromethyl)pyrazol-1-yl]borate, $K[H_2B\{3\text{-}(CF_3)pz\}_2]$, (0.322 g, 1.0 mmol) was then added and the reaction mixture stirred for 12 h. The solution was filtered and concentrated under vacuum and the resulting solid was recrystallized from diethyl ether/*n*-hexane (1:2) to give complex **5** (0.415 g) in 81% yield; m.p. 159–161 °C. Crude **5** was dissolved in diethyl ether/*n*-hexane to give a single crystal suitable for X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$, 293 K): δ = 1.44 (s, 18 H, CC*H*$_3$), 3.20 (br., 2 H, B*H*$_2$), 6.45 (d, 2 H, 4-C*H*), 7.60 (d, 2 H, 3-C*H*) ppm. ^{13}C{^{1}H}NMR ($CDCl_3$, 293 K): δ = 30.27 (C*C*H$_3$), 55.76 (*C*CH$_3$), 103.59 (4-*C*H), 121.93 (q, $^1J_{C,F}$ = 267.0 Hz, *C*F$_3$), 136.01 (5-*C*H), 139.58 (*C*N), 142.38 (q, $^2J_{C,F}$ = 36.4 Hz, 3-*C*CF$_3$) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –60.19 (s) ppm. IR: $\tilde{\nu}$ = 3144 (w), 2989 (m, CH), 2419 (br), 2389 (br., BH), 2182 (sh), 2161 (s, νCN), 1509 (w, C=C + C=N) cm^{-1}. ESI-MS (major negative-ions, CH_3OH): *m*/*z* (%) 283 (100) $[H_2B\{3\text{-}(CF_3)pz\}_2]^-$. ESI-MS (major positive-ions, CH_3OH): *m*/*z* (%) 230 (100) $[Cu(CNtBu)_2]^+$. $C_{18}H_{24}BCuF_6N_6$ (512.78): calcd. C 42.16, H 4.72, N 16.39; found C 41.98, H 4.59, N 16.15.

[{H$_2$B[3-(CF$_3$)pz]$_2$}Cu(CNCy)$_2$] (6): Complex **6** was prepared in a similar manner to compound **5** from cyclohexyl isocyanide (0.218 g, 2 mmol), CuI (0.190 g, 1.0 mmol), and $K[H_2B\{3\text{-}(CF_3)pz\}_2]$ (0.322 g, 1.0 mmol). The product was recrystallized from diethyl ether/*n*-hexane (1:2) to afford **6** (0.441 g) in 78% yield. Crude **6** was dissolved in diethyl ether/*n*-hexane solution to give a single crystal suitable for X-ray diffraction analysis; m.p. 99–100 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ = 1.33–2.00 (m, 20 H, Cy), 3.00 (br., 2 H, B*H*$_2$), 3.66 (m, 2 H, Cy), 6.45 (d, 2 H, 4-C*H*), 7.60 (d, 2 H, 3-C*H*) ppm. ^{13}C{^{1}H}NMR ($CDCl_3$, 293 K): δ = 23.02, 25.12, 32.30, 53.00 (Cy), 103.66 (4-*C*H), 121.97 (q, $^1J_{C,F}$ = 267.1 Hz, *C*F$_3$), 136.10 (5-*C*H), 140.90 (*C*N), 142.46 (q, $^2J_{C,F}$ = 37.1 Hz, 3-*C*CF$_3$) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –60.21 (s) ppm. IR: $\tilde{\nu}$ = 3157 (w), 2942 (m, CH), 2460 (sh), 2407 (m, BH), 2170 (s, νNC), 1512 (w, C=C + C=N) cm^{-1}. ESI-MS (major negative-ions, CH_3OH): *m*/*z* (%) 283 (100) $[H_2B\{3\text{-}(CF_3)pz\}_2]^-$, 589 (20) $[2H_2B\{3\text{-}(CF_3)pz\}_2 + Na]^-$. ESI-MS (major positive-ions, CH_3OH): *m*/*z* (%) 282 (100) $[Cu(CNCy)_2]^+$. $C_{22}H_{28}BCuF_6N_6$ (564.85): calcd. C 46.78, H 5.00, N 14.88; found C 46.63, H 4.86, N 14.48.

X-ray Data Collection and Structure Determinations: A suitable crystal of $[\{H_3B[5\text{-}(CF_3)pz]\}Cu(PPh_3)_2]$, $[\{H_2B[3\text{-}(CF_3)pz]_2\}Cu(CNtBu)_2]$, and $[\{H_2B[3\text{-}(CF_3)pz]_2\}Cu(CNCy)_2]$, covered with a layer of hydrocarbon oil, was selected, mounted with paratone-N oil on a cryo-loop, and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series Cryostream cooler, a graphite monochromator, and a Mo-K_α fine-focus sealed tube (λ = 0.710 73 Å). The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using Bruker SHELXTL software package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on boron were located from the difference maps and included and refined isotropically. The remaining hydrogen atoms in all complexes were placed at calculated positions and refined using a riding model. Selected X-ray data are given in Table 1.

CCDC-730631 (for **1**), -730632 (for **5**) and -730633 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Selected crystal data for $[\{H_3B[5\text{-}(CF_3)pz]\}Cu(PPh_3)_2]$ (**1**), $[\{H_2B[3\text{-}(CF_3)pz]_2\}Cu(CNtBu)_2]$ (**5**), and $[\{H_2B[3\text{-}(CF_3)pz]_2\}Cu(CNCy)_2]$ (**6**).

Compound	**1**	**5**	**6**
Empirical formula	$C_{40}H_{35}BCuF_3N_2P_2$	$C_{18}H_{24}BCuF_6N_6$	$C_{22}H_{28}BCuF_6N_6$
Formula weight	736.99	512.78	564.85
Temperature [K]	100(2)	100(2)	100(2)
Radiation (λ)	Mo-K_α (0.71073 Å)	Mo-K_α (0.71073 Å)	Mo-K_α (0.71073 Å)
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$Pna2_1$	$P2_1/n$
a [Å]	10.7379(7)	23.0511(16)	9.0812(7)
b [Å]	12.7836(9)	11.1720(8)	24.0163(17)
c [Å]	14.3449(10)	9.3674(7)	11.8333(8)
α [°]	82.708(1)	90	90
β [°]	71.515(1)	90	93.099(1)
γ [°]	72.329(1)	90	90
Volume [Å^3]	1778.4(2)	2412.4(3)	2577.0(3)
Z	2	4	4
Calcd. density [Mg m^{-3}]	1.376	1.412	1.456
Final *R* indices [$I > 2\sigma(I)$]			
R_1	0.0309	0.0260	0.0309
wR_2	0.0810	0.0646	0.0823
R indices (all data)			
R_1	0.0338	0.0269	0.0340
wR_2	0.0833	0.0652	0.0843

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Acknowledgments

This work was partially supported by Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) (PRIN 20078EWK9B). We are grateful to the Consorzio Interuniversitario di Ricerca in Chimica dei Metalli nei Sistemi Biologici (CIRCMSB). H. V. R. D. wishes to acknowledge the Welch Foundation (Y-1289) for financial support.

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Received: May 8, 2009
Published Online: July 29, 2009

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