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Silver(I) and Copper(I) Adducts of a Tris(pyrazolyl)borate Decorated with Nine Trifluoromethyl Groups

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S *Supporting Information*

ABSTRACT: Silver and copper ethylene adducts and the silver carbonyl complex of the tris(pyrazolyl)borate $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$ (which is based on one of the most acidic pyrazoles known) have been synthesized. ^{13}C NMR resonance signals of metal-bound ethylene carbon atoms of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ and $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Cu(C_2H_4)$ appear at δ 111.6 and 94.9, respectively. The CO stretching frequency of the silver adduct $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(CO)$ is significantly higher than that of free CO, but it appears at a region less sensitive to the ligand electronic effects of tris(azolyl)borate silver adducts.

Tris(pyrazolyl)borates are very popular auxiliary ligands in inorganic and organometallic chemistry.[1−3] It is possible to vary the steric and electronic properties of these ligands quite easily by changing the substituents on the boron atom or pyrazolyl moiety. In fact, a large number of tris(pyrazolyl)borate ligand varieties are now known. An area of research focus on in one of our laboratories concerns the development of fluorinated versions of these ligands and their use in various applications.[2] For example, we have reported the synthesis of several polyfluorinated tris(pyrazolyl)borates including $[HB(3\text{-}(CF_3)Pz)_3]^-$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (Figure 1) and boron-substituted varieties such as $[MeB(3\text{-}(CF_3)Pz)_3]^-$.[2] Metal adducts of fluorinated tris(pyrazolyl)borates feature more electrophilic metal sites and display interesting properties and reactivity compared to the nonfluorinated electron-rich tris(pyrazolyl)borate analogues.[4−6]

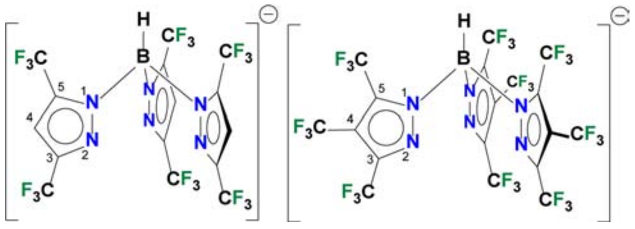

Figure 1. $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$.

Recently, a practical route to 3,4,5-tris(trifluoromethyl)-pyrazole $[3,4,5\text{-}(CF_3)_3PzH]$ was reported.[7] It is one of the most acidic pyrazoles known with a pK_a value of 4.5 (which is more acidic than acetic acid, with pK_a = 4.7)! Considering the importance of weakly coordinating ligands like $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (which is based on $3,5\text{-}(CF_3)_2PzH$ with a pK_a of 7.1)[8] in metal coordination chemistry and catalysis,[2] we set out to develop poly(pyrazolyl)borates based on $3,4,5\text{-}(CF_3)_3PzH$. In this Communication, we describe the synthesis of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$, which has nine trifluoromethyl groups on the periphery (Figure 1) and some of its copper and silver complexes.

The sodium salt $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Na$ was readily synthesized by the reaction of $NaBH_4$ with $3,4,5\text{-}(CF_3)_3PzH$ at ca. 190 °C in a solventless process. It was isolated as its tetrahydrofuran (THF) adduct after a workup involving THF. The ^{19}F NMR spectrum of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Na(THF)$ displays three peaks centered at δ −55.1, −57.0, and −62.3 corresponding to the fluorine atoms of CF_3 groups on pyrazolyl moieties. For comparison, fluorine atoms of the starting material, $3,4,5\text{-}(CF_3)_2PzH$, in $CDCl_3$ give rise to two peaks at δ −56.1 and −61.3 (1:2 ratio).

The treatment of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Na(THF)$ with AgOTf in THF under an atmosphere of ethylene affords the silver(I) ethylene complex $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$. It is a white powder and stable to loss of ethylene in a nitrogen atmosphere. The X-ray structure of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ is illustrated in Figure 2. Such structurally characterized silver(I) ethylene complexes are of interest because of their relevance in various industrial and biological processes.[2,9] The silver atom of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ adopts a pseudotetrahedral geometry. Interestingly, the ethylene moiety coordinates to the metal center in η^2 fashion but somewhat asymmetrically having one short bond and one long Ag−C bond, 2.294(4) and 2.337(4) Å. This asymmetric arrangement is atypical for ethylene even though that is common in arene silver complexes.[10,11] The $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$ moiety shows κ^3 coordination but with three different Ag−N distances [2.369(3), 2.399(3), and 2.444(3) Å]. Such variations in the metal−N distance are not unusual, and there are even κ^2-ligated

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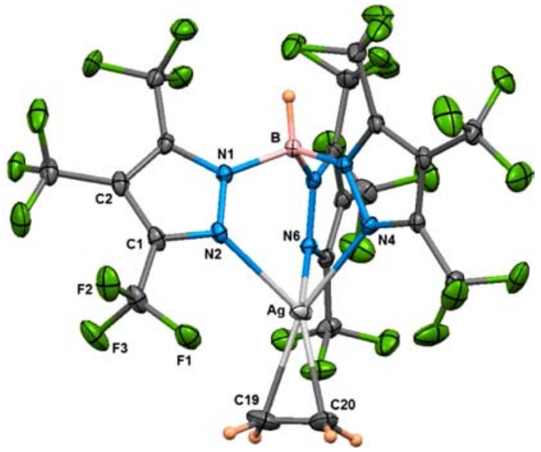

Figure 2. Molecular structure of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ (thermal ellipsoids at 40% probability). Selected distances (Å) and angles (deg): Ag−C20 2.294(4), Ag−C19 2.337(4), C19−C20 1.305(8), Ag−N4 2.369(3), Ag−N2 2.399(3), Ag−N6 2.444(3), Ag···B 3.39; C20−Ag−C19 32.73(19), N4−Ag−N2 80.76(10), N4−Ag−N6 78.74(10), N2−Ag−N6 82.61(10).

tris(pyrazolyl)borates, as we observed in $[HB(3,5\text{-}(CF_3)_2Pz)_3]Au(C_2H_4)$.[12,13] Detailed analysis of the ethylene C═C distance is not very useful because the C═C bond distance change as a result of coordination to silver(I) in these (and many of the other reported) adducts is small and is often overshadowed by experimental errors associated with routine X-ray crystallography, high estimated standard deviation values, libration effects, and the anisotropy of the electron density.[9,14]

The ^1H NMR signal of the protons of silver-bound ethylene of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ appears at δ 5.65. It is a notable downfield shift compared to the free ethylene signal (δ 5.40). The ^{13}C NMR spectrum of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ in CD_2Cl_2 shows a resonance at δ 111.6, which is assigned to carbon atoms of the silver-coordinated ethylene moiety. This is the smallest upfield shift relative to the free ethylene signal (δ 123.3) observed thus far for a coinage metal ethylene adduct supported by tris(azolyl)borates (see Table S1 in the Supporting Information, SI). The related $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$, for example, exhibits a corresponding signal at δ 104.9.[10] The ^{13}C NMR data suggest that the silver−ethylene interaction in these adducts is much closer to the T-shaped bonding extreme than the metallacyclopropane regime.[13] For comparison, $[Ni(i\text{Pr}_2\text{Im})_2(\eta^2\text{-}C_2H_4)]$, which features a high degree of metal → ethylene back-bonding [leading to near-metallacyclopropane-type bonding and a C−C distance of 1.420(4) Å], displays its ethylene carbon resonance at δ 24.85.[15] Bubbling excess ethylene into a $CDCl_3$ solution of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ at room temperature led to coalescence of the ^1H NMR signals of the coordinated ethylene, with the free ethylene producing a broad new signal at a weighted average position. This indicates that the bound ethylene exchanges rapidly with the free ethylene in the solution on the NMR time scale. The removal of excess ethylene by purging with nitrogen led to the reappearance of the ethylene peak of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$.

Solid $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ displays a sharp band in the Raman spectrum at 1581 cm^{-1}, which can be assigned to the C═C stretch of the ethylene moiety. This points to only a 42 cm^{-1} reduction from the C═C stretch of free ethylene (1623 cm^{-1}) as a result of silver(I) coordination. For comparison, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$ and the related tris(triazolyl)borate $[HB(3,5\text{-}(CF_3)_2Tz)_3]Ag(C_2H_4)$ (Tz = triazolyl) display the $\nu_{C=C}$ band at 1573 and 1576 cm^{-1}, respectively.[16] Overall, Raman data are in agreement with the findings from NMR spectroscopy and indicate only minor changes to the ethylene moiety in $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ compared to the free state. These data also point to the presence of a very electrophilic and only a weakly back-bonding silver site and a weakly donating tris(pyrazolyl)borate ligand in $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$.

The related copper analogue $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Cu(C_2H_4)$ was synthesized by treating $[HB(3,4,5\text{-}(CF_3)Pz)_3]Na(THF)$ with $[CuOTf]_2\cdot C_6H_6$ in the presence of ethylene. It is also possible to obtain this adduct by the metathesis of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ with CuCl. The ^1H NMR spectrum of the crude sample indicates the presence of two metal-bound ethylene adducts, out of which $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Cu(C_2H_4)$ is the major product. Solid $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Cu(C_2H_4)$ is stable in air at least for several days at room temperature. The ^1H NMR spectrum of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Cu(C_2H_4)$ exhibits a resonance at δ 5.06, which is due to the protons of the coordinated ethylene. This is a small but upfield shift from the free ethylene ^1H NMR signal that appears at δ 5.40. The related silver adduct, as noted earlier, shows a downfield shift of the ethylene ^1H NMR resonance. The ^{13}C NMR spectrum of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Cu(C_2H_4)$ in $CDCl_3$ displays the ethylene carbon signal at δ 94.9 (Table S1 in the SI). It is also the highest ^{13}C chemical shift value observed for copper ethylene adducts of poly(azolyl)borates. The corresponding signal for $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ was observed at δ 89.5, while $[HB(3,5\text{-}(CF_3)_2Tz)_3]Cu(C_2H_4)$ shows this resonance at δ 92.6.[16,17] Similar to $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$, a $CDCl_3$ solution of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Cu(C_2H_4)$ also shows rapid exchange of bound ethylene with added external ethylene on the NMR time scale. $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Cu(C_2H_4)$ is a crystalline solid, but the crystals we managed to obtain thus far show severe disorder.

It is also possible to synthesize the silver(I) carbonyl adduct supported by $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$. $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(CO)$ was obtained by replacing ethylene of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(C_2H_4)$ with CO (this is, however, a reversible process; the ethylene adduct can be regenerated by treating $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(CO)$ with ethylene in $CDCl_3$). $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(CO)$ is a stable white powder at room temperature under nitrogen. The X-ray structure of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(CO)$ is illustrated in Figure 3. It features a κ^3-bonded tris(pyrazolyl)borate with three somewhat similar Ag−N distances. The Ag−C−O moiety is essentially linear. The Ag−C bond distance 2.083(3) Å is longer than the corresponding distance observed for compounds like $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(CO)$ [2.037(5) Å][10] and $[MeB(3\text{-}(Mes)Pz)_3]Ag(CO)$ [1.994(3) Å].[18]

The IR spectrum of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(CO)$ shows the ν_{CO} band at 2177 cm^{-1}. It is significantly higher than the C−O stretching frequency of the free carbon monoxide (2143 cm^{-1}).[19] It also suggests the presence of a very electrophilic metal site with relatively low levels of M → CO π-back-bonding and considerable M−CO electrostatic component.[19] Interestingly, despite the presence of two different pyrazolyl moieties on the supporting ligands, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(CO)$ shows essentially an identical C−O stretch value (2178 cm^{-1}) in the IR spectrum. However, the corresponding silver ethylene adducts described above show two different chemical shifts for

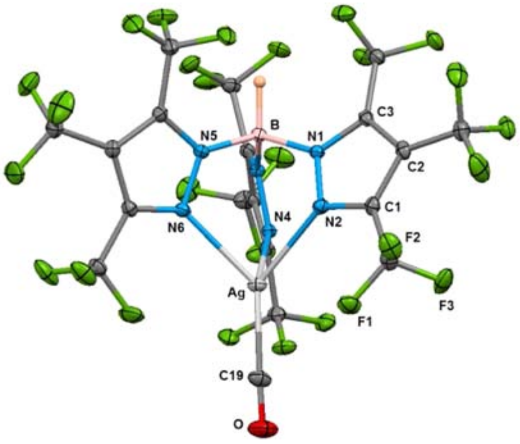

Figure 3. Molecular structure of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]Ag(CO)$ (thermal ellipsoids at 40% probability). Selected distances (Å) and angles (deg): Ag−C19 2.083(3), Ag−N6 2.352(2), Ag−N2 2.3654(19), Ag−N4 2.3799(18), C19−O 1.109(3), Ag···B 3.38; N6−Ag−N2 82.12(6), N6−Ag−N4 80.08(6), N2−Ag−N4 81.26(6), O−C19−Ag 175.4(2), C19−Ag···B 174.5.

their ethylene carbon atoms. This shows that, in contrast to the ethylene ^{13}C chemical shift, the CO stretching frequency value of these Ag−CO adducts lies in a region where the CO stretch of silver tris(pyrazolyl)borates is relatively insensitive to the donor properties of the supporting ligand.

Most chemists use the CO stretching frequency as a very convenient tool to probe the electronic properties at the metal site. It works well in the regions where M → CO π-back-donation dominates. However, the findings presented here and computational studies on cationic $[M{-}CO]^+$ (M = Cu, Ag, Au) species reported by Frenking, Strauss, and co-workers.[20] suggest that one has to be cautious when relating CO stretching frequency data to the metal-site electron densities of metal adducts when the $\bar{\upsilon}_{CO}$ values fall in the flatter region. This region is very likely unique to different classes of metal−ligand adducts and depends on many factors including the nature of the metal, charge, and supporting ligand. In fact, our previous work involving tris(pyrazolyl)borate and tris(triazolyl)borate adducts suggests that this flatter region is different for copper systems.[21]

Overall, this Communication describes the isolation of a very highly trifluoromethylated tris(pyrazolyl)borate. Silver and copper ethylene adducts of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$ are also reported, and the weakly donating nature of the supporting ligand is reflected in their ethylene ^{13}C chemical shift. Although the CO stretching frequency of the silver adduct is significantly higher than that of free CO, it is not different from the corresponding parameter of the less fluorinated $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(CO)$. We have shown that silver adducts of fluorinated tris(pyrazolyl)borates like $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ are very promising catalysts for various processes including C−H[2,4,5] and C−halogen bond activation.[2,6,22] The catalytic properties of $[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$ supported metal adducts, and related ligands with longer fluorocarbons are presently under study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and details of the synthesis, characterization, and physical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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