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Fluorinated Tris(pyrazolyl)borate Ligands without the Problematic Hydride Moiety: Isolation of Copper(I) Ethylene and Copper(I)–Tin(II) Complexes Using $[MeB(3\text{-}(CF_3)Pz)_3]^-$

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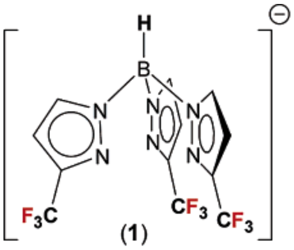
The thallium derivative of a fluorinated, B-methylated, tris(pyrazolyl)borate ligand, $[MeB(3\text{-}(CF_3)Pz)_3]^-$, has been synthesized via a two-step process using the corresponding pyrazole, $Li[MeBH_3]$, and thallium(I) acetate. Reaction of $[MeB(3\text{-}(CF_3)Pz)_3]Tl$ with CuBr in the presence of ethylene leads to $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$. It is a thermally stable solid. $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ reacts with $[(Bn)_2ATI]SnCl$ to yield $[MeB(3\text{-}(CF_3)Pz)_3]Cu{\leftarrow}Sn(Cl)[(Bn)_2ATI]$, featuring an unsupported Cu(I)–Sn(II) bond [2.4540(4) Å].

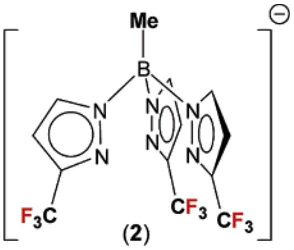
Tris(pyrazolyl)borates are some of the most widely utilized ligands in chemistry.[1] They are particularly attractive for many scientists because the steric and electronic properties of these ligands can be changed relatively easily by varying the substituents on the pyrazolyl moieties or on the boron center. Consequently, many different tris(pyrazolyl)borates have been synthesized and reported in the literature. However, tris(pyrazolyl)borate systems featuring fluorinated substituents on the pyrazolyl groups (e.g., **1**) or alkyl or aryl substituents on the boron are still relatively uncommon.[1−5] Over the past few years, we have described the synthesis of several highly fluorinated tris(pyrazolyl)borate ligand systems, e.g., $[HB(3\text{-}(CF_3)Pz)_3]^-$ (**1**) and $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]^-$.[6−8] Metal adducts of such fluorinated ligands often show chemistry very different from that of their nonfluorinated counterparts. Tris(pyrazolyl)borate ligands that lack the boron hydride moiety are also useful because the reactive B−H functionality creates problems in some applications.[1] In this paper, we describe the synthesis of a fluorinated tris(pyrazolyl)borate ligand with a methyl group on the boron and its use in the isolation of rare copper(I) ethylene and Cu(I)−Sn(II) adducts.

The thallium derivative of $[MeB(3\text{-}(CF_3)Pz)_3]^-$ (**2**) can be synthesized by a two-step procedure. The first step involves the preparation of $[MeB(3\text{-}(CF_3)Pz)_3]Li$ using $Li[MeBH_3]$ and the free pyrazole $3\text{-}(CF_3)PzH$. It can be used directly in the second step, which is a metathesis reaction with thallium(I) acetate. The formation of $[MeB(3\text{-}(CF_3)Pz)_3]Tl$ could be followed by NMR spectroscopy. For example, $3\text{-}(CF_3)PzH$ and $[MeB(3\text{-}(CF_3)Pz)_3]Li$ display a singlet in the ^{19}F NMR spectrum, whereas the thallium adduct exhibits a doublet centered at δ −59.14 ($^4J_{Tl-F} = 878$ Hz). The ^{19}F NMR data also suggest the formation of the $3\text{-}CF_3$ isomer rather than the $5\text{-}CF_3$ isomer.[9] The ^{11}B NMR spectrum of the thallium adduct $[MeB(3\text{-}(CF_3)Pz)_3]Tl$ shows only a broad singlet. In contrast, the ^{11}B NMR spectrum of $Li[MeBH_3]$ in DMSO-d_6 reveals a quartet of quartets (note that the ^1H NMR spectrum of $Li[MeBH_3]$ is very informative because it shows nicely resolved coupling between ^1H, ^{11}B, and ^{10}B isotopes).[2]



(1)

$[HB(3\text{-}(CF_3)Pz)_3]^-$



(2)

$[MeB(3\text{-}(CF_3)Pz)_3]^-$

The X-ray crystal structure of $[MeB(3\text{-}(CF_3)Pz)_3]Tl$ is illustrated in Figure 1. It contains a crystallographically

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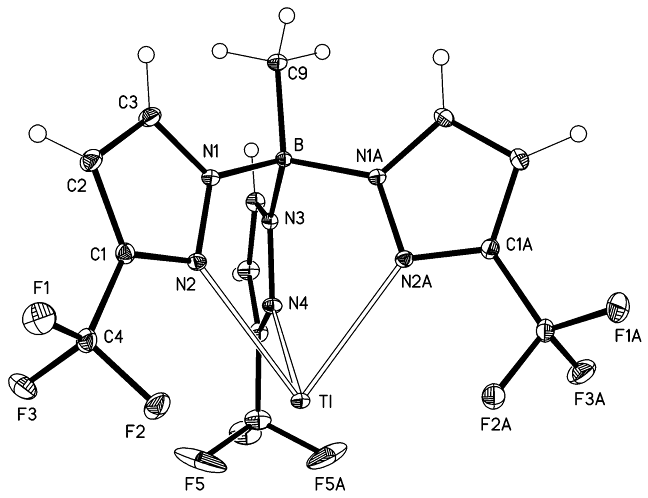

Figure 1. Molecular structure of $[MeB(3\text{-}(CF_3)Pz)_3]Tl$. Selected bond lengths (Å) and angles (deg): Tl−N4, 2.601(2); Tl−N2, 2.6228(15); Tl−N2A, 2.6228(15); B−N3, 1.563(4); B−N1, 1.567(2); B−N1A, 1.567(2); B−C9, 1.599(4); N4−Tl−N2, 70.17(5); N4−Tl−N2A, 70.17(5); N2−Tl−N2A, 73.38(7); N3−B−N1, 108.29(13); N3−B−N1A, 108.29(13); N1−B−N1A, 109.1(2); N3−B−C9, 110.7(2); N1−B−C9, 110.19(14); N1A−B−C9, 110.20(14).

imposed mirror plane involving Tl, B, and one of the pyrazolyl groups. $[MeB(3\text{-}(CF_3)Pz)_3]Tl$ exhibits the common tridentate coordination of the tris(pyrazolyl)borate ligand. There are no close Tl···Tl contacts (closest at 7.1 Å). The Tl−N [2.601(2), 2.6228(15), and 2.6228(15) Å] distances of $[MeB(3\text{-}(CF_3)Pz)_3]Tl$ are not significantly different from the Tl−N bond lengths of $[HB(3\text{-}(CF_3)\text{-}5\text{-}(thienyl)Pz)_3]Tl$[9] [2.603(2), 2.623(6), and 2.635(4) Å] and $[HB(3\text{-}(CF_3)\text{-}5\text{-}(Ph)\text{-}Pz)_3]Tl$[10] [2.618(2), 2.618(2), and 2.627(2) Å] but are shorter than those observed for the thallium salt of the more weakly coordinating ligand, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Tl$ [2.675(10), 2.725(7), and 2.724(7) Å].[11]

The treatment of $[MeB(3\text{-}(CF_3)Pz)_3]Tl$ with CuBr under an ethylene atmosphere led to the copper(I) ethylene complex $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ in very good yield. Solid samples of $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ can be handled in air for short periods without any apparent decomposition. In contrast, the related nonfluorinated adduct $[HB(3,5\text{-}(CH_3)_2Pz)_3]Cu(C_2H_4)$ oxidizes easily upon exposure to air.[12] Furthermore, unlike most copper(I) monoolefin complexes, $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ does not lose ethylene under reduced pressure. It was characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and by X-ray crystallography.

The ^1H NMR spectrum taken in $CDCl_3$ displays a signal corresponding to protons of the coordinated ethylene at δ 4.80. More importantly, no free ethylene signal (expected at δ 5.40 in $CDCl_3$) was detected in such solutions, indicating high solution stability of $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$.[8] Furthermore, two separate signals were observed in the ^1H NMR spectrum (corresponding to the protons of free and bound C_2H_4) when excess C_2H_4 was added at room temperature to an NMR tube containing a pure sample of $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ in $CDCl_3$. These NMR data also indicate that the ^1H NMR resonance due to ethylene protons shifts to a lower frequency upon coordination to copper(I). The change, however, is relatively small. This is similar to that observed for $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$.[8] The closely related nonfluorinated analogue $[HB(3,5\text{-}(CH_3)_2Pz)_3]Cu(C_2H_4)$ exhibits the corresponding peak at a much lower chemical shift value (δ 4.41 in CD_2Cl_2).[12] The upfield shift of the ^1H NMR resonance of ethylene protons of copper(I) adducts may be attributed to the increased shielding caused by the copper-to-ethylene π-back-donation. The relative magnitude of the upfield shift is consistent with the electron density at the copper center. The proton-coupled ^{13}C NMR spectrum of $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ displayed a triplet centered at δ 85.4. This can be assigned to the carbon atoms of the ethylene moiety. It is noteworthy that, because of the highly labile nature of the copper−olefin bonding interaction, little is known about the ^{13}C NMR chemical shifts or the C−H coupling constant values of copper-coordinated ethylene.[8,13,14] The corresponding peak in free ethylene appears at a much higher frequency (δ 123.5). The $^1J_{C-H}$ coupling constant of ethylene does not change very much upon coordination [156.4 Hz in the free ligand versus 161.2 Hz in $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$]. The $^1J_{C-H}$ values provide useful information about the hybridization state at the carbon.[15] The $^1J_{C-H}$ of 161.2 Hz suggests that in $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ the hybridization at the ethylene carbons remains essentially sp^2.

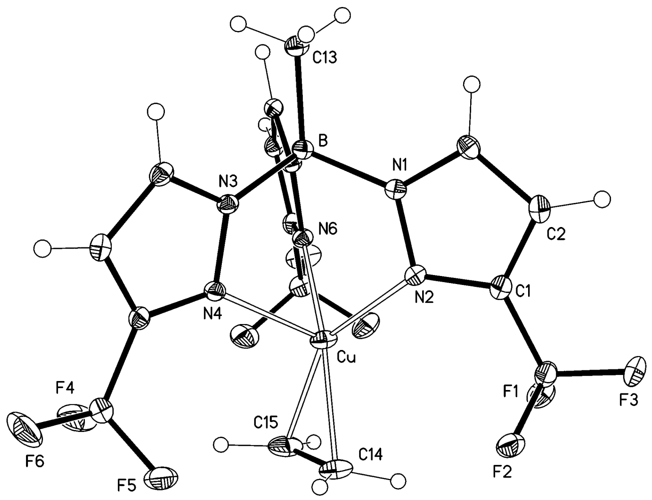

Figure 2. Molecular structure of $[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$. Selected bond lengths (Å) and angles (deg): Cu−N6, 2.0323(19); Cu−C15, 2.033(3); Cu−N2, 2.034(2); Cu−C14, 2.043(3); Cu−N4, 2.2716(19); B−N3, 1.560(3); B−N5, 1.568(3); B−N1, 1.570(3); B−C13, 1.596(3); C14−C15, 1.334(4); N6−Cu−N2, 91.07(8); C15−Cu−C14, 38.19(12); N6−Cu−N4, 87.32(7); N2−Cu−N4, 89.98(7); N3−B−N5, 107.68(18); N3−B−N1, 108.12(18); N5−B−N1, 107.65(18); C15−C14−Cu, 70.52(16); C14−C15−Cu, 71.29(17).

$[MeB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ affords good X-ray quality crystals from hexane (Figure 2). The structure shows that the ethylene molecule coordinates to copper(I) in typical η^2

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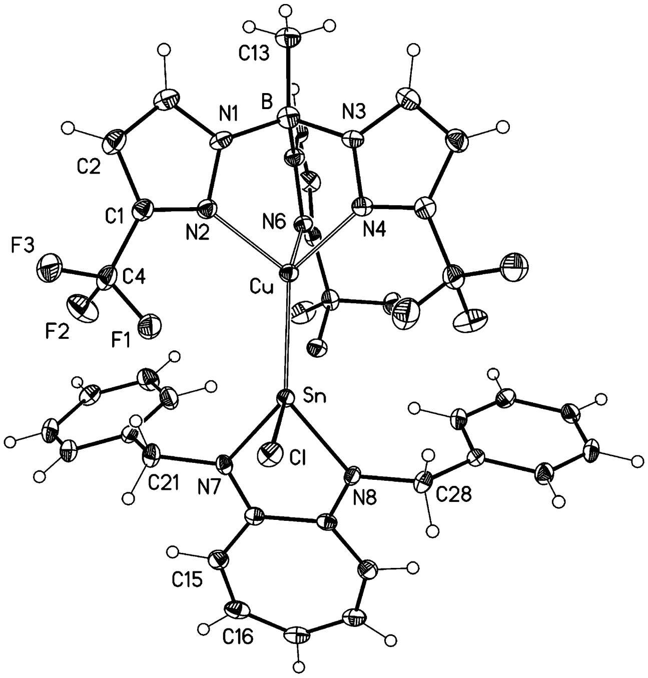

Figure 3. Molecular structure of $[MeB(3-(CF_3)Pz)_3]Cu \leftarrow Sn(Cl)[(Bn)_2ATI]$. Selected bond lengths (Å) and angles (deg): Cu−N4, 2.064(2); Cu−N2, 2.072(2); Cu−N6, 2.120(2); Cu−Sn, 2.4540(4); Cl−Sn, 2.4137(7); Sn−N8, 2.112(2); Sn−N7, 2.114(2); B−C13, 1.586(5); N4−Cu−N2, 92.71(10); N4−Cu−N6, 88.09(9); N2−Cu−N6, 93.03(9); N4−Cu−Sn, 124.62(7); N2−Cu−Sn, 121.91(7); N6−Cu−Sn, 126.57(7); N8−Sn−N7, 75.51(9); N8−Sn−Cl, 91.91(7); N7−Sn−Cl, 97.85(7); N8−Sn−Cu, 132.54(7); N7−Sn−Cu, 126.23(6); Cl−Sn−Cu, 120.55(2).

fashion. It did not suffer from the disorder problems previously observed in the related adducts.[8,12] The ethylene protons were located on the difference map and freely refined. The C═C bond distance of the coordinated ethylene [1.334(4) Å] is essentially the same as that for the free molecule [1.313 (expt) and 1.333 (calc) Å].[16,17] These data are consistent with the C−H coupling constant value, suggesting very few, if any, changes in the ethylene unit upon coordination. The tris(pyrazolyl)borate ligand coordinates to the copper ion in a tripodal fashion but shows two clearly different pyrazolyl nitrogen-to-copper distances: 2.0323(19), 2.034(2), and 2.2716(19) Å. It is interesting to note that the cell dimensions of $[MeB(3-(CF_3)Pz)_3]Cu(C_2H_4)$ and $[HB(3-(CF_3)Pz)_3]Cu(C_2H_4)$ show a remarkable similarity.[8] Preliminary studies involving the related Cu−CO adducts indicate that B-methylation does not affect their CO stretching frequency.[2,10]

Copper ethylene complexes have attracted significant interest because of their importance in biochemistry, in organic synthesis, and in industrial applications.[8,12,13,18] However, only a limited number of structurally characterized copper(I) ethylene complexes have been reported.[8] $[MeB(3-(CF_3)Pz)_3]Cu(C_2H_4)$ represents a new addition to this family.

The treatment of $[MeB(3-(CF_3)Pz)_3]Cu(C_2H_4)$ with $[(Bn)_2ATI]SnCl$ (where $[(Bn)_2ATI]^- = N$-benzyl-2-(benzylamino)troponiminate) leads to the elimination of ethylene and the formation of an interesting heterobimetallic species with an unsupported Cu(I)−Sn(II) bond. Such species are very rare, and to our knowledge, $(Me_3Si)_3SiCu \leftarrow Sn[Si(SiMe_3)_3](2,6-Mes_2C_6H_2)$ is the only Cu(I)−Sn(II) adduct in the literature that has been characterized using X-ray crystallography.[19] $[MeB(3-(CF_3)Pz)_3]Cu \leftarrow Sn(Cl)[(Bn)_2ATI]$ (Figure 3) has tetrahedral Cu and Sn sites. The substituents at the Cu and Sn sites adopt a sterically preferred staggered conformation. The Cu−Sn bond distance of 2.4540(4) Å in $[MeB(3-(CF_3)Pz)_3]Cu \leftarrow Sn(Cl)[(Bn)_2ATI]$ is shorter than the Cu−Sn separation [2.4992(5) Å] in $(Me_3Si)_3SiCu \leftarrow Sn[Si(SiMe_3)_3](2,6-Mes_2C_6H_2)$.[19]

Interestingly, despite the increase in the coordination number at Sn, the Sn−Cl and Sn−N distances shorten upon coordination to Cu(I). For example, the Sn−Cl distances of free ligand $[(Bn)_2ATI]SnCl$ and the copper adduct $[MeB(3-(CF_3)Pz)_3]Cu \leftarrow Sn(Cl)[(Bn)_2ATI]$ are 2.5148(4) and 2.4137(7) Å, respectively. This is perhaps the result of an increase in the *s* character of the Sn−Cl and Sn−N bonds due to Cu(I) ion coordination to the Sn center. Ionic effects could also play a role in shortening the bond distance.[20] We have observed similar trends in the Ag(I)−Ge(II) and Ag(I)−Sn(II) adducts. For example, the Sn−Cl distances of $[(n-Pr)_2ATI]SnCl$ and $[HB(3,5-(CF_3)_2Pz)_3]Ag \leftarrow Sn(Cl)[(n-Pr)_2ATI]$ are 2.504(1) and 2.4082(18) Å, respectively.[21] The Ag−Sn distance of this molecule is 2.5863(6) Å, which is longer than the Cu−Sn bond distance of $[MeB(3-(CF_3)Pz)_3]Cu \leftarrow Sn(Cl)[(Bn)_2ATI]$, as was expected because of the larger covalent radius of Ag(I).[22]

Overall, we have described the isolation of a trifluoromethylated tris(pyrazolyl)borate with a B−methyl substituent. Such ligands are particularly useful for investigating chemistry where B−H units typically create problems. We have used $[MeB(3-(CF_3)Pz)_3]^-$ to isolate rare, thermally stable copper(I) ethylene and Cu(I)−Sn(II) adducts. We are currently investigating the coordination chemistry of these B-protected, fluorine-rich ligand systems.

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Supporting Information Available: X-ray crystallographic data (CIF) and synthetic details (PDF) for $[MeB(3-(CF_3)Pz)_3]Tl$, $[MeB(3-(CF_3)Pz)_3]Cu(C_2H_4)$, and $[MeB(3-(CF_3)Pz)_3]Cu \leftarrow Sn(Cl)[(Bn)_2ATI]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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