Carbonyl and isocyanide complexes of copper and silver supported by fluorinated poly(pyridyl)borates

Mukundam Vanga, Anurag Noonikara-Poyil, Jiang Wu and H. V. Rasika Dias*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, USA

*Correspondence to: dias@uta.edu

Abstract:

The pyridine-based poly(pyridyl)borates are a recent addition to the scorpionate family. Furthermore, pyridyl ring substituted analogs are also rare. The synthesis of a bis(pyridyl)borate featuring trifluoromethyl substituted pyridyl donor arms and its utility in isocyanide and carbonyl chemistry of copper(I) and silver(I) have been described together with related molecules supported by a fluorinated tris(pyridyl)borate, and a comparison to the better-known poly(pyrazolyl)borate relatives. X-ray crystal structures of copper and silver complexes show that the B-arylated, bis- and tris(pyridyl)borate ligands use only two pyridyl moieties for metal ion coordination. Flanking B-aryl groups close to metal sites are also a common feature in copper and silver complexes supported by $[Ph_2B(6\text{-}(CF_3)Py)_2]^-$ and $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]^-$. The CN stretching frequencies of the *t*-BuNC complexes of Cu(I) and Ag(I) are notably higher than that of the free *t*-BuNC. The CO stretch of the analogous fluorinated poly(pyridyl)borate ligand supported metal carbonyls lie closer to that of the free CO, indicating the presence of fairly Lewis acidic metal sites. Metal bound carbonyl stretching frequencies of comparable species suggest that the poly(pyridyl)borates are slightly better donors relative to the related poly(pyrazolyl)borates.

Introduction:

Fluorine is the most electronegative element in the periodic table, and in association with carbon, forms some of the most robust, chemically inert single bonds (e.g., BDE of C-F and C-H bonds of CF_4 and CH_4 are 546.8 and 439.3 kJ/mol, respectively).[1] As a result, metal complexes of fluorinated ligands in comparison to their non-fluorinated, hydrocarbon counterparts, usually display different properties such as relatively high thermal and oxidative stability, volatility, and unique reactivity profiles.[2-6] They are also ideal for applications in fluorous-biphase media and supercritical CO_2.[7-9] Fluorinated poly(pyrazolyl)borates (which belong to a family known as scorpionates)[10-11] such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (**1**, Figure 1) and $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ (**2**) are a particularly useful group of ligands as they have facilitated the stabilization of rare species such silver(I)-acetylene,[12] copper(I) and silver(I)-organo azide,[13] and silver(I)-dimethyl diazomalonate[14] complexes and to probe their chemistry under readily accessible conditions. They are also valuable in applications involving catalysis including those in super-critical CO_2,[15-21] ethylene sensing,[22] to olefin-paraffin separations.[23] For example, fluorinated tris(pyrazolyl)borates have been useful in supporting catalytically active and fairly reactive copper complexes, without the ligand itself getting destroyed.[15, 24] The silver complex $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$ is an effective mediator for the functionalization of inert C-Cl bonds of halocarbons as well as C-H bonds of saturated hydrocarbons via catalytic carbene insertion chemistry.[16, 19, 25-26] The bis(pyrazolyl)borate $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu$ serves as an excellent non-porous material for the separation of ethylene from an ethylene/ethane mixture.[23]

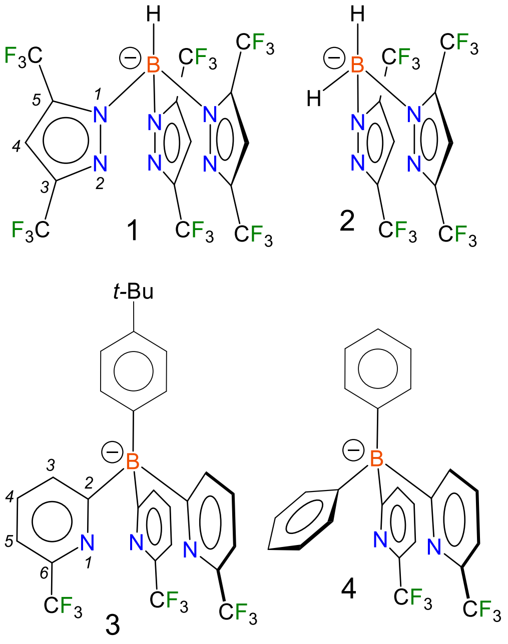


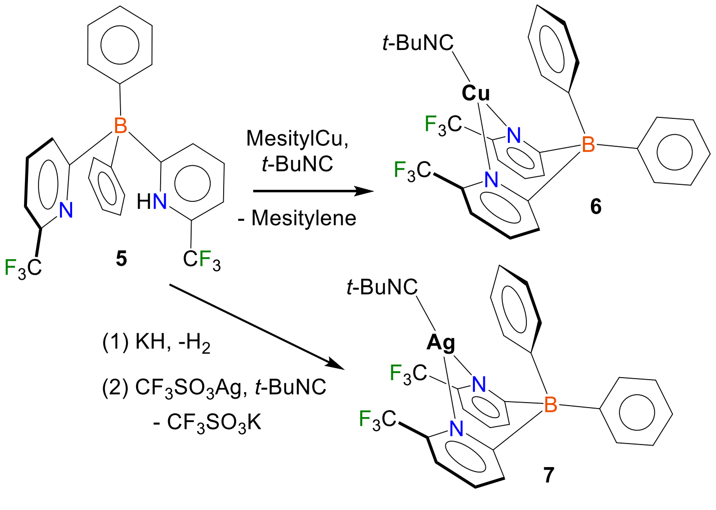
Figure 1. Structures of a tris(pyrazolyl)borate $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (**1**), bis(pyrazolyl)borate $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ (**2**), tris(2-pyridyl)borate $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]^-$ (**3**) and the new bis(2-pyridyl)borate $[Ph_2B(6\text{-}(CF_3)Py)_2]^-$ (**4**)

Considering the importance of fluorinated ligands and the successes with fluorinated poly(pyrazolyl)borates,[19, 27-29] we embarked on a project to develop the fluorinated versions of poly(pyridyl)borates. Recently we reported the assembly of first such ligand, a fluorinated tris(2-pyridyl)borate $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]^-$ (**3**, Figure 1), and demonstrated its utility in coinage metal ethylene chemistry.[30] In contrast to the pyrazole based poly(pyrazolyl)borates,[10-11] the pyridine based poly(pyridyl)borates are a recent addition to the scorpionate family.[31-32] The paucity of ligand variations apart from those based on the parent 2-pyridylborate is also noteworthy. Nevertheless, poly(2-pyridyl)borates are finding increasing utility as metal ion chelators,[31-43] as they bring different donor properties (pyridyl vs. pyrazolyl), backbone stabilities (attributable to less polar B-C linkages vs. B-N), and steric profiles (due to the involvement of six-membered pyridyl donor arms instead of the five-membered pyrazolyl moieties) relative to the pyrazolyl counterparts.[40]

In this paper, we describe the synthesis of a fluorinated bis(2-pyridyl)borate, $[Ph_2B(6\text{-}(CF_3)Py)_2]^-$ (**4**) and its effectiveness in copper and silver carbonyl and isocyanide chemistry. The related molecules supported by the tris(2-pyridyl)borate **3** as well as a copper(I) carbonyl complex of a fluorinated tris(1-pyrazolyl)borate are also presented. The carbonyl and isocyanide complexes were chosen for this study not only because of their importance[19, 44-56] but also since their CO and CN stretch could serve as a gauge of ligand electronic effects on the metal sites.[57] It is noteworthy that isolable silver carbonyl complexes are also quite rare.[12, 15, 58-67]

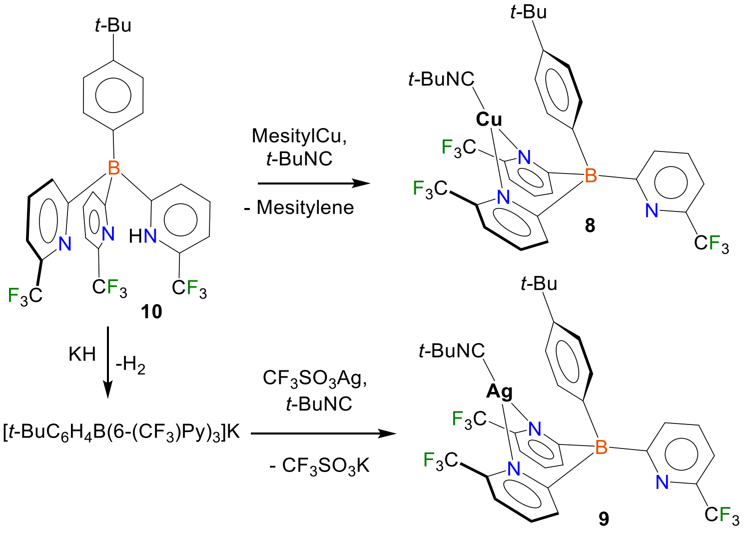
Results and discussion.

The fluorinated bis(2-pyridyl)borate ligand $[Ph_2B(6\text{-}(CF_3)Py)_2]^-$ (**4**) was synthesized by treating Ph_2BBr with the corresponding 2-pyridylmagnesium chloride (which was obtained from *i*-PrMgCl and 2-bromo-6-(trifluoromethyl)pyridine)[30] in THF. The protonated form of **4**, $[Ph_2B(6\text{-}(CF_3)Py)_2]H$ (**5**) was isolated as a white solid and characterized completely using NMR spectroscopy and elemental analysis. There are few bis(2-pyridyl)borate ligands such as $[Me_2B(Py)_2]^-$,[31] $[Ph_2B(Py)_2]^-$,[42] and $[\text{cyclooctane-1,5-diyl}B(Py)_2]^-$,[43] known, but they all feature the parent 2-pyridyl donor arms. There are also no reports to our knowledge of bis(2-pyridyl)borate ligands such as **4** bearing substituents at the pyridyl ring 6-position, which due to their proximity to the coordinated metal atom, should provide better protection to a metal site, relative to 6-unsubstitued bis(2-pyridyl)borate chelators such as $[Ph_2B(Py)_2]^-$. Furthermore, based on the chemistry observed with pyrazolyl ring substituted bis(pyrazolyl)borates (e.g., **2**),[18, 20-21, 23, 29] we expect ligands of the type **4** with substituents at the pyridyl ring 6-position to be quite useful.



Scheme 1. Synthesis of *t*-BuNC complexes $[Ph_2B(6\text{-}(CF_3)Py)_2]Cu(CNBu^t)$ (**6**) and $[Ph_2B(6\text{-}(CF_3)Py)_2]Ag(CNBu^t)$ (**7**) supported by the bis(2-pyridyl)borate $[Ph_2B(6\text{-}(CF_3)Py)_3]^-$ (**4**)

In order to evaluate the coordination prowess and features of $[Ph_2B(6\text{-}(CF_3)Py)_2]^-$ (**4**), we first set out to prepare its copper(I) and silver(I) complexes of *t*-BuNC. The copper(I) complex $[Ph_2B(6\text{-}(CF_3)Py)_2]Cu(CNBu^t)$ (**6**) was obtained by an arene elimination reaction between $[Ph_2B(6\text{-}(CF_3)Py)_2]H$ (**5**) and mesityl copper in the presence of *t*-BuNC (Scheme 1). The silver(I) analog $[Ph_2B(6\text{-}(CF_3)Py)_2]Ag(CNBu^t)$ (**7**) was synthesized using $K[Ph_2B(6\text{-}(CF_3)Py)_2]$ (prepared from KH and $[Ph_2B(6\text{-}(CF_3)Py)_2]H$), CF_3SO_3Ag and *t*-BuNC. Compounds **6** and **7** are obtained as colorless, air stable crystals from their hexane solutions at -20°C. Spectroscopic data suggest the formation of the expected products. For example, the CN stretch of the metal bound *t*-BuNC group of these molecules was observed at 2180 and 2200 cm^{-1}, respectively, in their IR spectra which is different from, and appears at a much higher value relative to, the $\overline{\upsilon}$(CN) of free *t*-BuNC at 2138 cm^{-1}. Chemical shifts and peak integration values of ^{1}H NMR data indicated the formation of mono *t*-BuNC complexes. The isocyanide carbon resonance of **6** and **7** was observed at δ 136.33 and 138.90 ppm, respectively in their ^{13}C NMR spectra, and shows an upfield shift from the free *t*-BuNC (which is observed at δ 153.6 ppm in $CDCl_3$).[68]



Scheme 2. Synthesis of *t*-BuNC complexes [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Cu(CNBu^t) (**8**) and [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Ag(CNBu^t) (**9**) supported by the tris(2-pyridyl)borate, [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]$^-$

We have also synthesized the related metal complexes supported by the tripodal ligand relative [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]$^-$ (**3**) for comparisons. The copper(I) and silver(I) complexes, [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Cu(CNBu^t) (**8**) and [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Ag(CNBu^t) (**9**) were prepared following analogous methods used for **6** and **7**, but using the tris(pyridyl)borate precursor [*t*-

BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]H (**10**)[30] instead of [Ph$_2$B(6-(CF$_3$)Py)$_2$]H (**5**) (Scheme 2). Compounds **8** and **9** are colorless solids and display strong bands at 2168 and 2198 cm^{-1} in their IR spectra for the CN stretch of *t*-BuNC group.

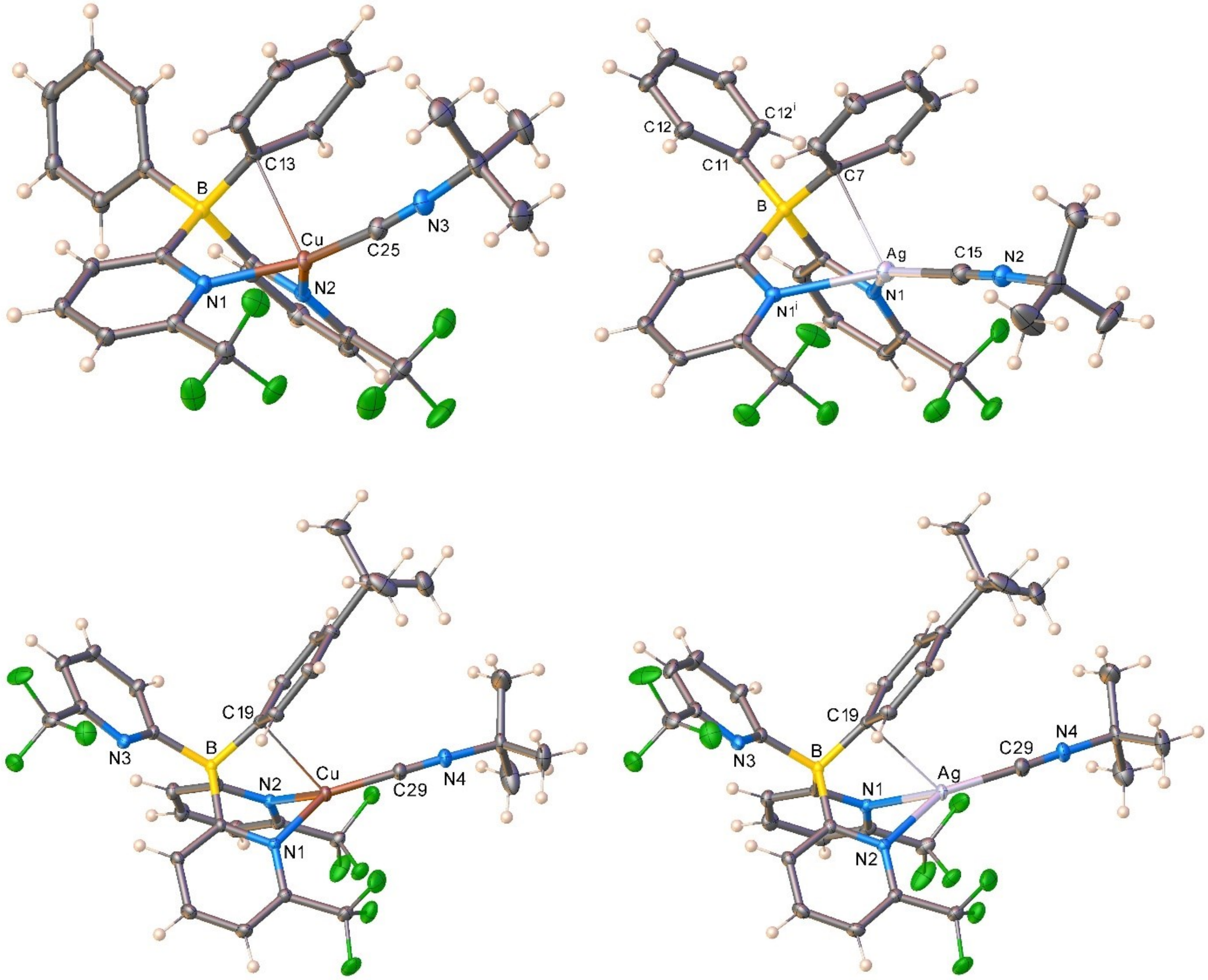


Figure 2. Molecular structure of [Ph$_2$B(6-(CF$_3$)Py)$_2$]Cu(CNBu^t) (**6**) (Top-left), [Ph$_2$B(6-(CF$_3$)Py)$_2$]Ag(CNBu^t) (**7**) (Top-right), [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Cu(CNBu^t) (**8**) (Bottom-left) and [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Ag(CNBu^t) (**9**) (Bottom-right). Selected bond distances (Å) and angles (°) are given in Table 1.

X-ray crystal structures of **6-9** are illustrated in Figure 2. Selected bond distances and angles are given in Table 1. The bis(pyridyl)borate ligand in [Ph$_2$B(6-(CF$_3$)Py)$_2$]Cu(CNBu^t) (**6**) and

$[Ph_2B(6\text{-}(CF_3)Py)_2]Ag(CNBu^t)$ (**7**), as expected uses both pyridyl donor-arms to chelate the metal site. In addition, one of the phenyl groups on boron sits above the metal site with somewhat close M•••C(B) separation (M = Cu and Ag) between the M and flanking phenyl group at 2.5314(12) and 2.560(2) Å. Although these distances are within Bondi's van der Waals contact separation of the Cu•••C and Ag•••C pairs (3.10 and 3.42 Å, respectively),[69] they are much longer than the typical Cu-C(sp^2) and Ag-C(sp^2) covalent distances (2.05 and 2.18 Å).[70] The metal sites are trigonal planar or nearly planar as evident from the sum of angles at copper (359.9°) and silver (355.1°) in **6** and **7** (Table 1).

Table 1. Selected bond distances (Å), angles (°) of $[Ph_2B(6\text{-}(CF_3)Py)_2]M(CNBu^t)$ and $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]M(CNBu^t)$ (M = Cu, Ag). The M•••C(B) is the ipso-carbon separation between the M and flanking phenyl group (value given in italics). ∑ at M represents the sum of angles at M involving two nitrogen atoms bonded to M and the carbon of *t*-BuNC.

Molecule/ Parameter	$[Ph_2B(6\text{-}(CF_3)Py)_2]Cu(CNBu^t)$ (**6**)	$[Ph_2B(6\text{-}(CF_3)Py)_2]Ag(CNBu^t)$ (**7**)	$[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Cu(CNBu^t)$ (**8**)	$[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Ag(CNBu^t)$ (**9**)
C-NBu^t	1.1537(17)	1.145(4)	1.1610(12)	1.147(2)
M-CNBu^t	1.8471(13)	2.085(3)	1.8598(9)	2.0781(15)
M-N	2.0243(10), 2.0482(10)	2.3741(16), 2.3741(16)	2.0495(7), 2.1175(7)	2.4083(12), 2.3033(12)
M••C(B)	*2.5314(12)*	*2.560(2)*	*2.4174(8)*	*2.5661(13)*
M-C-NBu^t	172.81(12)	179.6(3)	172.30(9)	171.32(14)
N-M-N	93.34(4)	82.11(7)	89.63(3)	81.41(4)
∑ at M	359.9	355.1	354.8	354.9

Interestingly, the tris(pyridyl)borate complexes **8** and **9** also feature essentially trigonal planar metal sites, with the scorpionate binding to the metal centers using only two pyridyl arms.

The B-aryl group, instead of the third pyridyl moiety sits above the metal sites. We have seen the same κ^2-mode of coordination in [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Cu(C$_2$H$_4$) and [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Ag(C$_2$H$_4$),[30] but they have side-on bonded ethylene ligands, unlike the end-on bonded *t*-BuNC. The M-N and M-CNBu^t bond distances are relatively longer in the silver complexes than the related distances of the copper, as expected considering the larger covalent radius of the former.[70]

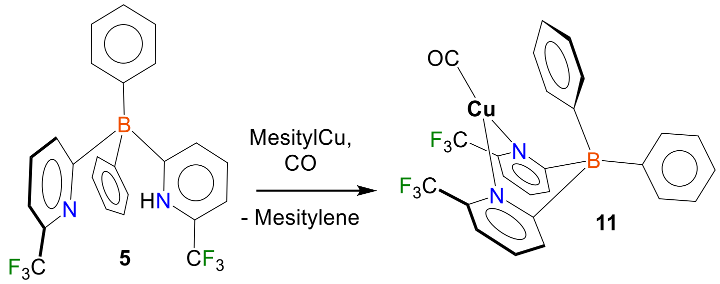
Table 2. Selected, structurally characterized Cu(I)-CNBu^t and Ag(I)-CNBu^t complexes of poly(pyridyl)borates and poly(pyrazolyl)borates and some of their structural and spectroscopic parameters. The $\overline{\upsilon}$(CN) of free *t*-BuNC = 2138 cm^{-1}.

Complex	**$\overline{\upsilon}$(CN)/cm^{-1}**	**M-C/Å**	**Ref.**
[Ph$_2$B(6-(CF$_3$)Py)$_2$]Cu(CNBu^t) (**6**)	2180	1.8471(13)	This work
[*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Cu(CNBu^t) (**8**)	2168	1.8598(9)	This work
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Cu(CNBu^t)	2196	1.827(6)	71
[H$_2$B(3-(NO$_2$)Pz)$_2$]Cu(CNBu^t)$_2$	2166, 2190sh	1.926(2) 1.903(2)	72
[H$_2$B(3-(CF$_3$)Pz)$_2$]Cu(CNBu^t)$_2$	2161, 2182sh	1.914(2) 1.9308(19)	73
{[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]Cu(CNBu^t)}$_2$	2196	1.855(3)	71
[Ph$_2$B(6-(CF$_3$)Py)$_2$]Ag(CNBu^t) (**7**)	2200	2.085(3)	This work
[*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Ag(CNBu^t) (**9**)	2198	2.0781(15)	This work
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(CNBu^t)	2214	2.059(4)	58
[HB(3,5-(CH$_3$)$_2$Pz)$_3$]Ag(CNBu^t)	2178	2.05(1)	74
[HB(3,5-(Ph)$_2$Pz)$_3$]Ag(CNBu^t)	2185	2.08(1)	74

The ^{1}H NMR of [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]M(CNBu^t) (M = Cu , Ag) complexes show an averaged set of signals in solution at room temperature for the coordinated and free N-donor arms with some broadening of the pyridyl proton signals, which could be due to fast κ^2- to κ^3-

interconversion on the NMR time scale. Interestingly, the ^{19}F NMR spectrum of [*t*-BuC_6H_4B(6-(CF_3)Py)$_3$]Cu(CNBu^t) shows partially resolved peaks for CF_3-groups of the two different pyridyl arms, whereas a single ^{19}F peak is observed for [*t*-BuC_6H_4B(6-(CF_3)Py)$_3$]Ag(CNBu^t) suggesting this fluxional process is relatively slower in the former adduct.

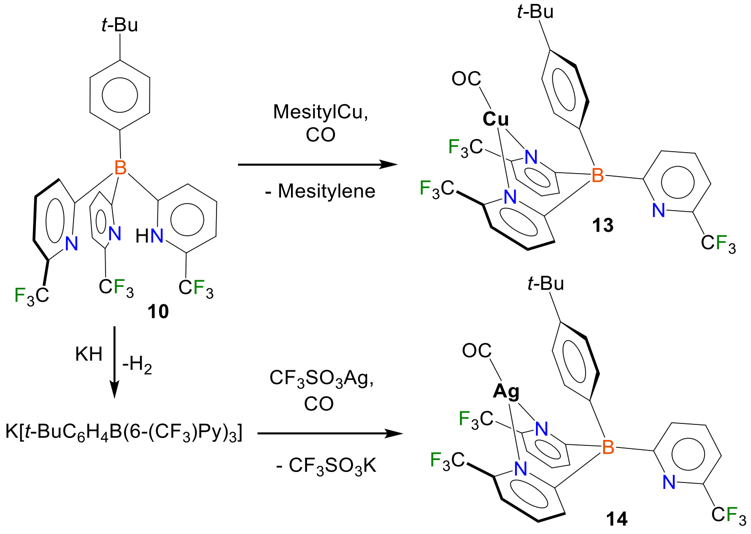
Literature reports on poly(pyridyl)borato copper and silver complexes of any type are very limited,[30, 75-78] and none of those feature isocyanide donors. There are however, several structurally characterized bis- and tris(pyrazolyl)borato copper and silver complexes of *t*-BuNC available for comparisons.[12, 58, 71-74] Interestingly, they are all 4-coordinate metal complexes (in contrast, **6-9** are basically three coordinate metal species).[79] As evident from the data presented in Table 2, M-CNBu^t distances of the poly(pyridyl)borate and poly(pyrazolyl)borate mono-isocyanide complexes do not vary much for a given metal (Cu or Ag) despite the differences in coordination number. Furthermore, at least based on the limited data available, the scorpionate ligand donor properties have no significant effect on the Ag-CNBu^t distance. The CN stretching frequency however is somewhat higher for the molecules supported by weakly donating fluorinated scorpionates, which is a result of the increased Lewis acidity at the metal (e.g., 2178 and 2198 cm^{-1} for [HB(3,5-(CH_3)$_2$Pz)$_3$]Ag(CNBu^t) and [*t*-BuC_6H_4B(6-(CF_3)Py)$_3$]Ag(CNBu^t), respectively). Also an analysis of $\bar{\upsilon}$(CN) data of **6-9** indicates that the copper analogs **6** and **8** have relatively lower CN stretching frequencies compared to the related silver adducts **7** and **9.** This could be a result of better backbonding prowess of the copper ion in comparison to the larger relative silver(I).[57] Nevertheless, they all display CN stretching frequencies clearly higher than that of the free *t*-BuNC (2138 cm^{-1}).



Scheme 3. Synthesis of copper(I) carbonyl complex [$Ph_2B(6-(CF_3)Py)_2$]Cu(CO) (**11**) supported by the bis(2-pyridyl)borate [$Ph_2B(6-(CF_3)Py)_3$]$^-$

Copper and silver carbonyl chemistry supported by the newly constructed [$Ph_2B(6-(CF_3)Py)_2$]$^-$ and the related tripodal analog, [*t*-$BuC_6H_4B(6-(CF_3)Py)_3$]$^-$ were also investigated in this work. Such metal-carbon monoxide complexes are of interest due to their importance ranging from fundamental aspects, catalysis to biochemistry.[19, 54] Copper carbonyl complexes are more common although thermally stable species are somewhat challenging to isolate.[18-19, 27, 80-91] In contrast, well-characterized silver carbonyl complexes are relatively rare.[19, 66-67] However, scorpionates are particularly useful for the stabilization of molecules with Ag(I)-CO moiety.[12, 15, 58-65, 92]

The copper(I) carbonyl complex [$Ph_2B(6-(CF_3)Py)_2$]Cu(CO) (**11**) was synthesized by treating [$Ph_2B(6-(CF_3)Py)_2$]H (**5**) with mesityl copper in the presence of carbon monoxide (Scheme 3). The synthesis of the silver(I) analog [$Ph_2B(6-(CF_3)Py)_2$]Ag(CO) (**12**) was attempted using K[$Ph_2B(6-(CF_3)Py)_2$], CF_3SO_3Ag and CO, but the resulting product (which shows a strong IR band at 2164 cm^{-1}) could not be characterized satisfactorily thus far due to facile CO loss. The copper complex **11** is a colorless solid and does not lose bound CO easily under reduced pressure. The IR spectrum of the crystalline material shows strong bands corresponding to the CO stretch at 2110 and 2100 cm^{-1} for **11**. The same two bands were observed in Nujol but at a different intensity ratio. The presence of two bands could be a result of having two slightly different environments for Cu-CO (as noted below, there are three crystallographically different molecules of **11** in the asymmetric unit). ^1H and ^{13}C NMR of $[Ph_2B(6\text{-}(CF_3)Py)_2]Cu(CO)$ at room temperature show one set of well resolved pyridyl proton signals and carbons and a singlet in ^{19}F NMR peaks indicating the presence of equivalent pyridyl donor arms.



Scheme 4. Synthesis of copper(I) and silver(I) carbon monoxide complexes $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Cu(CO)$ (**13**) and $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Ag(CO)$ (**14**) supported by the tris(2-pyridyl)borate, $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]^-$

The tris(pyridyl)borate versions of copper(I) and silver(I) complexes, $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Cu(CO)$ (**13**) and $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Ag(CO)$ (**14**) were prepared following analogous methods utilized for the **8** and **9**, but using CO (~ 1 atm) instead of *t*-BuNC (Scheme 4). These compounds are obtained as colorless crystalline solids from their hexane solutions saturated with carbon monoxide at -20 °C. The Cu-CO interaction in [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Cu(CO) (**13**) appears to be fairly strong, which is evidenced from the stability towards CO loss under reduced pressure, whereas [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Ag(CO) (**14**) loses its CO under reduced pressure quite easily. They display typically strong bands in their IR spectra at 2103 and 2144 cm^{-1} for the CO stretch. Note that the $\overline{\upsilon}$(CO) of **14** is essentially the same as that of the free CO, which is quite rare as the vast majority of silver-CO complexes have much higher CO frequencies.

The copper(I) complex [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Cu(CO) (**13**) shows two different sets of signals for bound and free pyridyl arms in its ^1H, ^{13}C and ^{19}F NMR spectra, at room temperature, indicating the κ^2-mode of coordination of the scorpionate. The NMR data [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Ag(CO) (**14**) were collected in the presence of excess CO in $CDCl_3$ to minimize the by-product formation due to CO loss. The ^1H NMR spectrum shows averaged and broadened signals for the pyridyl arms at room temperature. The silver bounds carbon monoxide ^{13}C resonance was observed at δ 176.4 ppm, which is in good agreement with the literature reports.[59]

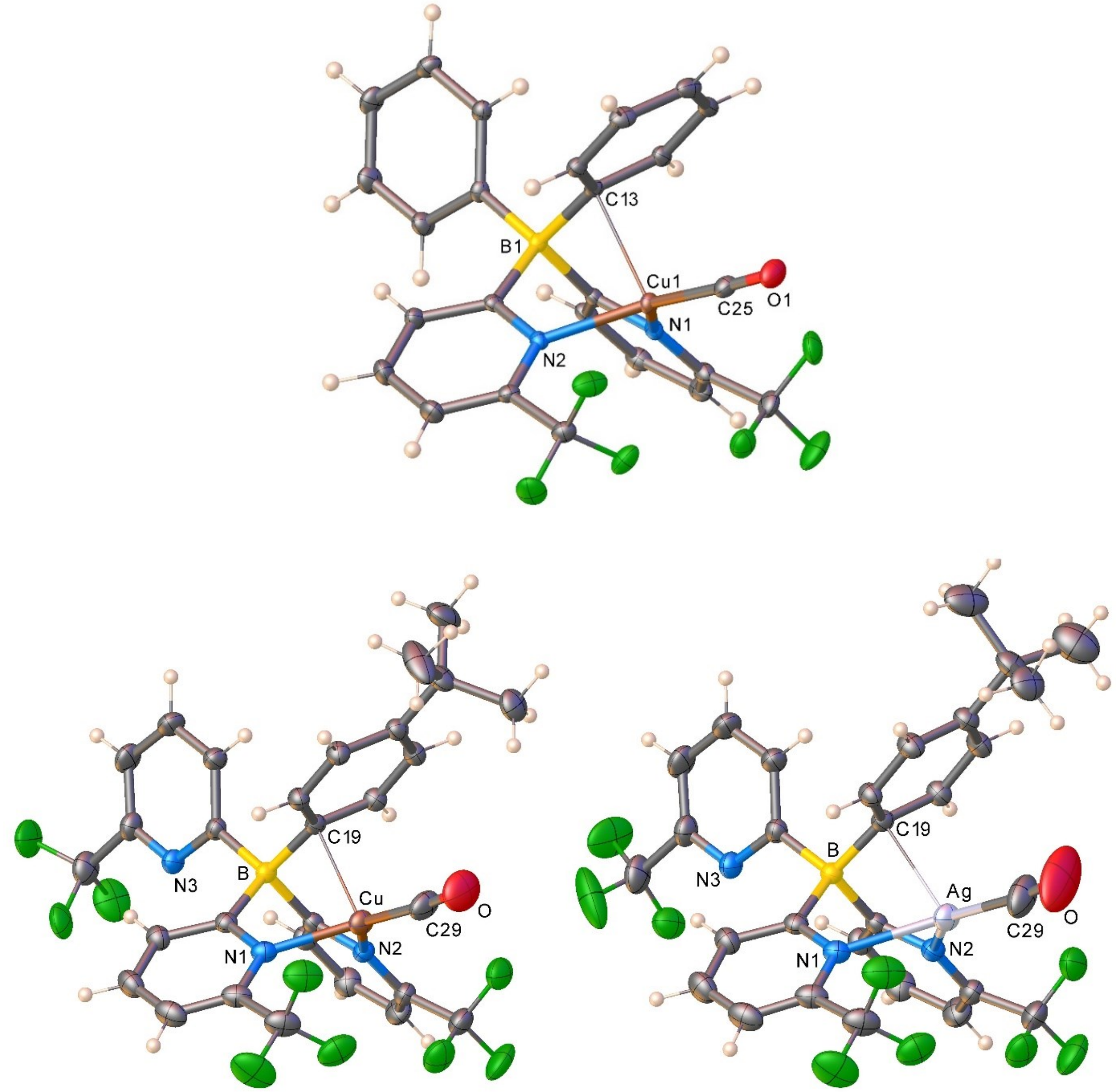


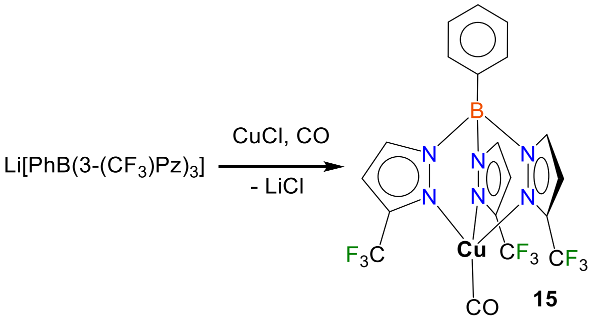
Figure 3. Molecular structure of [$Ph_2B(6\text{-}(CF_3)Py)_2$]Cu(CO) (**11**) (Top), [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Cu(CO) (**13**) (Bottom-left) and [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Ag(CO) (**14**) (Bottom-right). Selected bond distances (Å) and angles (°) are given in Table 3.

Compounds **11, 13** and **14** produced quality crystals suitable for X-ray crystallography. The [$Ph_2B(6\text{-}(CF_3)Py)_2$]Cu(CO) (**11**) crystallizes with three chemically similar but crystallographically different molecules in the asymmetric unit. The molecular structures of **11, 13** and **14** are illustrated in Figure 3. Selected bond distances and angles are given in Table 3. All three complexes feature essentially trigonal planar metal sites (e.g., sum of the angles at M involving two nitrogen atoms and carbonyl carbon deviate only very little from the ideal 360°), and κ^2-bound poly(pyrazolyl)borates. They have flanking B-aryl groups in close proximity to metal sites, but the closest M•••C(aryl) distances are much longer than the typical Cu-C(sp^2) and Ag-C(sp^2) covalent distances (2.05 and 2.18 Å).[70] The Cu•••C(B) separation in **11** and **13** is much shorter than those found in the related isocyanide complexes. This could be a result of having a smaller ligand CO (instead of *t*-BuNC) on copper in **11** and **13** and reduced steric interactions with the flanking aryl groups. The difference in Ag•••C(B) distance in **14** and **9** is much smaller. Most other features, however, are similar between the analogous metal fragments with CO and *t*-BuNC donors (see Tables 1 and 3).

Table 3. Selected bond distances (Å), angles (°), and IR spectroscopic data (carbonyl stretch in cm^{-1}) of $[Ph_2B(6\text{-}(CF_3)Py)_2]M(CO)$ and $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]M(CO)$ (M = Cu, Ag). The M•••C(B) is the ipso-carbon separation between the M and flanking phenyl group (value given in italics). ∑ at M represents the sum of angles at M involving two nitrogen atoms bonded to M and the carbon of CO.

Molecule/Parameter	$[Ph_2B(6\text{-}(CF_3)Py)_2]Cu(CO)$[a] (**11**)	$[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Cu(CO)$ (**13**)	$[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Ag(CO)$ (**14**)
C-O	1.115(3)	1.115(5)	1.099(4)
M-C	1.822(3)	1.807(4)	2.038(3)
M-N	2.038(2), 2.036(2)	2.046(3) 2.043(3)	2.3085(17), 2.2977(16)
M••C(B)	*2.374(2)*	*2.354(3)*	*2.5251(17)*
M-C-O	176.9(3)	175.5(4)	173.4(3)
N-M-N	93.14(8)	92.50(10)	84.69(6)
∑ at M	356.8	357.0	357.6
$\overline{\upsilon}$(CO)	2110, 2100	2103	2144

[a] Data from only one of the three chemically similar molecules in the asymmetric unit are listed here. Complete details are in the ESI section.



Scheme 5. Synthesis of [PhB(3-(CF$_3$)Pz)$_3$]Cu(CO) (**15**) supported by a tris(pyrazolyl)borate

The tris(1-pyrazolyl)borate [PhB(3-(CF$_3$)Pz)$_3$]$^-$ may be considered as a close relative of the "fluoroalkyl-lined" tris(2-pyridyl)borate ligand [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]$^-$ (**3**).[93-94] Thus, to further compare those two ligand families, we prepared the copper(I) carbonyl complex of the former. The [PhB(3-(CF$_3$)Pz)$_3$]Cu(CO) (**15**) was obtained from a reaction between Li[PhB(3-(CF$_3$)Pz)$_3$] and CuCl and CO (1 atm) (Scheme 5). This molecule displays its CO stretch in the IR spectrum at 2112 cm^{-1}. The crystal structure of **15** is illustrated in Figure 4. It is a tetrahedral copper complex. Interestingly, the tris(pyrazolyl)borate in **15** acts as a typical tripodal κ^3-ligand which uses all three pyrazolyl donor arms (in contrast to **13**, which uses only two N-donors).

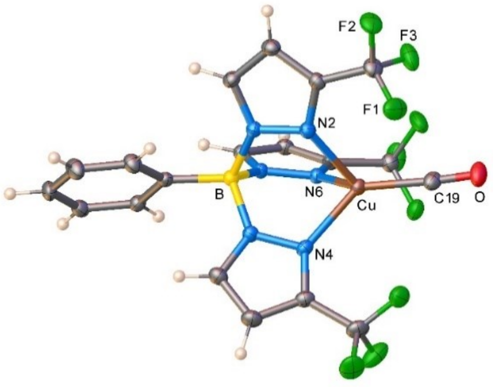


Figure 4. Molecular structure of [PhB(3-(CF$_3$)Pz)$_3$]Cu(CO) (**15**). Selected bond distances (Å) and angles (°): Cu-N2 2.0742(18), Cu-N4 2.0248(18), Cu-N6 2.0563(18), Cu-C19 1.804(2), O-C19 1.126(3), N4-Cu-N2 90.02(7), N4-Cu-N6 88.39(7), N6-Cu-N2 90.82(7), O-C19-Cu 176.0(2)

Table 4. Selected, structurally characterized Cu(I)-CO and Ag(I)-CO complexes of poly(pyridyl)borates and poly(pyrazolyl)borates and some of their structural and spectroscopic parameters. The ū(CO) of free CO = 2143 cm^{-1}. Data for the second and third molecule in the asymmetric unit in *italics*.

Complex	**ū(CO)/cm^{-1}**	**M-C/Å**	**Ref.**
[Ph$_2$B(6-(CF$_3$)Py)$_2$]Cu(CO) (**11**)	2110, 2101	1.822(3) *1.813(3)* *1.816(3)*	This work
[*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Cu(CO) (**13**)	2103	1.808(5)	This work
[Ph$_2$B(3-(CF$_3$)Pz)$_2$]Cu(CO)	2117	1.8028(16)	18
[Ph$_2$B(3-(SF$_5$)Pz)$_2$]Cu(CO)	2121	1.803(2) *1.807(2)*	18
[PhB(3-(CF$_3$)Pz)$_3$]Cu(CO) (**15**)	2112	1.804(2)	This work
[HB(3-(CF$_3$)Pz)$_3$]Cu(CO)	2100	1.790(4)	95
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Cu(CO)	2137	1.808(4)	80
[HB(3,5-(CH$_3$)$_2$Pz)$_3$]Cu(CO)	2060	1.785(4)	96-97
[HB(3,5-(*i*-Pr)$_2$Pz)$_3$]Cu(CO)	2056	1.769(8)	98
[*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Ag(CO) (**14**)	2144	2.038(3)	This work
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(CO)	2178	2.037(5)	58
[MeB(3-(C$_2$F$_5$)Pz)$_3$]Ag(CO)	2153	2.030(4)	59
[MeB(3-(Mes)Pz)$_3$]Ag(CO)	2125	1.994(3)	60

Table 4 provides a list of related scorpionate ligand supported copper and silver carbonyl complexes and some key parameters. Note that one of the reasons for investigating these Cu-CO and Ag-CO complexes **11, 13-15** is to probe the scorpionate ligand effects on the metal site using the CO stretch, and to compare the new poly(pyridyl)borate and better-known poly(pyrazolyl)borate systems. Computational analysis[30, 99] of molecules such as [Ph$_2$B(3-(CF$_3$)Pz)$_2$]Cu(CO), [Ph$_2$B(3-(CH$_3$)Pz)$_2$]Cu(CO), [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(CO), and [MeB(3-

(Mes)Pz)$_3$]Ag(CO) indicate that the LM and CO (L = scorpionate) is mainly electrostatic. Traditional σ-donor/π-acceptor interactions usually explained by the Dewar-Chatt-Duncanson model are also significant.[100-101] Overall, the strength of the electrostatic attraction and the degree of π-backbonding between LM and CO fragments correlate well with the observed $\bar{\upsilon}$(CO), which gets higher with more weakly donating ligand support on a metal. Computational work on the above systems also shows that the copper complexes display stronger LCu→CO π-backdonation relative to their silver counterparts.

The [Ph$_2$B(6-(CF$_3$)Py)$_2$]Cu(CO) (**11**) and [Ph$_2$B(3-(CF$_3$)Pz)$_2$]Cu(CO)[18] are closely related and their $\bar{\upsilon}$(CO) suggest that the former has a slightly more electron-rich metal site. Compounds **13** and **15** also provide $\bar{\upsilon}$(CO) data to support the contention that the poly(pyridyl)borates are slightly better donors relative to the related poly(pyrazolyl)borates. Keep in mind however that the coordination modes are very different in **13** and **15** making this latter comparison less reliable. The computed proton affinities of [PhB(6-(CF$_3$)Py)$_3$]$^-$ and [PhB(3-(CF$_3$)Pz)$_3$]$^-$ are 1120.0 and 1069.2 kJ/mol, respectively, indicate that the pyridyl-borate analog is a better donor. Among the reported silver-carbonyl complexes, the [MeB(3-(C$_2$F$_5$)Pz)$_3$]Ag(CO) is perhaps the closest relative of [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Ag(CO) (**14**). Compound **14** has a slightly lower CO stretch value, suggesting that its metal site is less Lewis acidic, perhaps due to slightly better donor feature of [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]$^-$ ligand. Unfortunately, these silver(I) complexes also feature different coordination modes (i.e., κ^3 and κ^2) of the scorpionate. Overall, more closely related systems from two scorpionate ligand families are needed for a better comparison of, and to reach a solid conclusion on, ligand donor features.

The data presented in Table 4 show that molecules with weakly donating supporting ligands have slightly longer M-CO distances, but esds associated with the measurement overshadows the differences when ligand donor properties are similar. The Cu-CO distances are clearly longer than the Ag-CO bond distances, because the latter involves a metal ion with a larger covalent radius. The longer distances in Ag-CO bonds could also contribute to the lower Ag→CO backbonding, resulting in higher ῡ(CO) values.

Conclusions

A new, chemically robust, bis(2-pyridyl)borate $[Ph_2B(6\text{-}(CF_3)Py)_2]^-$ with fluoro-alkyl groups adjacent to the metal coordination pocket has been synthesized and utilized as a ligand support for copper(I) and silver(I) ions containing *t*-BuNC and carbon monoxide donors. Related molecules involving a tris(2-pyridyl)borate were also investigated. These poly(pyridyl)borate metal complexes, including those with three pyridyl donor arms, use only two pyridyl moieties for metal ion coordination, and feature trigonal planar geometry at the metal. The tris(pyrazolyl)borate $[PhB(3\text{-}(CF_3)Pz)_3]Cu(CO)$ in contrast acts as a κ^3-donor, generating a tetrahedral copper site. Flanking B-aryl groups close to metal sites are also a common feature in copper and silver complexes supported by $[Ph_2B(6\text{-}(CF_3)Py)_2]^-$ and $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]^-$. Isolable carbonyl complexes of silver(I) such as $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Ag(CO)$ stabilized here are rare among metal carbonyls. The CN stretching frequencies of fluorinated poly(2-pyridyl)borate supported *t*-BuNC complexes of Cu(I) and Ag(I) are notably higher than that of the free *t*-BuNC. The CO stretch of the analogous metal carbonyls lies closer to that of the free CO, indicating the presence of fairly Lewis acidic metal sites. The CO stretching frequencies suggest that poly(pyridyl)borates are slightly better donors relative to the related poly(pyrazolyl)borates. We are currently developing additional poly(2-pyridyl)borate chelators involving different substituents on boron and pyridyl rings, and their chemistry with metal ions.

Experimental:

All preparations and manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a MBraun drybox equipped with a -25 °C refrigerator. Commercially available solvents were purified and dried by standard methods. Glassware was oven dried overnight at 150 ˚C. NMR spectra were acquired at 25 ˚C, on a JEOL Eclipse 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 126 MHz; ^{19}F, 471 MHz). ^{19}F NMR values were referenced to external $CFCl_3$. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were referenced internally to solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR; DMSO-d_6: 2.50 ppm for ^{1}H NMR, 39.52 ppm for ^{13}C NMR), or externally to $SiMe_4$ (0 ppm). ^{1}H NMR chemical shifts are reported in ppm and coupling constants (J) are reported in Hertz (Hz). Abbreviations used for signal assignments: Ph = phenyl, Py = pyridyl, Py^n = non-coordinated pyridine, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, brs = broad singlet. NMR solvents were purchased from Cambridge Isotopes Laboratories and used as received. Carbon monoxide (UHP grade) gas was purchased from Airgas. Elemental analyses were performed using a Perkin-Elmer Model 2400 CHN analyzer. Bromodiphenylborane,[102] mesityl copper,[102-103] [t-$BuC_6H_4B(6$-$(CF_3)Py)_3]H$ (**10**),[30] K[t-$BuC_6H_4B(6$-$(CF_3)Py)_3$],[30] $\{(6$-(CF_3)-2-$Py)MgCl\}_2\bullet(THF)_3$,[30] $Li[PhB(3$-$(CF_3)Pz)_3]$[93] were prepared according to literature procedures. All other reagents were obtained from commercial sources and used as received. Silver complexes were prepared in reaction vessels protected from light using aluminum foil.

Synthesis of [$Ph_2B(6\text{-}(CF_3)Py)_2$]H (5)

Bromodiphenylborane (2.50 g, 10.21 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of {(6-(CF_3)-2-Py)MgCl}$_2$•(THF)$_3$ (7.05 g, 14.23 mmol) in CH_2Cl_2 (40 mL) at 0 ˚C. The resulting dark red mixture was slowly warmed to room temperature and kept stirring for 48 h. The reaction mixture was then poured into an aqueous Na_2CO_3 solution (14.0 g in 120 mL H_2O) and stirred for 1 h, and then extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue dissolved in CH_2Cl_2 (50 mL), activated charcoal was added and then filtered through small pad of celite and evaporated to dryness. The resulting residue was recrystallized from acetone to obtain the desired [Ph_2B(6-(CF_3)Py)$_2$]H as white crystalline solid. Yield: 4.20 g (90%). Anal. Calc. $C_{24}H_{17}B_1F_6N_2$: C, 62.91; H, 3.74; N, 6.11%. Found: C, 62.04; H, 3.65; N, 5.75. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.91 (s, 1H, NH), 7.87 (d, *J* = 8.0 Hz, 2H, Py), 7.81 (t, *J* = 7.8 Hz, 2H, Py), 7.60 (dd, *J* = 7.5, 1.0 Hz, 2H, Py), 7.27 – 7.15 (m, 10H, Ph). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.79 (q, $^1J_{C\text{-}B}$ = 51.6 Hz, Py), 154.82 (q, $^1J_{C\text{-}B}$ = 52.8 Hz, Ph), 140.27 (q, $^2J_{C\text{-}F}$ = 37.2 Hz, Py), 137.89 (Py), 135.94 (Py), 134.89 (Ph), 127.53 (Ph), 125.07 (Ph), 121.02 (q, $^1J_{C\text{-}F}$ = 274.7 Hz, CF_3), 117.63 (Py). ^{19}F NMR (471 MHz, $CDCl_3$): δ = -66.83 (s).

Synthesis of [$Ph_2B(6\text{-}(CF_3)Py)_2$]Cu(CNBu^t) (6)

To a mixture of [Ph_2B(6-(CF_3)Py)$_2$]H (130 mg, 284 μmol) and mesityl copper (57 mg, 312 μmol) in a 50 mL Schlenk flask were added anhydrous toluene (15 mL) and *t*-BuNC (0.34 mL, 1.1 M in toluene, 369 µmol) under inert atmosphere and kept stirring for 3 h. The solvent was then removed reduced pressure, and the compound was recrystallized from hexane at -20 ˚C to obtain colorless X-ray quality single crystals of $[Ph_2B(6\text{-}(CF_3)Py)_2]Cu(CNBu^t)$. Yield: 125 mg (77%). Anal. Calc. $C_{29}H_{25}B_1Cu_1F_6N_3$: C, 57.68; H, 4.17; N, 6.96%. Found: C, 57.43; H, 4.07; N, 6.69%. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.8 Hz, 2H, Py), 7.61 (t, *J* = 7.8 Hz, 2H, Py), 7.45 (dd, *J* = 7.7, 1.1 Hz, 2H, Py), 7.24 -7.18 (m, 6H, Ph), 6.97 (brs, 4H, Ph), 1.38 (s, 9H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 187.19 (q, $^1J_{C\text{-}B}$ = 51.6 Hz, Py), 153.78 (q, $^1J_{C\text{-}B}$ = 49.2 Hz, Ph), 145.54 (q, $^2J_{C\text{-}F}$ = 33.6 Hz, Py), 137.13 (Ph), 136.33 (CN), 134.95 (Py), 133.02 (Py), 127.07 (Ph), 124.85 (Ph), 122.03 (q, $^1J_{C\text{-}F}$ = 273.5 Hz, CF_3), 116.80 (Py), 55.48 ($C\text{-}CH_3$), 30.45 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$): δ = -66.82. ATR-IR (single crystals, selected peaks, cm^{-1}): 2178 (CN stretch).

Synthesis of $K[Ph_2B(6\text{-}(CF_3)Py)_2]$

To a suspension of KH (0.26 g, 6.55 mmol) in anhydrous THF (25 mL) at 0 °C was slowly added a solution of $[Ph_2B(6\text{-}(CF_3)Py)_2]H$ (2.00 g, 4.36 mmol) in THF (25 mL). After complete ceasing of hydrogen gas evolution, the reaction mixture was allowed to warm to room temperature and then kept stirring for 12 h. The solution was filtered through a celite packed frit to remove unreacted KH. The solvent in the filtrate collected was removed under reduced pressure to obtain $K[Ph_2B(6\text{-}(CF_3)Py)_2]$ as a white solid. The compound was further dried at 90 °C for 6 h under reduced pressure to remove all trace solvent. Yield: 2.00 (92%). This was used directly in the next steps. ^1H NMR (500 MHz, DMSO-d_6): δ = 7.46 (t, *J* = 7.7 Hz, 2H, Py), 7.40 (d, *J* = 7.8 Hz, 2H, Py), 7.28 (d, *J* = 7.4 Hz, 2H, Py), 7.24 (brs, 4H, Ph), 6.96 (t, *J* = 7.4 Hz, 4H, Ph), 6.86 (t, *J* = 7.2 Hz, 2H, Ph). ^{13}C NMR (126 MHz, MHz, DMSO-d_6): δ = 189.52 (q, $^1J_{C\text{-}B}$ = 53.9 Hz, Py), 161.10 (q, $^1J_{C\text{-}B}$ = 50.4

Hz, Ph), 140.39 (q, ${}^2J_{C\text{-}F}$ = 28.8 Hz, Py), 135.43 (Py/Ph), 132.58 (Py/Ph), 125.56 (Py/Ph), 122.26 (Py/Ph), 122.85 (q, ${}^1J_{C\text{-}F}$ = 274.7 Hz, CF_3), 113.84 (Py/Ph). ^{19}F NMR (471 MHz, DMSO-d_6): δ = - 66.12.

Synthesis of [$Ph_2B(6\text{-}(CF_3)Py)_2$]Ag(CNBu^t) (7)

To a mixture of of K[$Ph_2B(6\text{-}(CF_3)Py)_2$] (130 mg, 209 µmol) and AgOTf (56 mg, 219 µmol) in a 50 mL Schlenk flask, covered with aluminum foil were added anhydrous dichloromethane (20 mL) and *t*-BuNC (0.38 mL, 1.0 M in toluene, 418 µmol) under inert atmosphere, kept stirring for 3 h. The reaction mixture was then cannula filtered through a celite packed frit to remove KOTf. The solvent was then removed reduced pressure and the compound was recrystallized from hexane at -20 ˚C to obtain colorless X-ray quality single crystals of [$Ph_2B(6\text{-}(CF_3)Py)_2$]Ag(CNBu^t). Yield: 140 mg (86%). Anal. Calc. $C_{29}H_{25}Ag_1B_1F_6N_3$: C, 53.74; H, 3.89; N, 6.48%. Found: C, 53.18; H, 3.80; N, 6.29%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.9 Hz, 2H, Py), 7.56 (t, *J* = 7.8 Hz, 2H, Py), 7.39 (dd, *J* = 7.7, 1.1 Hz, 2H, Py), 7.25 – 7.22 (m, 4H, Ph), 7.18 – 7.04 (m, 6H, Ph), 1.47 (s, 9H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 187.70 (q, ${}^1J_{C\text{-}B}$ = 49.2 Hz, Py), 154.65 (q, ${}^1J_{C\text{-}B}$ = 50.4 Hz, Ph), 146.17 (q, ${}^2J_{C\text{-}F}$ = 32.4 Hz, Py), 138.90 (CN), 136.28 (Ph), 134.84 (Py), 133.26 (Py), 127.18 (Ph), 124.45 (Ph), 122.15 (q, ${}^1J_{C\text{-}F}$ = 274.7 Hz, CF_3), 116.06 (Py), 56.65 (C-CH_3), 30.28 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$): δ = -67.65. ATR-IR (single crystals, selected peaks, cm^{-1}): 2200 (CN stretch).

Synthesis of [*t*-$BuC_6H_4B(6\text{-}(CF_3)Py)_3$]Cu(CNBu^t) (8)

To a mixture of [*t*-$BuC_6H_4B\{2\text{-}(6\text{-}(CF_3)Py)\}_3$]H (0.13 g, 223 µmol) and mesityl copper (45 mg, 245 µmol) in a 50 ml Schlenk flask were added anhydrous toluene (15 mL) and *t*-BuNC (0.67 mL, 1.0 M in toluene, 670 µmol) under inert atmosphere and kept stirring for 3 h. The solvent was then removed reduced pressure, and the compound was recrystallized from hexane at -20 ˚C to obtain colorless X-ray quality single crystals of [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Cu(CNBu^t). Yield: 125 mg (77%). Anal. Calc. C$_{33}$H$_{31}$B$_1$ Cu$_1$F$_9$N$_4$: C, 54.37%; H, 4.29%; N, 7.69%. Found: C, 53.91%; H, 4.38%; N, 7.33%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.00 (brs, 3H, Py), 7.57 (t, *J* = 7.3 Hz, 3H, Py), 7.42 (dd, *J* = 7.8, 1.0 Hz, 3H, Py), 7.24 (d, *J* = 8.1 Hz, 2H, Ph), 6.80 (s, 2H, Ph), 1.40 (s, 9H, CH$_3^{t\text{BuNC}}$), 1.35 (s, 9H, CH$_3^{t\text{BuPh}}$). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 185.30 (brs, Py$_{\text{C-B}}$), 148.72 (Ph), 145.78 (brs, CCF$_3$), 137.37 (Ph), 135.15 (Py), 132.71 (Py), 122.28 (q, $^1J_{C\text{-}F}$ = 274.7 Hz, CF$_3$), 124.23 (Ph), 116.52 (Py), 55.65 (C-CH$_3^{t\text{BuNC})}$, 34.48 (C-CH$_3^{t\text{BuPh}}$), 31.78 (CH$_3^{t\text{BuPh}}$), 30.43 (CH$_3^{t\text{BuNC})}$, Ph$_{\text{C-B}}$ not observed, Cu-CN not observed. ^{19}F NMR NMR (471 MHz, CDCl$_3$): δ = -66.71 (br), -67.77 (br). ATR-IR (single crystals, selected peaks, cm^{-1}): 2168 (CN stretch).

Synthesis of [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Ag(CNBu^t) (9)

To a mixture of of K[*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$] (130 mg, 209 µmol) and AgOTf (56 mg, 219 µmol) in a 50 ml Schlenk flask, covered with aluminum foil were added anhydrous dichloromethane (20 mL) and *t*-BuNC (0.63 mL, 1.0 M in toluene, 630 µmol) under inert atmosphere, kept stirring for 3 h. The reaction mixture was then cannula filtered through a celite packed frit to remove KOTf. The solvent was then removed reduced pressure and the compound was recrystallized from hexane at -20 ˚C to obtain colorless X-ray quality single crystals of [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Ag(CNBu^t). Yield: 135 mg (83%). Anal. Calc. C$_{33}$H$_{31}$ Ag$_1$B$_1$F$_9$N$_4$: C, 51.26%; H, 4.04%; N, 7.25%. Found: C, 50.90%; H, 3.99%; N, 6.89%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.76 (brs, 3H, Py), 7.52 (t, *J* = 7.8 Hz, 3H, Py), 7.37 (dd, *J* = 7.7, 1.1 Hz, 3H, Py), 7.28 (d, *J* = 8.2 Hz, 2H, Ph), 6.91 (brs, 2H, Ph), 1.46 (s, 9H, CH$_3^{t\text{BuNC}}$), 1.33 (s, 9H, CH$_3^{t\text{BuPh}}$). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 184.93 (q, $^1J_{C\text{-}B}$ = 57.6 Hz, Py), 147.93 (Ph), 147.42 (q, $^1J_{C\text{-}B}$ = 40.8 Hz, Ph), 145.94 (q, $^2J_{C\text{-}F}$ = 28.8 Hz, Py), 139.87

(CN), 136.30 (Ph), 134.93 (Py), 132.88 (Py), 124.52 (Ph), 122.40 (q, $^1J_{C\text{-}F}$ = 273.5 Hz, CF_3), 115.90 (Py), 56.67 ($C\text{-}CH_3^{tBuNC)}$,$^{)}$, 34.45 ($C\text{-}CH_3^{tBuPh}$), 31.64 (CH_3^{tBuPh}),, 30.30 ($CH_3^{tBuNC)}$. ^{19}F NMR (471 MHz, $CDCl_3$): δ = -67.29. ATR-IR (single crystals, selected peaks, cm^{-1}): 2198 (CN stretch).

Synthesis of $[Ph_2B(6\text{-}(CF_3)Py)_2]Cu(CO)$ (11)

To a mixture of $[Ph_2B(6\text{-}(CF_3)Py)_2]H$ (130 mg, 284 µmol) and mesityl copper (57 mg, 312 µmol) was added anhydrous toluene and then bubbled with carbon monoxide. The reaction mixture was kept stirring for 3 h and then solvent was removed reduced pressure. The resulted compound was dissolved in carbon monoxide saturated hexane and kept at -20 °C freezer overnight to get X-ray quality colorless crystals of $[Ph_2B(6\text{-}(CF_3)Py)_2]Cu(CO)$. Yield: 105 mg (67%). Anal. Calc. $C_{25}H_{16}B_1Cu_1F_6N_2O_1$: C, 54.72; H, 2.94; N, 5.10%. Found: C, 54.13; H, 2.84; N, 4.79%. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.8 Hz, 2H, Py), 7.69 (t, *J* = 7.8 Hz, 2H, Py), 7.51 (dd, *J* = 7.7, 1.3 Hz, 2H, Py), 7.27 (br, 8H, Ph), 6.80 (brs, 2H, Ph). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 186.94 (q, $^1J_{C\text{-}B}$ = 49.2 Hz, Py), 170.36 (CO), 152.54 (br, $Ph_{C\text{-}B}$), 145.58 (q, $^2J_{C\text{-}F}$ = 33.6 Hz, Py), 138.85 (Ph), 136.01 (Py), 133.15 (Py), 127.59 (Ph), 126.69 (Ph), 122.80 (q, $^1J_{C\text{-}F}$ = 274.7 Hz, CF_3), 117.27 (Py). ^{19}F NMR (471 MHz, $CDCl_3$): δ = -67.19 (s). ATR-IR (single crystals, selected peaks, cm^{-1}): 2110 (C≡O stretch), 2100 (C≡O stretch); samples in Nujol: 2111 (C≡O stretch), 2101 (C≡O stretch).

Synthesis of $[t\text{-}BuC_6H_4B(6\text{-}(CF_3)Py)_3]Cu(CO)$ (13)

To a mixture of $[t\text{-}BuC_6H_4B\{2\text{-}(6\text{-}(CF_3)Py)\}_3]H$ (100 mg, 171 µmol) and mesityl copper (35 mg, 282 µmol) was added anhydrous toluene and then bubbled with carbon monoxide. The reaction mixture was kept stirring for 3 h and then solvent was removed reduced pressure. The resulted compound was dissolved in carbon monoxide saturated hexane and kept at -20 °C freezer overnight to get X-ray quality colorless crystals of [*t*-BuC$_6$H$_4$B{2-(6-(CF$_3$)Py)}$_3$]Cu(CO). Yield: 90 mg (78%). Anal. Calc. C$_{29}$H$_{22}$B$_1$ Cu$_1$F$_9$N$_3$O$_1$: C, 51.69%; H, 3.29%; N, 6.24%. Found: C, 51.56%; H, 3.24%; N, 6.07%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.15 (d, *J* = 7.8 Hz, 2H, Py), 7.68 (t, *J* = 7.8 Hz, 2H, Py), 7.55 (t, *J* = 7.7 Hz, 1H, Py^n), 7.47 (two overlapped doublets, 2H, Py; 1H, Py^n), 7.34 (d, *J* = 8.0 Hz, 2H, Py), 6.86 (brs, 3H, Py; 1H Py^n), 1.34 (s, 9H, CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 185.48 (q, $^1J_{C\text{-}B}$ = 51.6 Hz, Py), 180.42 (q, $^1J_{C\text{-}B}$ = 72.0 Hz, Py^n), 170.46 (CO), 150.85 (Ph), 146.66 (q, $^2J_{C\text{-}F}$ = 35.6 Hz, Py^n), 145.36 (q, $^2J_{C\text{-}F}$ = 34.8 Hz, Py), 144.40 (q, $^1J_{C\text{-}B}$ = 49.2 Hz, Ph), 138.58 (Ph), 136.34 (Py), 135.22 (Py^n), 133.05 (Py), 132.50 (Py^n), 125.03 (Ph), 122.76 (q, $^1J_{C\text{-}F}$ = 274.7 Hz, CF$_3$- Py^n), 121.81 (q, $^1J_{C\text{-}F}$ = 273.5 Hz, CF$_3$- Py), 117.28 (Py), 116.00 (Py^n), 34.62 (C-CH$_3$), 31.59 (CH$_3$). ^{19}F NMR NMR (471 MHz, CDCl$_3$): δ = -67.26 (s, 6F, CF$_3$-Py), -67.96 (s, 3F, CF$_3$-Py^n). ATR-IR (single crystals, selected peaks, cm^{-1}): 2103 (C≡O stretch).

Synthesis of [*t*-BuC$_6$H$_4$B(6-(CF$_3$)Py)$_3$]Ag(CO) (14)

To a mixture of K[*t*-BuC$_6$H$_4$B{2-(6-(CF$_3$)Py)}$_3$] (100 mg, 161 µmol) and AgOTf (43 mg, 169 mmol) in a 50 mL Schlenk flask, covered with aluminum foil was added anhydrous dichloromethane and then bubbled with carbon monoxide. The reaction mixture was kept stirring for 3 h then cannula filtered through a celite packed frit to remove KOTf. The solvent was then removed reduced pressure and the compound was recrystallized from carbon monoxide saturated hexane at -20 ˚C to obtain colorless X-ray quality single crystals of [*t*-BuC$_6$H$_4$B{2-(6-(CF$_3$)Py)}$_3$]Ag(CO). Yield: 90 mg (78%). The CO loss is facile too facile to dry the sample for CHN analysis. ATR-IR (single crystals, selected peaks, cm^{-1}): 2144 (C≡O stretch). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.27 (brs, 3H, Py), 7.58 (brs, 3H, Py), 7.42 (d, *J* = 7.7 Hz, 3H, Py), 7.36 (d, *J* = 8.1 Hz, 2H, Ph), 6.94 (br, 2H, Ph), 1.34 (s, 9H,

CH_3). ^{19}F NMR (471 MHz, $CDCl_3$): δ = -67.75 (s). ^{13}C NMR (126 MHz, $CDCl_3$, selected peaks): δ = 176.4 (CO).

Synthesis of [PhB(3-(CF_3)Pz)$_3$]Cu(CO) (15)

Li[PhB(3-(CF_3)Pz$_3$)] (0.26 g, 0.520 mmol) and CuCl (0.06 g, 0.6 mmol) were mixed in a Schlenk tube filled with 20 mL of degassed CH_2Cl_2 at room temperature. This mixture stirred for about 1 h at CO atmosphere and was filtered. The solvent was removed from the filtrate under reduced pressure to obtain the product as a grayish-white powder with a yield of 90%. It was recrystallized from hexane/CH_2Cl_2 to obtain colorless crystal of [PhB(3-(CF_3)Pz)$_3$]CuCO. Anal. Calc. for $C_{19}H_{14}BCuF_9N_6O$: C, 38.83; H, 2.40; N, 14.30%, Found: C, 38.51; H, 2.10; N, 13.82. ^1H NMR (500MHz, $CDCl_3$): δ 7.87 (br, 3H, Pz-*H*), 7.55 (br, 5H, Ph-*H*), 6.46 (s, 3H, Pz-*H*). ^{19}F NMR (471 MHz, $CDCl_3$): δ -60.9 (s, C*F$_3$*). ATR-IR (selected peaks, cm^{-1}): 2112 (C≡O stretch).

X-ray Data Collection and Structure Determinations

A suitable crystal covered with a layer of hydrocarbon/Paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data of [Ph_2B(6-(CF_3)Py)$_2$]Cu(CNBu^t) (**6**), [Ph_2B(6-(CF_3)Py)$_2$]Ag(CNBu^t) (**7**), [*t*-BuC_6H_4B(6-(CF_3)Py)$_3$]Ag(CNBu^t) (**9**), [Ph_2B(6-(CF_3)Py)$_2$]Cu(CO) (**11**) , [*t*-BuC_6H_4B(6-(CF_3)Py)$_3$]Ag(CO) (**14**), and [PhB(3-(CF_3)Pz)$_3$]Cu(CO) (**15**) were on a Bruker instrument with Smart ApexII detector, while the data of [*t*-BuC_6H_4B(6-(CF_3)Py)$_3$]Cu(CNBu^t) (**8**) and [*t*-BuC_6H_4B(6-(CF_3)Py)$_3$]Cu(CO) (**13**) were collected on a Bruker D8 Quest with a PHOTON II 7 CPAD detector. Both instruments were equipped with an Oxford Cryosystems 700 series cooler, a graphite monochromator, and a Mo

Kα fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed using the Bruker Apex program suite. Data were collected at 100(2) K (except the data of **13** and **14** at 200(2) K and 150(2) K, respectively, due to crystal cracking issues). Absorption corrections were applied by using SADABS for all except, for which TWINABS was used.[104] Compound **13** shows non-merohedral twinning (over two domains), which was resolved satisfactorily using Cell_Now. Initial atomic positions were located by SHELXT,[105] and the structures of the compounds were refined by the least-squares method using SHELXL[106] within Olex2 GUI.[107] All the non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were included in their calculated positions and refined as riding on the atoms to which they are joined. Compound **11** crystallizes in P -1 space group with three chemically identical molecules in the asymmetric unit. Molecules of **7** sit on a mirror plane containing Ag, B and *t*-BuNC moieties. X-ray structural figures were generated using Olex2.[107]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H, and other NMR spectra, IR spectra, crystallographic data and additional figures (PDF)

Accession Codes

CCDC 2157354-2157361 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

H. V. Rasika Dias
Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, United States; orcid.org/0000-0002-2362-1331; Email: dias@uta.edu

Authors

Mukundam Vanga
Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, USA

Anurag Noonikara-Poyil
Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, USA

Jiang Wu
Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, USA

Notes

The authors declare no competing financial interest

Acknowledgements

This material is based upon work supported by the Robert A. Welch Foundation (Grant Y-1289, HVRD) and National Science Foundation under grant number (CHE-1954456, HVRD).

References

1. Eisenstein, O.; Milani, J.; Perutz, R. N., Selectivity of C-H Activation and Competition between C-H and C-F Bond Activation at Fluorocarbons. *Chem. Rev.* **2017,** *117* (13), 8710-8753.

2. Mishra, S.; Daniele, S., Metal-Organic Derivatives with Fluorinated Ligands as Precursors for Inorganic Nanomaterials. *Chem. Rev.* **2015,** *115* (16), 8379-8448.

3. Chen, T.-H.; Popov, I.; Zenasni, O.; Daugulis, O.; Miljanic, O. S., Superhydrophobic perfluorinated metal-organic frameworks. *Chem. Commun.* **2013,** *49* (61), 6846-6848.

4. Grushin, V. V.; Herron, N.; LeCloux, D. D.; Marshall, W. J.; Petrov, V. A.; Wang, Y., New, efficient electroluminescent materials based on organometallic Ir complexes. *Chem. Commun.* **2001,** (16), 1494-1495.

5. Ritter, T.; Day, M. W.; Grubbs, R. H., Rate Acceleration in Olefin Metathesis through a Fluorine-Ruthenium Interaction. *J. Am. Chem. Soc.* **2006,** *128* (36), 11768-11769.

6. Dehnen, S.; Schafer, L. L.; Lectka, T.; Togni, A., Fluorine: A Very Special Element and Its Very Special Impacts on Chemistry. *Inorg. Chem.* **2021,** *86* (23), 16213–16219.

7. Horváth, I. T., Fluorous Biphase Chemistry. *Acc. Chem. Res.* **1998,** *31* (10), 641-650.

8. Carter, C. A. G.; Baker, R. T.; Tumas, W.; Nolan, S. P., Enhanced regioselectivity of rhodium-catalyzed alkene hydroboration in supercritical carbon dioxide. *Chem. Commun.* **2000,** (5), 347-348.

9. Palo, D. R.; Erkey, C., Homogeneous catalytic hydroformylation of 1-octene in supercritical carbon dioxide using a novel rhodium catalyst with fluorinated arylphosphine ligands. *Ind. Eng. Chem. Res.* **1998,** *37* (10), 4203-4206.

10. Trofimenko, S., Recent advances in poly(pyrazolyl)borate (scorpionate) chemistry. *Chem. Rev.* **1993,** *93* (3), 943-80.

11. Pettinari, C.; Santini, C., Polypyrazolylborate and scorpionate ligands. *Compr. Coord. Chem. II* **2004,** *1*, 159-210.

12. Dias, H. V. R.; Wang, Z.; Jin, W., Synthesis and Chemistry of [Hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borato]silver(I) Complexes. *Inorg. Chem.* **1997,** *36* (27), 6205-6215.

13. Dias, H. V. R.; Polach, S. A.; Goh, S.-K.; Archibong, E. F.; Marynick, D. S., Copper and Silver Complexes Containing Organic Azide Ligands: Syntheses, Structures, and Theoretical Investigation of [HB(3,5-$(CF_3)_2$Pz$)_3$]CuNNN(1-Ad) and [HB(3,5-$(CF_3)_2$Pz$)_3$]AgN(1-Ad)NN (Where Pz = Pyrazolyl and 1-Ad = 1-Adamantyl). *Inorg. Chem.* **2000,** *39* (17), 3894-3901.

14. Dias, H. V. R.; Polach, S. A., An Isolable, Oxygen-Coordinated Silver(I) Complex of Dimethyl Diazomalonate: Synthesis and Characterization of $[HB(3,5-(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ (Where Pz = Pyrazolyl). *Inorg. Chem.* **2000,** *39* (21), 4676-4677.

15. Gava, R.; Olmos, A.; Noverges, B.; Varea, T.; Álvarez, E.; Belderrain, T. R.; Caballero, A.; Asensio, G.; Pérez, P. J., Discovering Copper for Methane C–H Bond Functionalization. *ACS Catal.* **2015,** *5* (6), 3726-3730.

16. Munoz-Molina, J. M.; Belderrain, T. R.; Perez, P. J., Trispyrazolylborate coinage metals complexes: Structural features and catalytic transformations. *Coord. Chem. Rev.* **2019,** *390*, 171-189.

17. Olmos, A.; Asensio, G.; Perez, P. J., Homogeneous Metal-Based Catalysis in Supercritical Carbon Dioxide as Reaction Medium. *ACS Catal.* **2016,** *6* (7), 4265-4280.

18. Noonikara-Poyil, A.; Munoz-Castro, A.; Boretskyi, A.; Mykhailiuk, P. K.; Dias, H. V. R., When SF_5 outplays CF_3: effects of pentafluorosulfanyl decorated scorpionates on copper. *Chem. Sci.* **2021,** *12* (43), 14618-14623.

19. Dias, H. V. R.; Lovely, C. J., Carbonyl and Olefin Adducts of Coinage Metals Supported by Poly(pyrazolyl)borate and Poly(pyrazolyl)alkane Ligands and Silver Mediated Atom Transfer Reactions. *Chem. Rev.* **2008,** *108* (8), 3223-3238.

20. Ponduru, T. T.; Sun, Z.; Cundari, T. R.; Dias, H. V. R., Nitrene Insertion into Aromatic and Benzylic C-H Bonds Catalyzed by Copper Complexes of Fluorinated Bis- and Tris(pyrazolyl)borates. *ChemCatChem* **2019,** *11* (19), 4966-4973.

21. Noonikara-Poyil, A.; Ridlen, S. G.; Dias, H. V. R., Isolable Copper(I) η^2-Cyclopropene Complexes. *Inorg. Chem.* **2020,** *59* (24), 17860-17865.

22. Esser, B.; Schnorr, J. M.; Swager, T. M., Selective detection of ethylene gas using carbon nanotube-based devices: Utility in determination of fruit ripeness. *Angew. Chem., Int. Ed.* **2012,** *51* (23), 5752-5756.

23. Noonikara-Poyil, A.; Cui, H.; Yakovenko, A. A.; Stephens, P. W.; Lin, R.-B.; Wang, B.; Chen, B.; Dias, H. V. R., A Molecular Compound for Highly Selective Purification of Ethylene. *Angew. Chem., Int. Ed.* **2021,** *60*, 27184–27188.

24. Hu, Z.; Williams, R. D.; Tran, D.; Spiro, T. G.; Gorun, S. M., Re-engineering Enzyme-Model Active Sites: Reversible Binding of Dioxygen at Ambient Conditions by a Bioinspired Copper Complex. *J. Am. Chem. Soc.* **2000,** *122* (14), 3556-3557.

25. Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J., Activation of Alkyl Halides via a Silver-Catalyzed Carbene Insertion Process. *J. Am. Chem. Soc.* **2003,** *125* (31), 9270-9271.

26. Dias, H. V. R.; Browning, R. G.; Richey, S. A.; Lovely, C. J., Silver(I) Scorpionate Mediated Insertion of Carbenes into Aliphatic C-H Bonds. *Organometallics* **2004,** *23* (6), 1200-1202.

27. Dias, H. V. R.; Kim, H.-J., Novel Tris(pyrazolyl)borates Bearing Perfluoroalkyl Pigtails. Syntheses and Characterization of the Sodium and Copper(I) Complexes of $[HB(3\text{-}(R)Pz)_3]^-$ (R = C_2F_5, C_3F_7; Pz = Pyrazolyl). *Organometallics* **1996,** *15* (25), 5374-5379.

28. Dias, H. V. R.; Jin, W.; Kim, H.-J.; Lu, H.-L., Polyfluorinated Tris(pyrazolyl)borates. Syntheses and Spectroscopic and Structural Characterization of Group 1 and Group 11 Metal Complexes of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[HB(3\text{-}(CF_3)Pz)_3]^-$. *Inorg. Chem.* **1996,** *35* (8), 2317-2328.

29. Dias, H. V. R.; Gorden, J. D., Synthesis and Characterization of Copper(II), Zinc(II), and Potassium Complexes of a Highly Fluorinated Bis(pyrazolyl)borate Ligand. *Inorg. Chem.* **1996,** *35* (2), 318-324.

30. Vanga, M.; Munoz-Castro, A.; Dias, H. V. R., Fluorinated tris(pyridyl)borate ligand support on coinage metals. *Dalton Trans.* **2022,** *51* (4), 1308-1312.

31. Hodgkins, T. G.; Powell, D. R., Derivatives of the Dimethylbis(2-pyridyl)borate(1-) Ion: Synthesis and Structure. *Inorg. Chem.* **1996,** *35* (7), 2140-2148.

32. Cui, C.; Lalancette, R. A.; Jäkle, F., The elusive tripodal tris(2-pyridyl)borate ligand: a strongly coordinating tetraarylborate. *Chem. Commun.* **2012,** *48* (55), 6930-6932.

33. Khaskin, E.; Zavalij, P. Y.; Vedernikov, A. N., Facile Arene C-H Bond Activation and Alkane Dehydrogenation with Anionic $LPt^{II}Me_2^-$ in Hydrocarbon-Water Systems (L = Dimethyldi(2-pyridyl)borate). *J. Am. Chem. Soc.* **2006,** *128* (40), 13054-13055.

34. Garcia, F.; Hopkins, A. D.; Kowenicki, R. A.; McPartlin, M.; Silvia, J. S.; Rawson, J. M.; Rogers, M. C.; Wright, D. S., Pyridyl 'ring-flipping' in the dimers $[Me_2E(2\text{-}py)]_2$ (E = B, Al, Ga; 2-py = 2-pyridyl). *Chem. Commun.* **2007,** (6), 586-588.

35. Khaskin, E.; Zavalij, P. Y.; Vedernikov, A. N., Oxidatively induced methyl transfer from boron to platinum in dimethyldi(2-pyridyl)boratoplatinum complexes. *Angew. Chem., Int. Ed.* **2007,** *46* (33), 6309-6312.

36. Cui, C.; Shipman, P. R.; Lalancette, R. A.; Jäkle, F., Tris(2-pyridylborate) (Tpyb) Metal Complexes: Synthesis, Characterization, and Formation of Extrinsically Porous Materials with Large Cylindrical Channels. *Inorg. Chem.* **2013,** *52* (16), 9440-9448.

37. Bhunya, S.; Roy, L.; Paul, A., Mechanistic Details of Ru-Bis(pyridyl)borate Complex Catalyzed Dehydrogenation of Ammonia-Borane: Role of the Pendant Boron Ligand in Catalysis. *ACS Catal.* **2016,** *6* (7), 4068-4080.

38. Jeong, S. Y.; Lalancette, R. A.; Lin, H.; Lupinska, P.; Shipman, P. O.; John, A.; Sheridan, J. B.; Jäkle, F., "Third-Generation"-Type Functional Tris(2-pyridyl)borate Ligands and Their Transition-Metal Complexes. *Inorg. Chem.* **2016,** *55* (7), 3605-3615.

39. Qian, J.; Comito, R. J., A Robust Vanadium(V) Tris(2-pyridyl)borate Catalyst for Long-Lived High-Temperature Ethylene Polymerization. *Organometallics* **2021,** *40* (12), 1817-1821.

40. Pawar, G. M.; Sheridan, J. B.; Jäkle, F., Pyridylborates as a New Type of Robust Scorpionate Ligand: From Metal Complexes to Polymeric Materials. *Eur. J. Inorg. Chem.* **2016,** *2016* (15-16), 2227-2235.

41. Goura, J.; McQuade, J.; Shimoyama, D.; Lalancette, R. A.; Sheridan, J. B.; Jäkle, F., Electrophilic and nucleophilic displacement reactions at the bridgehead borons of tris(pyridyl)borate scorpionate complexes. *Chem. Commun.* **2022,** *58* (7), 977-980.

42. Khaskin, E.; Zavalij, P. Y.; Vedernikov, A. N., Bidirectional Transfer of Phenyl and Methyl Groups between PtIV and Boron in Platinum Dipyridylborato Complexes. *J. Am. Chem. Soc.* **2008,** *130* (31), 10088-10089.

43. Pal, S.; Zavalij, P. Y.; Vedernikov, A. N., Oxidative C(sp^3)-H bond cleavage, C-C and C:C coupling at a boron center with O_2 as the oxidant mediated by platinum(II). *Chem. Commun.* **2014,** *50* (40), 5376-5378.

44. Peng, J.-B.; Geng, H.-Q.; Wu, X.-F., The Chemistry of CO: Carbonylation. *Chem* **2019,** *5* (3), 526-552.

45. Wright, M. A.; Wright, J. A., PhotoCORMs: CO release moves into the visible. *Dalton Trans.* **2016,** *45* (16), 6801-6811.

46. Lupinetti, A. J.; Strauss, S. H.; Frenking, G., Nonclassical metal carbonyls. *Prog. Inorg. Chem.* **2001,** *49*, 1-112.

47. Fujimori, S.; Inoue, S., Carbon Monoxide in Main-Group Chemistry. *J. Am. Chem. Soc.* **2022,** *144* (5), 2034-2050.

48. Singleton, E.; Oosthuizen, H. E., Metal isocyanide complexes. *Adv. Organomet. Chem.* **1983,** *22*, 209-310.

49. Massarotti, A.; Brunelli, F.; Aprile, S.; Giustiniano, M.; Tron, G. C., Medicinal Chemistry of Isocyanides. *Chem. Rev.* **2021,** *121* (17), 10742-10788.

50. Knorn, M.; Lutsker, E.; Reiser, O., Isonitriles as supporting and non-innocent ligands in metal catalysis. *Chem. Soc. Rev.* **2020,** *49* (21), 7730-7752.

51. Yurino, T.; Ohkuma, T., Nucleophilic Isocyanation. *ACS Omega* **2020,** *5* (10), 4719-4724.

52. Smith, C. S.; Mann, K. R., Exceptionally Long-Lived Luminescence from [Cu(I)(isocyanide)$_2$(phen)]$^+$ Complexes in Nanoporous Crystals Enables Remarkable Oxygen Gas Sensing. *J. Am. Chem. Soc.* **2012,** *134* (21), 8786-8789.

53. Sutton, G. D.; Olumba, M. E.; Nguyen, Y. H.; Teets, T. S., The diverse functions of isocyanides in phosphorescent metal complexes. *Dalton Trans.* **2021,** *50* (48), 17851-17863.

54. Pike, R. D., Structure and Bonding in Copper(I) Carbonyl and Cyanide Complexes. *Organometallics* **2012,** *31* (22), 7647-7660.

55. Kealey, S.; Miller, P. W.; Long, N. J.; Plisson, C.; Martarello, L.; Gee, A. D., Copper(I) scorpionate complexes and their application in palladium-mediated [^{11}C]carbonylation reactions. *Chem. Commun.* **2009,** (25), 3696-3698.

56. Boyarskiy, V. P.; Bokach, N. A.; Luzyanin, K. V.; Kukushkin, V. Y., Metal-Mediated and Metal-Catalyzed Reactions of Isocyanides. *Chem. Rev.* **2015,** *115* (7), 2698-2779.

57. Elschenbroich, C., *Organometallics, 3rd, Completely Revised and Extended Edition*. 3rd ed.; Wiley: Weinheim, 2006; p 817 pp.

58. Dias, H. V. R.; Jin, W., Chemistry of Trifluoromethylated Tris(pyrazolyl)borate: Synthesis and Characterization of Carbonyl and Isonitrile Adducts of Silver(I). *J. Am. Chem. Soc.* **1995,** *117* (45), 11381-11382.

59. Dias, H. V. R.; Wang, X., Silver(I) carbonyl and silver(I) ethylene complexes of a B-protected fluorinated tris(pyrazolyl)borate ligand. *Dalton Trans.* **2005,** (18), 2985-2987.

60. Dias, H. V. R.; Fianchini, M., A classical silver carbonyl complex [{MeB[3-(Mes)pz]$_3$}Ag(CO)] and the related silver ethylene adduct [{MeB[3-(Mes)pz]$_3$}Ag(C$_2$H$_4$)]. *Angew. Chem., Int. Ed.* **2007,** *46* (13), 2188-2191.

61. Despagnet-Ayoub, E.; Jacob, K.; Vendier, L.; Etienne, M.; Alvarez, E.; Caballero, A.; Diaz-Requejo, M. M.; Perez, P. J., A New Perfluorinated F21-Tp Scorpionate Ligand: Enhanced Alkane Functionalization by Carbene Insertion with (F21-Tp)M Catalysts (M = Cu, Ag). *Organometallics* **2008,** *27* (18), 4779-4787.

62. Rangan, K.; Fianchini, M.; Singh, S.; Dias, H. V. R., Silver(I) complexes of fluorinated scorpionates: Ligand effects in silver catalyzed carbene insertion into C-H bonds in alkanes. *Inorg. Chim. Acta* **2009,** *362* (12), 4347-4352.

63. Fuentes, M. A.; Munoz, B. K.; Jacob, K.; Vendier, L.; Caballero, A.; Etienne, M.; Perez, P. J., Functionalization of Non-Activated C-H Bonds of Alkanes: An Effective and Recyclable Catalytic System Based on Fluorinated Silver Catalysts and Solvents. *Chem. - Eur. J.* **2013,** *19* (4), 1327-1334.

64. Jayaratna, N. B.; Gerus, I. I.; Mironets, R. V.; Mykhailiuk, P. K.; Yousufuddin, M.; Dias, H. V. R., Silver(I) and Copper(I) Adducts of a Tris(pyrazolyl)borate Decorated with Nine Trifluoromethyl Groups. *Inorg. Chem.* **2013,** *52* (4), 1691-1693.

65. Ridlen, S. G.; Kulkarni, N. V.; Dias, H. V. R., Partially fluorinated Scorpionate $[HB(3-(CF_3),5-(Ph)Pz)_3]^-$ as a supporting ligand for silver(I)-benzene, -carbonyl, and -PPh_3 complexes. *Polyhedron* **2017,** *125*, 68-73.

66. Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H., $Ag(CO)B(OTeF_5)_4$: the first isolatable silver carbonyl. *J. Am. Chem. Soc.* **1991,** *113* (16), 6277-6278.

67. Hurlburt, P. K.; Rack, J. J.; Dec, S. F.; Anderson, O. P.; Strauss, S. H., Bis(carbonyl)silver tetrakis(pentafluorooxotellurato)borate: the first structurally characterized $M(CO)_2$ complex. *Inorg. Chem.* **1993,** *32* (4), 373-374.

68. Knol, D.; Koole, N. J.; de Bie, M. J. A., A ^{13}C NMR investigation of some tetrakisisocyanocopper(I) tetrafluoroborate complexes: Chemical shift of, and coupling to, the isocyano carbon. *Org. Magn. Reson.* **1976,** *8* (4), 213-218.

69. Bondi, A., van der Waals Volumes and Radii. *J. Phys. Chem.* **1964,** *68* (3), 441-451.

70. Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S., Covalent radii revisited. *Dalton Trans.* **2008,** (21), 2832-2838.

71. Dias, H. V. R.; Lu, H.-L.; Gorden, J. D.; Jin, W., Copper(I) Isocyanide Complexes of Highly Fluorinated Poly(pyrazolyl)borates. *Inorg. Chem.* **1996,** *35* (7), 2149-51.

72. Pellei, M.; Papini, G.; Lobbia, G. G.; Ricci, S.; Yousufuddin, M.; Dias, H. V. R.; Santini, C., Scorpionates bearing nitro substituents: mono-, bis- and tris-(3-nitro-pyrazol-1-yl)borate ligands and their copper(I) complexes. *Dalton Trans.* **2010,** *39* (38), 8937-8944.

73. Dias, H. V. R.; Gioia Lobbia, G.; Papini, G.; Pellei, M.; Santini, C., Copper(I) Isocyanide and Phosphane Complexes of Fluorinated Mono- and Bis(pyrazolyl)borates. *Eur. J. Inorg. Chem.* **2009,** (26), 3935-3941.

74. Gioia Lobbia, G.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H., Synthesis, structural and spectroscopic characterization of new silver(I) poly(pyrazolyl)borate complexes containing isonitrile ligands. *Inorg. Chim. Acta* **2000,** *298* (2), 146-153.

75. Leitl, M. J.; Krylova, V. A.; Djurovich, P. I.; Thompson, M. E.; Yersin, H., Phosphorescence versus Thermally Activated Delayed Fluorescence. Controlling Singlet-Triplet Splitting in Brightly Emitting and Sublimable Cu(I) Compounds. *J. Am. Chem. Soc.* **2014,** *136* (45), 16032-16038.

76. Shipman, P. O.; Cui, C.; Lupinska, P.; Lalancette, R. A.; Sheridan, J. B.; Jäkle, F., Nitroxide-Mediated Controlled Free Radical Polymerization of the Chelate Monomer 4-Styryl-tris(2-pyridyl)borate (StTpyb) and Supramolecular Assembly via Metal Complexation. *ACS Macro Lett.* **2013,** *2* (12), 1056-1060.

77. Krylova, V. A.; Djurovich, P. I.; Conley, B. L.; Haiges, R.; Whited, M. T.; Williams, T. J.; Thompson, M. E., Control of emission colour with N-heterocyclic carbene (NHC) ligands in phosphorescent three-coordinate Cu(I) complexes. *Chem. Commun.* **2014,** *50* (54), 7176-7179.

78. Shi, S.; Djurovich, P. I.; Thompson, M. E., Synthesis and characterization of phosphorescent three-coordinate copper(I) complexes bearing bis(amino)cyclopropenylidene carbene (BAC). *Inorg. Chim. Acta* **2018,** *482*, 246-251.

79. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C., The Cambridge Structural Database. *Acta Crystallogr., Sect. B Struct. Sci., Cryst. Eng. Mater.* **2016,** *72* (2), 171-179.

80. Dias, H. V. R.; Lu, H.-L., Copper(I) Carbonyl Complex of a Trifluoromethylated Tris(pyrazolyl)borate Ligand. *Inorg. Chem.* **1995,** *34* (21), 5380-5382.

81. Ivanova, S. M.; Ivanov, S. V.; Miller, b. S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H., Mono-, Di-, Tri-, and Tetracarbonyls of Copper(I), Including the Structures of $Cu(CO)_2(1\text{-}Bn\text{-}CB_{11}F_{11})$ and $[Cu(CO)_4][1\text{-}Et\text{-}CB_{11}F_{11}]$. *Inorg. Chem.* **1999,** *38* (17), 3756-3757.

82. Polyakov, O. G.; Ivanova, S. M.; Gaudinski, C. M.; Miller, S. M.; Anderson, O. P.; Strauss, S. H., $Cu(CO)_2(N(SO_2CF_3)_2)$. The First Structurally Characterized Copper(I) Polycarbonyl. *Organometallics* **1999,** *18* (19), 3769-3771.

83. Das, A.; Dash, C.; Yousufuddin, M.; Dias, H. V. R., Coordination and Ligand Substitution Chemistry of Bis(cyclooctyne)copper(I). *Organometallics* **2014,** *33* (7), 1644-1650.

84. Dash, C.; Das, A.; Yousufuddin, M.; Dias, H. V. R., Isolable, Copper(I) Dicarbonyl Complexes Supported by N-Heterocyclic Carbenes. *Inorg. Chem.* **2013,** *52* (3), 1584-1590.

85. Dias, H. V. R.; Singh, S., Copper(I) Complexes of Fluorinated Triazapentadienyl Ligands: Synthesis and Characterization of $[N\{(C_3F_7)C(Dipp)N\}_2]CuL$ (Where L = $NCCH_3$, $CNBu^t$, CO; Dipp = 2,6-Diisopropylphenyl). *Inorg. Chem.* **2004,** *43* (19), 5786-5788.

86. Dias, H. V. R.; Singh, S.; Flores, J. A., Syntheses of Highly Fluorinated 1,3,5-Triazapentadienyl Ligands and Their Use in the Isolation of Copper(I)-Carbonyl and Copper(I)-Ethylene Complexes. *Inorg. Chem.* **2006,** *45* (22), 8859-8861.

87. Fianchini, M.; Cundari, T. R.; De Yonker, N. J.; Dias, H. V. R., A non-classical copper carbonyl on a tri-alkene hydrocarbon support. *Dalton Trans.* **2009,** (12), 2085-2087.

88. Parasar, D.; Jayaratna, N. B.; Munoz-Castro, A.; Conway, A. E.; Mykhailiuk, P. K.; Dias, H. V. R., Carbonyl complexes of copper(I) stabilized by bridging fluorinated pyrazolates and halide ions. *Dalton Trans.* **2019,** *48* (19), 6358-6371.

89. Ridlen, S. G.; Kulkarni, N. V.; Dias, H. V. R., Monoanionic, Bis(pyrazolyl)methylborate $[(Ph_3B)(CH(3,5\text{-}(CH_3)_2Pz)_2)]^-$ as a Supporting Ligand for Copper(I)-ethylene, *cis*-2-Butene, and Carbonyl Complexes. *Inorg. Chem.* **2017,** *56* (12), 7237-7246.

90. Bruce, M. I.; Ostazewski, A. P. P., Group IB metal chemistry. I. Preparation and reactions of the carbonyl(hydrotripyrazol-1-ylborato)copper(I) complex. *J. Chem. Soc., Dalton Trans.* **1973,** (22), 2433-6.

91. Bruce, M. I.; Ostazewski, A. P. P., Stable copper carbonyl complex. *J. Chem. Soc., Chem. Commun.* **1972,** (20), 1124-1125.

92. Kou, X.; Dias, H. V. R., Carbon monoxide and ethylene complexes of copper and silver supported by a highly fluorinated tris(triazolyl)borate. *Dalton Trans.* **2009,** (36), 7529-7536.

93. Dias, H. V. R.; Wu, J.; Wang, X.; Rangan, K., Structural Variations of Silver Ethylene Complexes Supported by Boron-Protected Fluorinated Scorpionates and the Isolation of a Ligand-Directed Silver Helix. *Inorg. Chem.* **2007,** *46* (6), 1960-1962.

94. Wu, J., "Coinage Metal Complexes of Alkenes and Alkynes", Ph.D. dissertation,The University of Texas at Arlington, 2010.

95. Dias, H. V. R.; Kim, H.-J.; Lu, H.-L.; Rajeshwar, K.; de Tacconi, N. R.; Derecskei-Kovacs, A.; Marynick, D. S., Investigation of the Electronic and Geometric Effects of Trifluoromethyl Substituents on Tris(pyrazolyl)borate Ligands Using Manganese(I) and Copper(I) Complexes. *Organometallics* **1996,** *15* (13), 2994-3003.

96. Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A., Structural studies of copper(I) binding by hydrotris(1-pyrazolyl)borate and hydrotris(3,5-dimethyl-1-pyrazolyl)borate in the solid state and in solution. *J. Am. Chem. Soc.* **1976,** *98* (3), 711-718.

97. Blake, A. J.; Carling, D. A.; George, M. W.; Hubberstey, P.; Lopez Garcia, R.; Wilson, C., Carbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato]copper(I) acetonitrile solvate. *Acta Cryst.* **2002,** *E58* (2), m41-m42.

98. Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Morooka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A., A new model for dioxygen binding in hemocyanin. Synthesis, characterization, and molecular structure of the μ-η^2:η^2 peroxo dinuclear copper(II) complexes, $[Cu(HB(3,5\text{-}R_2pz)_3)]_2(O_2)$ (R = isopropyl and Ph). *J. Am. Chem. Soc.* **1992,** *114* (4), 1277-1291.

99. Fernández, I.; Noonikara-Poyil, A.; Dias, H. V. R., Bonding situation in isolable silver(I) carbonyl complexes of the Scorpionates. *J. Comput. Chem.* **2022,** *43* (11), 796-803.

100. Chatt, J.; Duncanson, L. A., Olefin coördination compounds. III. Infrared spectra and structure: attempted preparation of acetylene compounds. *J. Chem. Soc.* **1953**, 2939-2947.

101. Dewar, M. J. S., A review of the π-complex theory. *Bull. Soc. Chim. Fr.* **1951**, C71-79.

102. Ohashi, M.; Adachi, T.; Ishida, N.; Kikushima, K.; Ogoshi, S., Synthesis and Reactivity of Fluoroalkyl Copper Complexes by the Oxycupration of Tetrafluoroethylene. *Angew. Chem., Int. Ed.* **2017,** *56* (39), 11911-11915.

103. Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C., Polynuclear aryl derivatives of Group 11 metals. Synthesis, solid state-solution structural relationship, and reactivity with phosphines. *Organometallics* **1989,** *8* (4), 1067-1079.

104. *Bruker Apex3 software suite*. Bruker AXS Inc.: Madison, WI, USA, 2020.

105. Sheldrick, G., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A: Found. Adv.* **2015,** *71* (1), 3-8.

106. Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C: Struct. Chem.* **2015,** *71* (1), 3-8.

107. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42* (2), 339-341.

TOC. Bis(pyridyl)borate and tris(pyridyl)borate ligands with fluorine-lined coordination pockets allow the stabilization and detailed investigation of copper and silver complexes of *tert*-butyl isocyanide and CO.