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Structural Variations of Silver Ethylene Complexes Supported by Boron-Protected Fluorinated Scorpionates and the Isolation of a Ligand-Directed Silver Helix

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Silver(I) ethylene adducts $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ and $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ have been synthesized using the corresponding lithium salts, AgOTf, and ethylene. X-ray data show that $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ has a planar three-coordinate silver center whereas $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ features a tetrahedral silver site. The ethylene-free $\{[PhB(3\text{-}(CF_3)Pz)_3]Ag\}_n$ adopts a helical structure with a hexagonal pore.

Silver(I) complexes of ethylene are of significant fundamental and practical interest. For example, silver plays an important role in the ethylene epoxidation and olefin separation.[1−9] In addition, there are numerous spectroscopic investigations and computational studies of silver(I) ethylene adducts.[10−19] Yet, isolable silver(I) ethylene complexes are rare.[18−22] Silver(I) in general forms very labile ethylene adducts because of its weak σ-acceptor and very poor π-donor nature.[23] Light sensitivity of silver adducts, the oxidizing nature of silver, and the easy displacement of the coordinated ethylene by other weakly donating species (including common solvents) present further synthetic challenges.[18,20−22]

We have been exploring the use of tris(pyrazolyl)borate (scorpionate)[24] supporting ligands in the isolation of thermally stable silver ethylene adducts. The synthesis of molecules like $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$ suggests that they are indeed promising ligands for this purpose.[20] In this paper, we describe the successful use of two *B−H-free* tris(pyrazolyl)borate ligands in this field (Figure 1). In addition, we also show the effect of having a B−phenyl group on the structure and properties of tris(pyrazolyl)boratosilver(I) ethylene adducts.

The B−phenyl-substituted $[PhB(3\text{-}(CF_3)Pz)_3]Li$ was synthesized from $[PhBH_3]Li$ and free pyrazole $3\text{-}(CF_3)PzH$. It reacts with silver(I) triflate under an ethylene atmosphere to afford $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$. The X-ray crystal structure shows that, in contrast to $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$[20] and $[MeB(3\text{-}(C_2F_5)Pz)_3]Ag(C_2H_4)$,[21] the tris(pyrazolyl)borate ligand in $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ coordinates to silver through just two pyrazolyl groups while the third pyrazolyl moiety remains free, pointed away from the Ag atom (Figure 2). The B−phenyl group sits above the Ag atom facing the $Ag{-}C_2H_4$ plane with two close Ag−phenyl C distances [2.868 Å (Ag$\cdots$C−B) and 3.074 Å (Ag$\cdots$C$_{ortho}$)]. Although these contacts are shorter than the sum of Ag and C van der Waals radius (3.42 Å),[25] they are not strong enough to distort the silver site from planar three-coordinate geometry, as is evident from the sum of the angles at silver (360.7°). The κ^2 mode of coordination observed here (rather than the common tripodal κ^3 mode)[24,26] is most likely a steric effect

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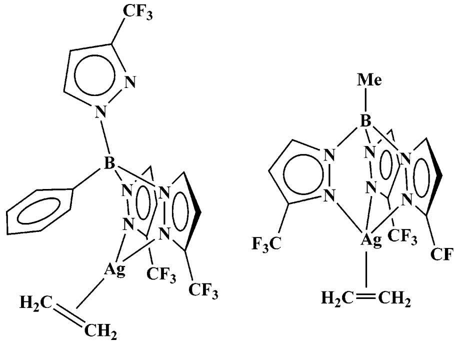

Figure 1. Silver ethylene complexes $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ and $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$.

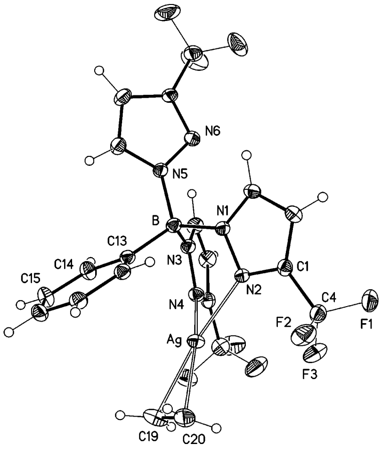

Figure 2. Molecular structure of $[PhB(3\text{-}CF_3)Pz)_3]Ag(C_2H_4)$. Selected bond lengths (Å) and angles (deg): Ag−C19 2.262(4), Ag−C20 2.267(4), Ag−N2 2.273(3), Ag−N4 2.248(3), C19−C20 1.296(7), Ag−C13 2.868, Ag···B 3.157; N4−Ag−N2 84.23(9), N4−Ag−C19 122.88(15), N2−Ag−C20 120.31(16), C19−Ag−C20 33.25(18).

of having a Ag atom in a B−phenylated tris(pyrazolyl)borate system. This is because a relatively large Ag atom would force the tripod resulting from κ^3 coordination to open up, causing adverse contacts between the B−phenyl group and one of the pyrazolyl groups (in particular, ortho C−H of B−phenyl and the C−H at the pyrazolyl ring 5 position). Bidentate coordination as seen in Figure 1 would alleviate this problem. The C═C bond distance of the coordinated ethylene [1.296(7) Å] in $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ is essentially the same as that of the free ethylene (1.313 Å).[27] The average Ag−N [2.261(3) Å] bond distance in the three-coordinate $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ is significantly shorter than the corresponding distances observed for the four-coordinate analogues (also see below).[20,21] However, the Ag−C(ethylene) distance is not significantly different from that observed in $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$.

The silver(I) ethylene complex $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ was synthesized from $[MeB(3\text{-}(CF_3)Pz)_3]Li$ and silver(I) triflate in order to study the effect of having a methyl group on the B atom of the tris(pyrazolyl)borate ligand. In contrast to the B−phenyl analogue, the tris(pyrazolyl)borate ligand in $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ coordinates to the Ag ion in the typical tripodal fashion (Figure 3) with an average

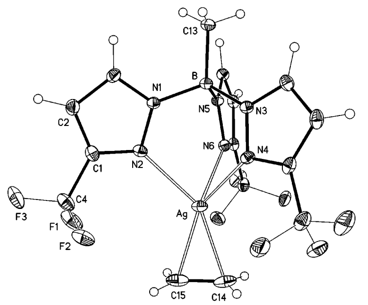

Figure 3. Molecular structure of $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$. Selected bond lengths (Å) and angles (deg): Ag−C14 2.2853(18), Ag−C15 2.2791(19), Ag−N2 2.2676(12), Ag−N4 2.3192(13), Ag−N6 2.4492(14), C14−C15 1.340(4), Ag···B 3.390; N2−Ag−N4 82.89(4), N2−Ag−N6 82.61(5), N4−Ag−N6 80.69(4), C14−Ag−C15 34.15(9).

Ag−N distance of [2.3453(13) Å]. The corresponding distance of 2.358(4) Å in $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$ is not significantly different, although it has a much more weakly donating ligand.[28] The ethylene moiety of $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ resides slightly off center from the Ag−B axis and on the side that has the longer Ag−N bond. The C═C bond distance of the silver(I)-bound ethylene [1.340(4) Å] is essentially the same as that for the free molecule.

The ^1H NMR signal of coordinated ethylene of $[MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ in $CDCl_3$ appears at δ 5.47 ppm, which is a marginal *downfield* shift compared to that of free ethylene (δ 5.40 ppm).[29] A similar trend is observed for silver(I) ethylene complexes of κ^3-coordinated tris(pyrazolyl)borates such as δ 5.56 ppm for $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$ and δ 5.48 ppm for $[MeB(3\text{-}(C_2F_5)Pz)_3]Ag(C_2H_4)$. In contrast, the ^1H NMR signal of coordinated ethylene of $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ in $CDCl_3$ appears at δ 4.72 ppm, which is an *upfield* shift compared to that of free ethylene. In general, the *upfield* shift of ethylene proton signals in diamagnetic molecules is explained on the basis of metal-to-ligand π back-bonding.[30] However, silver(I) is a very poor π-back-bond donor. It is also coordinated to a weakly donating tris(pyrazolyl)borate ligand. Furthermore, the ethylene C═C bond and Ag−C bond distances in these silver ethylene complexes vary only within a narrow range. Thus, the *upfield* shift of coordinated ethylene protons in $[PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)$ could not be a sign of significant increase in silver → ethylene back-bonding. Rather, it is probably a result of other factors like shielding caused by the ring-current effect of the B−phenyl ring facing the silver ethylene unit. Alternatively, one could also argue that the lower coordination number (i.e., 3 vs 4) may have an effect. Three-coordinate silver(I) adducts $[HC\{(CF_3)C(3,5\text{-}(CF_3)_2C_6H_3)N\}_2]Ag(C_2H_4)$,[22] $[\{(Ph)CH(MesCH_2)NH\}_2Ag(C_2H_4)][BF_4]$,[19] and $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$[18] are available for comparisons. The first two that have ethylene units flanked by aryl groups show relatively *upfield*-shifted ethylene protons (δ 3.78 ppm in C_6D_6 and δ 4.21 ppm in CD_2Cl_2, respectively). $[Ag(C_2H_4)_3]$-

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$[\mathrm{Al}\{\mathrm{OC(CF_3)_3}\}_4]$, which does not have aryl groups, shows the ethylene proton signal at δ 5.77 ppm in $\mathrm{CD_2Cl_2}$. There are, however, key differences between these molecules, including the supporting ligand and the solvent used for NMR studies. Thus, further supporting evidence is required before coming to a firm conclusion on the reasons behind the chemical shift difference. ^{13}C NMR signals corresponding to the bound ethylene of $[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$ and $[\mathrm{MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$ appear at δ 101.7 and 104.0 ppm, respectively, as broad signals. For comparison, the ^{13}C NMR resonance of the free ethylene has been observed at δ 123.5 ppm.

$[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$ and $[\mathrm{MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$ are colorless solids. In contrast to $[\mathrm{HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)}$[20] and $[\mathrm{MeB(3\text{-}(C_2F_5)Pz)_3]Ag(C_2H_4)}$,[21] these samples lose ethylene even in the solid form. The ethylene in these molecules is also labile in solution. The addition of excess ethylene to $\mathrm{CDCl_3}$ solutions of these adducts at room temperature led to the coalescence of ^{1}H and ^{13}C NMR signals of the coordinated ethylene with the free ethylene. The signal reappeared upon purging of the solution with dinitrogen to remove the excess free ethylene.

Hexane or $\mathrm{CH_2Cl_2}$ solutions of $[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$ and $[\mathrm{MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$ lose bound ethylene if purged with dinitrogen for *an extended period of time* or more easily if concentrated under vacuum, forming sparingly soluble solids, which are probably aggregated forms (e.g., dimers, polymers) of the silver tris(pyrazolyl)borates. The corresponding ethylene complexes can be reformed by bubbling ethylene into these mixtures. We were able to obtain a polymeric silver tris(pyrazolyl)borate via an independent route. For example, the treatment of $[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Li}$ and silver(I) triflate under a dinitrogen atmosphere led to $\{[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag}\}_n$. The X-ray-quality crystals of $\{[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag}\}_n$ were obtained from the $\mathrm{CH_2Cl_2}$ solution layered with hexane under dinitrogen at ambient temperature. $\{[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag}\}_n$ has a very interesting chain structure (Figure 4). $[\mathrm{PhB(3\text{-}(CF_3)Pz)_3}]^-$ serves as a bridging ligand between two silver sites. The Ag ion is positioned in a distorted tetrahedral environment coordinated to one tris(pyrazolyl)borate in a bidentate fashion with Ag−N bond distances of 2.377(18) and 2.314(8) Å and also to a pyrazolyl group [Ag−N of 2.304(10) Å] and a phenyl C [Ag−C of 2.43(2) Å] of a neighboring tris(pyrazolyl)borate ligand. Top and side views of the polymer show that it has a hexagonal helical structure.[31] All of the phenyl groups of $\{[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag}\}_n$ point inward, forming a hydrophobic core and a wheel-shaped channel (the shortest Ag···Ag separation between opposite silver sites is about 14 Å, and the estimated pore diameter based on a space-filling model is about 3.1 Å).

In summary, we report the isolation of two rare silver ethylene complexes using B−H-free tris(pyrazolyl)borate ligands. $[\mathrm{PhB(3\text{-}(CF_3)Pz)_3}]^-$ is also a new fluorinated tris(pyrazolyl)borate ligand. This work shows that a boron substituent can cause structural variations, as is seen with the three-coordinate $[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$ and four-coordinate $[\mathrm{MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$. The ethylene-free $\{[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag}\}_n$ features a supramolecular helical structure and a new coordination mode for a tris(pyrazolyl)borate ligand. Preliminary studies show that these silver ethylene complexes are good catalysts for C−H and C−X activation via carbene insertion. We are presently exploring the effect of a boron substituent on the catalytic activity.

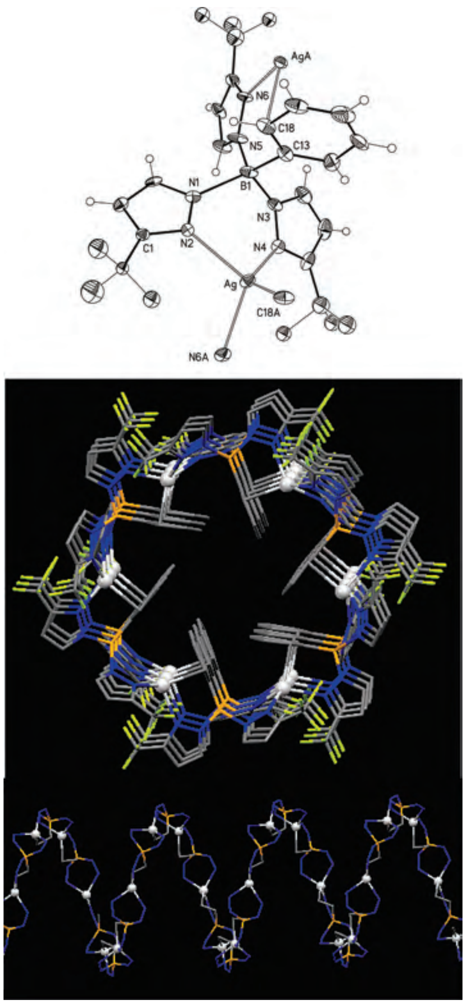

Figure 4. Top: Repeating unit of $\{[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag}\}_n$ and the contact points with the neighbors [Ag(A), N6(A), C18(A)]. Selected bond lengths (Å) and angles (deg): Ag−N2 2.377(18), Ag−N4 2.314(8), Ag−N6A 2.304(10), Ag−C18A 2.430(20); N2−Ag−N4 85.6(5), N2−Ag−N6A 111.0(5), N4−Ag−N6A 121.4(3), N2−Ag−C18A 122.9(8), N4−Ag−C18A 127.7(7), N6A−Ag−C18A 90.6(5). Middle: Top view of the $\{[\mathrm{PhB(3\text{-}CF_3)Pz)_3]Ag}\}_n$ helix. H atoms are omitted for clarity. Atom color code: C, gray; Ag, silver; N, blue; F, green; B, orange. Bottom: Side view showing the helical nature. Only selected atoms have been included.

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Supporting Information Available: X-ray crystallographic data (in CIF format) for $[\mathrm{MeB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$, $[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag(C_2H_4)}$, and $\{[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Ag}\}_n$ and experimental details for silver adducts and $[\mathrm{PhB(3\text{-}(CF_3)Pz)_3]Li}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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