Partially fluorinated Scorpionate [HB(3-(CF₃),5-(Ph)Pz)₃][−] as a supporting ligand for silver(I)-benzene, -carbonyl, and –PPh₃ complexes

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Abstract: The benzene, CO, and PPh₃ adducts [HB(3-(CF₃),5-(Ph)Pz)₃]AgL (L = C₆H₆, CO, or PPh₃) have been synthesized by a metathesis process using [HB(3-(CF₃),5-(Ph)Pz)₃]Na(THF), CF₃SO₃Ag, and the corresponding co-ligands. These silver(I) adducts have been characterized by NMR spectroscopy, and by X-ray crystallography. In all cases the Scorpionate is bound to silver in typical κ^3 -fashion. The X-ray crystallographic data of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(η^2 -C₆H₆) show that it has a η^2 -bound benzene molecule. NMR data point to fluxional behavior in solution. The ¹³C NMR resonance corresponding to the CO moiety of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) appears as a single peak at δ 177.4 ppm and the $\bar{\nu}_{\text{CO}}$ is observed at 2148 cm⁻¹. These values indicate the presence of a fairly Lewis acidic silver atom in [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) and significantly diminished Ag→CO π -backbonding. Interesting coupling is observed in the solution ¹⁹F and ¹⁹P NMR spectra of the Ag(I) adduct [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(PPh₃). A detailed analysis of the spectral and structural features of these complexes has been described herein.

Introduction: Poly(pyrazolyl)borates are a very popular class of ligands in coordination chemistry.[1-5] Since some modes of poly(pyrazolyl)borate ligand-metal ion interactions resemble hunting habits of a scorpion, they are often referred to as Scorpionates.[1] Poly(pyrazolyl)borates are also remarkably versatile group of ligands because, their steric and electronic properties can be modified quite easily by varying the number and type of substituents on the pyrazolyl moieties and on the boron atom. Many Poly(pyrazolyl)borate ligand varieties are known and the majority contain various

hydrocarbon substituents (e.g., Me, *i*-Pr, *t*-Bu, Ph, Mesityl) on the pyrazolyl moieties.[2, 5]

Figure 1. Fluorinated tris(pyrazolyl)borate ligands $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]^-$ and $[\text{HB}(3\text{-(CF}_3)_2,5\text{-(Ph)Pz})_3]^-$

An area of research focus in our laboratory concerns the chemistry of fluorinated poly(pyrazolyl)borates[6-11] and other azolyl analogs like tris(triazolyl)borates.[12, 13] For example, we have reported the synthesis of $[\text{HB}(3\text{-(CF}_3)_2\text{Pz})_3]^-$, [8] $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]^-$ (Figure 1), [7, 8] $[\text{HB}(3,4,5\text{-(CF}_3)_3\text{Pz})_3]^-$, [14] $[\text{HB}(3,5\text{-(CF}_3)_2,4\text{-(Cl)Pz})_3]^-$, [15] $[\text{HB}(3,5\text{-(CF}_3)_2,4\text{-(NO}_2\text{)Pz})_3]^-$, [15] $[\text{H}_2\text{B}(3,5\text{-(CF}_3)_2\text{Pz})_2]^-$, [9] as well as the B-alkylated and B-arylated systems like $[\text{MeB}(3\text{-(CF}_3)_2\text{Pz})_3]^-$ and $[\text{PhB}(3\text{-(CF}_3)_2\text{Pz})_3]^-$. [16, 17] Scorpionates bearing longer fluoroalkyl substituents on the pyrazolyl moieties are also known. [18-20]

Ligands such as $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]^-$ have electron withdrawing fluoroalkyl groups and are significantly less electron-rich and weaker donors compared to the non-fluorinated systems like $[\text{HB}(3,5\text{-(CH}_3)_2\text{Pz})_3]^-$. [21] Metal adducts of fluorinated

tris(pyrazolyl)borates therefore possess more electrophilic metal sites. They display greater catalytic activity in certain reactions like in the C-H and C-halogen bond functionalization chemistry via carbene insertion, compared to the non-fluorinated, electron rich tris(pyrazolyl)borate analogs.[15, 22-29] Fluorinated Scorpionates like $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]^-$ and $[\text{HB}(3\text{-(CF}_3),5\text{-(CH}_3\text{)Pz})_3]^-$ are also of interest because perfluoroalkyl groups at the pyrazolyl moiety 3-positions provide a robust environment around the metal site. The C-F bonds are strong and less prone to intramolecular activation (compared for example, to C-H bonds) when reactive species are generated at the metal site. Fluorinated tris(pyrazolyl)borates are useful as effective supporting ligands in metal mediated oxidation chemistry.[30-33] Other fluorinated Scorpionates and Scorpionates bearing other types of electron withdrawing substituents such as nitro groups, cyanides, and halogens have been reported as well.[34-49]

In this paper, we describe the successful use of a mixed aryl-perfluoroalkyl substituent bearing tris(pyrazolyl)borate ligand in silver chemistry. In particular, we report the synthesis and complete characterization of Ag(I)-benzene, Ag(I)-carbonyl, and Ag(I)-PPh₃ adducts supported by $[\text{HB}(3\text{-(CF}_3),5\text{-(Ph)Pz})_3]^-$. Isolation of silver(I) Scorpionates is challenging because they have a tendency to decompose thermally or photochemically producing metallic silver, especially when reducing borohydride moieties are present on the supporting ligand backbone.

Results and Discussion: The Scorpionate precursor $[\text{HB}(3\text{-(CF}_3),5\text{-(Ph)Pz})_3]\text{Na}(\text{THF})$ used in this work has been reported previously.[50] The silver(I)-benzene complex $[\text{HB}(3\text{-(CF}_3),5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$ was obtained by treating $[\text{HB}(3\text{-(CF}_3),5\text{-(Ph)Pz})_3]\text{Na}(\text{THF})$ with AgNO_3 in CH_2Cl_2 .

(Ph)Pz)₃]Na(THF) with CF₃SO₃Ag in a dichloromethane-benzene solvent mixture. It is a white solid, and forms very good quality colorless crystals with well-defined faces.

Figure 2. Top: ORTEP diagram of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(η²-C₆H₆) (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (°): Ag-N2 2.4170(9), Ag-N4 2.3505(9), Ag-N6 2.3463(9), Ag-C31 2.4507(12), Ag-C32 2.4480(12), Ag... (C31-C32 centroid) 2.347, Ag...B 3.343; N4-Ag-N2 80.61(3), N4-Ag-N6 81.56(3), N2-Ag-N6 84.41(3), C31-Ag-C32 33.29(4), B...Ag... (C31-C32 centroid) 161.3. Bottom: A view down Ag...B axis

X-ray crystallographic data of $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$ show that it has a η^2 -bound benzene molecule (Figure 2). The Ag-C31 and Ag-C32 distances are equal. The benzene molecule is tilted relative to the Scorpionate face, and the angle between Ag-C31-C32 plane and benzene ring plane is about 102° . The silver atom adopts a distorted tetrahedral geometry, with the Scorpionate showing κ^3 -coordination mode. There are no reports of structurally characterized silver Scorpionates with benzene co-ligands for comparisons.[51] However, related toluene complexes $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(CH}_3\text{)Pz})_3]\text{Ag}(\eta^2\text{-toluene})$ and $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$ are known and they also have η^2 -bound arenes.[52, 53] Interestingly, in contrast to $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$, the silver-arene bonding in $[\text{HB}(3,5\text{-(CF}_3\text{)}_2\text{Pz})_3]\text{Ag}(\eta^2\text{-toluene})$ which has a very weakly donating Scorpionate, is rather asymmetric with significantly different Ag-C distances (range 2.414-2.505 Å for two molecules in the asymmetric unit). The average Ag-C distances however, do not show a large difference (e.g., av. Ag-C of 2.449, 2.425, 2.448 Å for $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$, $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(CH}_3\text{)Pz})_3]\text{Ag}(\eta^2\text{-toluene})$ and $[\text{HB}(3,5\text{-(CF}_3\text{)}_2\text{Pz})_3]\text{Ag}(\eta^2\text{-toluene})$, respectively). Average Ag-N distances also do not show a major variation (2.371, 2.367, and 2.390 Å, respectively, for the three adducts listed above with the highest value not unexpectedly associated with the more weakly donating Scorpionate).

The solution NMR spectra of $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$ in CD_2Cl_2 at room temperature show only one sharp proton and one carbon signal for the benzene moiety, and one fluorine signal for the Scorpionate. This indicates the presence of a fluxional benzene ligand. The ^1H resonance of C_6H_6 in $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$

C₆H₆) (δ 7.42 ppm) shows a small down-field shift compared to the corresponding peak of free benzene in the same solvent (δ 7.35 ppm).[54]

The silver(I) carbonyl adduct [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) was synthesized by treating a mixture of [HB(3-(CF₃),5-(Ph)Pz)₃]Na(THF)[50] and CF₃SO₃Ag in dichloromethane with carbon monoxide (1 atm). It is a white solid. The characteristic $\bar{\nu}_{\text{CO}}$ band of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) can be observed at 2148 cm⁻¹ in the IR spectrum, which is higher than the $\bar{\nu}_{\text{CO}}$ of the free CO (2143 cm⁻¹). This is indicative of a significantly high electrostatic component in the Ag-CO interaction and diminished Ag→CO π -backbonding, which is not surprising since the silver(I) atom supported by the fluorinated [HB(3-(CF₃),5-(Ph)Pz)₃]⁻ is expected to be fairly electrophilic.[50] A comparison of $\bar{\nu}_{\text{CO}}$ values to silver carbonyl adducts supported by more weakly and strongly donating Scorpionates [HB(3,5-(CF₃)₂Pz)₃]Ag(CO) and [MeB(3-(Mes)Pz)₃]Ag(CO) show that the CO stretch of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) is in the expected range (Table 1). We have also observed the ¹³C NMR resonance corresponding to the CO moiety of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO). It appears as a singlet at δ 177.4 ppm in CD₂Cl₂ at room temperature. The absence of ^{107/109}Ag-¹³C coupling in solution probably an indication for the presence of a labile CO ligand in [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) that dissociates-coordinates rapidly in CD₂Cl₂ on the NMR timescale. For comparison, the corresponding signals of [HB(3,5-(CF₃)₂Pz)₃]Ag(CO) and free CO were reported at δ 175.5 and 184 ppm, respectively. Based on these IR and NMR data, [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) can be considered as a non-classical metal carbonyl adduct.[55] The classical metal carbonyls like Cr(CO)₆ with significant metal→CO π -backbonding, in contrast, show low CO stretching

frequencies (e.g., 2000 cm⁻¹)[56] and higher ¹³C NMR chemical shifts (e.g., δ 212.3 ppm),[57] relative to the corresponding values for the free CO.

The treatment of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) with excess benzene in dichloromethane led to the loss of CO and the formation of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(η^2 -C₆H₆). It is also possible to regenerate [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) from [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(η^2 -C₆H₆) by exposing it to CO in dichloromethane. This suggest the presence of rather labile CO and benzene co-ligands in these two silver Scorpionate adducts.

Figure 3. Top: ORTEP diagram of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (°): Ag-N2 2.2931(18), Ag-N4 2.3197(18), Ag-N6 2.3051(18), Ag-C31 2.019(2), O1-C31 1.110(3), Ag...B 3.317; N4-Ag-N2 85.13(6), N4-Ag-N6 82.74(6), N2-Ag-N6 80.34(6), O1-C31-Ag 177.1(3), B...Ag-C31 176.5.

X-ray crystal structure of $[\text{HB}(\text{3}-(\text{CF}_3),\text{5}-(\text{Ph})\text{Pz})_3]\text{Ag}(\text{CO})$ shows that it features a κ^3 -bonded tris(pyrazolyl)borate and a pseudo-tetrahedral silver site (Figure 3). The Ag-CO moiety is essentially linear. Isolable silver(I) adducts are rare. Search of Cambridge Structural Database show that there are only four structurally characterized tris(pyrazolyl)boratosilver(I) carbonyl complexes in the literature. Some of their structural and spectroscopic features are summarized in Table 1 with several other related adducts observed spectroscopically. The Ag-C bond distances of these adducts range from 2.083(3) to 1.994(3) Å. The corresponding distance of 2.019(2) Å observed for the $[\text{HB}(\text{3}-(\text{CF}_3),\text{5}-(\text{Ph})\text{Pz})_3]\text{Ag}(\text{CO})$ lies closer to the shorter end of the spectrum. For comparison, the copper(I) analog $[\text{HB}(\text{3}-(\text{CF}_3),\text{5}-(\text{Ph})\text{Pz})_3]\text{Cu}(\text{CO})$ [50] is known and it has a much shorter Cu-C distance (1.773(5) Å), consistent with the smaller atomic radius of copper.[60-62] The characteristic $\bar{\nu}_{\text{CO}}$ band of the copper analog appears at 2103 cm^{-1} in the IR spectrum, which is lower than the $\bar{\nu}_{\text{CO}}$ of free CO.[50]

The reaction between $[\text{HB}(\text{3}-(\text{CF}_3),\text{5}-(\text{Ph})\text{Pz})_3]\text{Na}(\text{THF})$ and $\text{CF}_3\text{SO}_3\text{Ag}$ in the presence of PPh_3 afforded $[\text{HB}(\text{3}-(\text{CF}_3),\text{5}-(\text{Ph})\text{Pz})_3]\text{Ag}(\text{PPh}_3)$, which was isolated as a white solid in 80% yield. It was characterized by ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectroscopy. The ^{19}F and ^{31}P NMR spectra are the most interesting as they not only show coupling to each other but also to spin active silver nuclei ($I = \frac{1}{2}$; ^{109}Ag (48.2%) and ^{107}Ag (51.8%)). For example, the ^{19}F resonance corresponding to the CF_3 groups at pyrazolyl moiety 3-positions appear as a doublet of doublet at δ -60.27 ppm due to coupling to ^{31}P and $^{107/109}\text{Ag}$ nuclei (Figure 4). For comparison, the corresponding signal in $[\text{HB}(\text{3},\text{5}-(\text{CF}_3)_2\text{Pz})_3]\text{Ag}(\text{PPh}_3)$ also appears as a doublet of doublet, whereas in the copper adduct $[\text{HB}(\text{3},\text{5}-(\text{CF}_3)_2\text{Pz})_3]\text{Cu}(\text{PPh}_3)$, it shows up as a doublet.[8] The ^{31}P

NMR spectrum of $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\text{PPh}_3)$ is equally informative as the phosphorus signal of silver bound PPh_3 appears as a doublet of doublet of multiplet centered at δ 17.8 ppm (Figure 4). The coupling of ^{31}P to the two silver isotopes is well resolved with $^1\text{J}(^{31}\text{P}\text{-}^{107}\text{Ag}) = 634$ Hz and $^1\text{J}(^{31}\text{P},^{109}\text{Ag}) = 732$ Hz. The $^1\text{J}(^{31}\text{P},^{109}\text{Ag})/^1\text{J}(^{31}\text{P}\text{-}^{107}\text{Ag})$ ratio is consistent with the $^{109}\text{Ag}/^{107}\text{Ag}$ gyromagnetic ratio of 1.149. The magnitude of $^1\text{J}(\text{Ag-P})$ coupling is at the higher end of four-coordinate silver phosphine complexes.[63] Each of these signals also shows spin-spin coupling to nine fluorine atoms of the CF_3 groups. Such long range coupling has been observed in the ^{31}P NMR spectra of $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Ag}(\text{PPh}_3)$ and $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(CH}_3\text{)Pz})_3]\text{Ag}(\text{PPh}_3)$ adducts.[64-66] The well resolved coupling in $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\text{PPh}_3)$ points to the lack of Scorpionate and PPh_3 ligand dissociation on the NMR timescale.

Although further studies are needed to ascertain whether these “long-range” $^5\text{J}(\text{P-F})$ couplings are a result of through bond or through-space interaction between phosphorous and fluorine spins, we note that the closest nonbonded intramolecular $\text{P}\cdots\text{F}$ distance in crystalline $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\text{PPh}_3)$ is short at 3.62 Å, and may be close enough to permit through space, Fermi-contact spin-spin coupling by the interaction between phosphorus with fluorines of the CF_3 groups. In fact, the closest separation in solution would be even less and estimated to be about 3.2-3.3 Å (which is near the sum of the P and F van der Waals radii of 3.27 or 3.36 Å according to Bondi or Alvarez),[67] because in the crystal structure, Ag and P atoms lie on a plane which dissects the F-C-F angle of CF_3 groups. It is also noteworthy that very large (>800 Hz), long-range TI-F coupling has been reported in fluorinated Scorpionate complexes of thallium such as $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(2-thienyl)Pz})_3]\text{TI}$ and $[\text{MeB}(3\text{-(CF}_3\text{)Pz})_3]\text{TI}$. [16, 44]

Figure 4. Top: ^{19}F NMR spectrum of $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\text{PPh}_3)$, **Bottom:** $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\text{PPh}_3)$

The X-ray crystal structure of $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3]\text{Ag}(\text{PPh}_3)$ is illustrated in Figure 5. The Scorpionate is bonded to the silver atom in a typical κ^3 -fashion. The Ag-P and average Ag-N bond distances are within the normal range observed for silver-

Solid samples of C₆H₆, CO, and PPh₃ adducts [HB(3-(CF₃),5-(Ph)Pz)₃]AgL (L = C₆H₆, CO, or PPh₃) can be exposed to air and indoor lighting at room temperature for several minutes without obvious signs of decomposition and do not lose co-ligand under reduced pressure. Although they are moderately air stable, these complexes should be kept under nitrogen and protected from light for long term storage. The complex [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(PPh₃) shows excellent solution stability and does not decompose after being exposed to air and ambient light for several days. Conversely, [HB(3-

(CF₃),5-(Ph)Pz)₃]Ag(C₆H₆) and [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) slowly form black precipitates over several hours when dissolved in chlorinated solvents, even when protected from exposure to air and indoor lighting.

Conclusions:

In summary, we have reported the isolation and characterization of three new silver(I) complexes supported by [HB(3-(CF₃),5-(Ph)Pz)₃]⁻ ligand. The benzene and carbonyl adducts of silver Scorpionates are particularly rare. [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(η^2 -C₆H₆) has an η^2 -bound benzene on silver(I). The $\bar{\nu}_{\text{CO}}$ of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) appear at 2148 cm⁻¹ and can be considered as a non-classical metal carbonyl complex. The phosphine adduct [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(PPh₃) shows interesting ¹⁹F and ¹⁹P NMR spectra with coupling to each other and spin active silver. Silver Scorpionates supported by weakly coordinating ligands are useful in catalysis and are good ligand transfer agents. We are currently exploring the coordination chemistry of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag with various other co-ligands.

Experimental:

General: All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmosphere single-station glovebox equipped with a -25 °C refrigerator. Solvents were purchased from commercial sources and purified prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at 25 °C on a JEOL Eclipse 500 (¹H, 500.16 MHz; ¹³C, 125.77 MHz; ¹⁹F, 470.62 MHz; and ³¹P, 121.66 MHz). Proton and carbon chemical shifts are referenced using the residual proton or carbon signals of the deuterated solvent. ¹⁹F NMR values

were referenced to external CFCl_3 , and ^{31}P NMR values were referenced to external H_3PO_4 (85%). Melting points were obtained on a Mel-Temp II apparatus. Elemental analyses were performed at Intertek Pharmaceutical Services. IR spectra were collected at room temperature on a Shimadzu IRPrestige-21 FTIR containing an ATR attachment. Silver(I) trifluoromethanesulfonate ($\text{CF}_3\text{SO}_3\text{Ag}$) was purchased from Sigma-Aldrich and carbon monoxide gas was purchased from Airgas. $[\text{HB}(3\text{-(CF}_3)_5\text{-(Ph)Pz})_3]\text{Na}(\text{THF})[50]$ was prepared via a reported procedure.

$[\text{HB}(3\text{-(CF}_3)_5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$: $[\text{HB}(3\text{-(CF}_3)_5\text{-(Ph)Pz})_3]\text{Na}(\text{THF})$ (0.25 g, 0.34 mmol) and $\text{CF}_3\text{SO}_3\text{Ag}$ (0.095 g, 0.37 mmol) were placed in a Schlenk flask under nitrogen atmosphere and the flask was covered aluminum foil to protect it from light. Dichloromethane (20 mL) and benzene (2.0 mL) were combined in a separate Schlenk flask and slowly added via syringe. The resulting solution was stirred overnight at room temperature and filtered through a bed of Celite to remove the insoluble material. The filtrate was concentrated under reduced pressure and placed in a freezer maintained at $-20\text{ }^\circ\text{C}$. X-ray quality crystals of $[\text{HB}(3\text{-(CF}_3)_5\text{-(Ph)Pz})_3]\text{Ag}(\eta^2\text{-C}_6\text{H}_6)$ were obtained after several days at $-20\text{ }^\circ\text{C}$. Yield: 0.234 g, 83%; m.p. $83\text{--}120\text{ }^\circ\text{C}$ (slowly decomposes over this wide temperature range with a final melting point of the residue at $211\text{ }^\circ\text{C}$). ^1H NMR (CD_2Cl_2 , 500.16 MHz, 298 K) δ (ppm): 7.42 (s, 6H, C_6H_6), 7.23 (t, 3H, Ph-*H*, $^3J_{\text{HH}} = 7.25\text{ Hz}$), 6.95 (t, 6H, Ph-*H*, $^3J_{\text{HH}} = 8.00\text{ Hz}$), 6.90 (d, 6H, Ph-*H*, $^3J_{\text{HH}} = 6.6\text{ Hz}$), 6.57 (s, 3H, Pz-*CH*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125.77 MHz, 298 K) δ (ppm): 152.2 (s, $\text{C}(\text{C}_6\text{H}_5)$), 143.0 (q, $^2J(\text{C},\text{F}) = 37\text{ Hz}$, CCF_3), 131.6 (s, Ph), 130.2 (s, Ph), 128.5 (s, Ph), 128.5 (s, C_6H_6), 128.2 (s, Ph), 121.1 (q, $^1J(\text{C},\text{F}) = 269\text{ Hz}$, CF_3), 105.0 (s, CH). ^{19}F NMR (CD_2Cl_2 , 470.62

MHz, 298 K) δ (ppm): -61.98 (s, 9F). ATR-FTIR (Selected peak, cm^{-1}): $\bar{\nu}$ = 2628 (B-H).
Analysis Calcd. for $\text{C}_{36}\text{H}_{25}\text{AgBF}_9\text{N}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 50.17; H, 3.00; N, 9.62%. Found. C, 50.38; H, 2.99; N, 9.86%.

[HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO): [HB(3-(CF₃),5-(Ph)Pz)₃]Na(THF) (0.25 g, 0.34 mmol) and CF₃SO₃Ag (0.087 g, 0.34 mmol) were placed in a Schlenk flask under a nitrogen atmosphere and the flask was covered aluminum foil to protect it from light. An atmosphere of CO was established and dichloromethane (25 mL) was added to the flask. The resulting mixture was stirred at RT for 1 h while gently bubbling CO, to obtain a solution with some black precipitate. It was filtered through a bed of Celite to obtain a clear colorless solution. The solution was concentrated by bubbling CO and placed in a freezer maintained at -20 °C overnight under a positive pressure of CO to obtain x-ray quality colorless crystals. Yield 0.197 g, 75%; m.p. 106-192 °C (slowly decomposes over this wide temperature range and finally melts 192 °C). ¹H NMR (CD₂Cl₂, 500.16 MHz, 298 K) δ (ppm): 7.24 (t, 3H, Ph), 6.90 (m, 12H, Ph), 6.56 (s, 3H). ¹³C{¹H} NMR (CD₂Cl₂, 125.77 MHz, 298 K) δ (ppm): 177.4 (s, CO), 151.2 (s, C(C₆H₅)), 143.2 (q, ²J(C,F) = 36 Hz, CCF₃), 131.2 (s, Ph), 130.2 (s, Ph), 128.9 (s, Ph), 128.3 (s, Ph), 121.9 (q, ¹J(C,F) = 269 Hz, CF₃), 105.0 (s, CH). ¹⁹F NMR (CD₂Cl₂, 470.62 MHz, 298 K) δ (ppm): -61.68 (s, 9F). ATR-FTIR (Selected peak, cm^{-1}): $\bar{\nu}$ = 2629 (B-H), 2148 (CO).
Analysis Calcd. for $\text{C}_{31}\text{H}_{19}\text{AgBF}_9\text{N}_6\text{O}$: C, 47.66; H, 2.45; N, 10.76%. Found. C, 47.27; H, 2.07; N, 10.67%.

[HB(3-(CF₃),5-(Ph)Pz)₃]Ag(PPh₃): [HB(3-(CF₃),5-(Ph)Pz)₃]Na(THF) (0.25 g, 0.34 mmol) and PPh₃ (0.089 g, 0.34 mmol) were dissolved in THF (10 mL) and this mixture was slowly added to a stirring solution of CF₃SO₃Ag (0.087 g, 0.33 mmol) in THF (10 mL) at 0 °C under an atmosphere of nitrogen. The flask was covered aluminum foil to protect it from light. After 1 h, the solution was allowed to warm to room temperature and stirred for additional 30 min. The reaction solvent was removed under vacuum, and the residue was extracted into toluene. The resulting mixture was filtered through bed of Celite and the solvent was removed under reduced pressure to obtain a white solid, which was thoroughly washed with hexanes and dried under vacuum. X-ray quality crystals were obtained from a dichloromethane solution stored at -20 °C. Yield: 0.274 g, 80%; m.p. 96-154 °C (slowly decomposes over this wide temperature range with a final melting point of the residue at 224 °C). ¹H NMR (C₆D₆, 500.16 MHz, 298 K) δ (ppm): 7.89 (m, 6H, Ph), 7.18, (m, 12H, Ph), 7.12 (m, 3H, Ph), 6.99 (m, 3H, Ph), 6.78 (m, 12H, Ph), 6.34 (s, 3H, Pz-CH). ¹³C{¹H} NMR (C₆D₆, 125.77 MHz, 298 K) δ (ppm): 151.8 (s, CPh), 144.1 (q, ²J(C,F) = 36 Hz, CCF₃), 135.0 (d, ²J(C,P) = 17 Hz, PPh₃), 133.3 (dd, ¹J = 34, ²J = 5 Hz, PPh₃), 132.2 (s, PPh₃), 130.9 (s, Ph), 130.5 (s, Ph), 129.3 (d, ³J(C,P) = 11 Hz, PPh₃), 122.4 (q, ¹J(C,F) = 268 Hz, CF₃), 105.8 (s, CH). ¹⁹F NMR (C₆D₆, 470.62 MHz, 298 K) δ (ppm): -60.27 (dd, ⁵J(F,P) = 7.8 Hz, ⁴J(F,Ag) = 1.3 Hz. ³¹P{¹H} NMR (C₆D₆, 121.65 MHz, 298 K) δ (ppm): 17.8 (¹J(P,¹⁰⁷Ag) = 633.9 Hz, ¹J(P,¹⁰⁹Ag) = 732.4 Hz, ⁵J(F,P) = 7.6 Hz). ATR-FTIR (Selected peak, cm⁻¹): $\bar{\nu}$ = 2623 (B-H). Analysis Calcd. for C₄₈H₃₄AgBF₉N₆P: C, 56.77; H, 3.37; N, 8.28%. Found. C, 56.12; H, 3.30; N, 8.25%.

X-ray crystallographic data:

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 for $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{C}_6\text{H}_6)]$, $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{CO})]$ and $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{PPh}_3)]$ were measured at 100(2) K or at 106(2) K on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo $\text{K}\alpha$ fine-focus sealed tube ($\lambda = 0.71073 \text{ \AA}$). Intensity data were processed using the Bruker ApexII program suite. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14). Initial atomic positions were located by direct methods using XS, and the structures of the compounds were refined by the least-squares method using SHELXL.[72] Absorption corrections were applied by using SADABS. All the non-hydrogen atoms were refined anisotropically. X-ray structural figures were generated using Olex2.[73] The hydrogen atom on boron and hydrogen atoms of benzene carbons (C31 and C32) bonded to silver in $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{C}_6\text{H}_6)]$ were located in a Fourier difference synthesis and refined satisfactorily. All the remaining hydrogen atoms of $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{C}_6\text{H}_6)]$ as well as hydrogens of $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{CO})]$ and $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{PPh}_3)]$ were placed at calculated positions and refined using a riding model. $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{CO})]$ crystallizes with a molecule of CH_2Cl_2 in the asymmetric unit. The fluorine atoms of one CF_3 group in $[\text{HB}(3\text{-(CF}_3\text{)},5\text{-(Ph)Pz})_3\text{Ag}(\text{CO})]$ and the CH_2Cl_2 show positional disorder over two sites, but these disorders were modeled satisfactorily. Further details are given in Table 3. The CCDC

1495609, 1495610, 1495611 contain the supplementary crystallographic data for [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(C₆H₆), [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) and [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(PPh₃), respectively. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK).

Supporting material: Additional details and figures of [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(C₆H₆), [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO) and [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(PPh₃)

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Table 1. Selected spectroscopic and structural data for tris(pyrazolyl)borato-silver(I) carbonyls

Scorpionate	$\delta(^{13}\text{CO})$ (NMR, ppm)	$\bar{\nu}(\text{CO})$ (IR, cm^{-1})	Ag-C ($\text{\AA}$)	Ref.
$[\text{HB}(3-(\text{CF}_3),5-(\text{Ph})\text{Pz})_3]^-$	177.4 (CD_2Cl_2)	2148 (neat)	2.019(2)	This work
$[\text{HB}(3,5-(\text{CF}_3)\text{Pz})_3]^-$	175.5 (CD_2Cl_2)	2178 (nujol)	2.037(5)	[52]
$[\text{HB}(3,4,5-(\text{CF}_3)\text{Pz})_3]^-$		2177 (KBr)	2.083(3)	[14]
$[\text{HB}(3,5-(\text{CF}_3),4-\text{BrPz})_3]^-$		2167 (soln.)		[58]
$[\text{HB}(3,4,5-(\text{Br})_3\text{Pz})_3]^-$		2153 (THF)		[37]
$[\text{MeB}(3-(\text{C}_2\text{F}_5)\text{Pz})_3]^-$	176.1 (CDCl_3)	2153 (KBr)	2.030(4)	[19]
$[\text{MeB}(3-(\text{CF}_3)\text{Pz})_3]^-$		2152 (hexane)		[25]
$[\text{MeB}(3-(\text{Mes})\text{Pz})_3]^-$		2128 (hexane)	1.994(3)	[59]
<i>Free CO</i>	184	2143		[6, 55]

Table 2. Selected spectroscopic and structural data for tris(pyrazolyl)borato-silver(I) PPh_3 complexes

Scorpionate	$\delta(^{31}P)$ (NMR, ppm)	Ag-P (Å)	Average Ag-N (Å)	$^1J(^{31}P-^{107}Ag)$	$^1J(^{31}P-^{109}Ag)$	Ref.
$[HB(3-(CF_3),5-(Ph)Pz)_3]^-$	17.9 (C_6D_6)	2.3690(7)	2.391	633.9	732.4	This work
$[HB(3-(CF_3),5-(CH_3)Pz)_3]^-$	16.53 ($CDCl_3$)	2.3642(5)	2.386	631.8	729.0	[53]
$[HB(3,5-(CF_3)_2Pz)_3]^-$	17.8 (C_6D_6)	2.376(1)	2.432	657.5	758.8	[8]
$[HB(3,5-(CH_3)_2Pz)_3]^-$	17.9 ($CDCl_3$)	2.347(6)	2.345	576	665	[63, 68]
$[HB(4-BrPz)_3]^-$	16.9 ($CDCl_3$)	2.345(3)	2.374	613	707	[63]
$[HB(Pz)_3]^-$	17.0 ($CDCl_3$)	2.337(3)	2.341	607	700	[63]
$[HB(3,5-(Ph)_2Pz)_3]^-$	13.4 ($CDCl_3$)	2.360(1)	2.370	600	693	[69]
$[HB(3,5-(Me),4-(C_5H_4N)Pz)_3]^-$	18.2 ($CDCl_3$)	2.3403(6)	2.338	584	675	[70]
<i>Free PPh₃</i>	-6.0					[71]

Table 3. Crystal Data and Summary of Data Collection and Refinement for [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(η^2 -C₆H₆), [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(CO)•CH₂Cl₂ and [HB(3-(CF₃),5-(Ph)Pz)₃]Ag(PPh₃)

Compound	[HB(3-(CF ₃),5-(Ph)Pz) ₃]Ag(η^2 -C ₆ H ₆)	[HB(3-(CF ₃),5-(Ph)Pz) ₃]Ag(CO)•CH ₂ Cl ₂	[HB(3-(CF ₃),5-(Ph)Pz) ₃]Ag(PPh ₃)
Empirical formula	C ₃₆ H ₂₅ AgBF ₉ N ₆	C ₃₂ H ₂₁ AgBCl ₂ F ₉ N ₆ O	C ₄₈ H ₃₄ AgBF ₉ N ₆ P
Formula weight	831.30	866.13	1015.46
Temperature	100.01 K	99.99 K	106.78 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P2(1)/n	Pbcn	P2(1)/n
Unit-cell dimensions	a = 13.3013(5) Å	a = 23.8118(17) Å	a = 13.1909(9) Å
	b = 12.7215(4) Å	b = 16.7916(12) Å	b = 18.2128(12) Å
	c = 20.7889(7) Å	c = 17.0571(12) Å	c = 18.3172(12) Å
	$\alpha = 90^\circ$	$\alpha = 90^\circ$	$\alpha = 90^\circ$
	$\beta = 104.6960(10)^\circ$	$\beta = 90^\circ$	$\beta = 94.006(2)^\circ$
	$\gamma = 90^\circ$	$\gamma = 90^\circ$	$\gamma = 90^\circ$
Volume	3402.7(2) Å ³	6820.1(8) Å ³	4389.8(5) Å ³
Z	4	8	4
Density (calculated)	1.623 Mg/m ³	1.687 Mg/m ³	1.536 Mg/m ³
Absorption coefficient	0.679 mm ⁻¹	0.835 mm ⁻¹	0.577 mm ⁻¹
Final R indices [I > 2 σ (I)]	R1 = 0.0316, wR2 = 0.0644	R1 = 0.0322, wR2 = 0.0759	R1 = 0.0343, wR2 = 0.0824
R indices (all data)	R1 = 0.0473, wR2 = 0.0689	R1 = 0.0392, wR2 = 0.0805	R1 = 0.0455, wR2 = 0.0929

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