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Synthesis and Chemistry of [Hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borato]silver(I) Complexes

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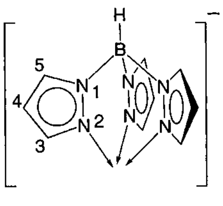
The syntheses, spectroscopy, and structures of silver(I) hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate complexes with tetrahydrofuran (THF), toluene, carbon monoxide, ethylene, acetylene, phenylacetylene, *tert*-butyl isocyanide, and *tert*-butyl cyanide ligands are presented. These complexes can be synthesized conveniently starting from the sodium salt of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand. The toluene ligand of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ exhibits fluxional behavior in solution and η^2-coordination in the solid state. The Ag−C distances, however, are not equal. The toluene ligand can be displaced reversibly with CO. $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ has mainly a σ-type Ag−CO bonding interaction. The Ag−C and C−O distances are 2.037(5) and 1.116(7) Å, respectively. $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(H_2C{=}CH_2)$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ have similar solid state structures. The $H_2C{=}CH_2$ and $HC{\equiv}CH$ bind symmetrically to silver ion. The Ag−C distances of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(H_2C{=}CH_2)$ are 2.294(7) and 2.307(7) Å. In $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CPh)$, the alkyne unit coordinates to silver ion in an asymmetric fashion with Ag−C distances of 2.263(5) and 2.407(5) Å. The $\upsilon_{C\equiv C}$ is about 69 cm^{-1} lower than that for free $HC{\equiv}CPh$. The coordinated alkyne moiety shows only a small bending-back angle (6.7°). The C−C bond distances of $H_2C{=}CH_2$, $HC{\equiv}CH$, and $HC{\equiv}CPh$ ligands remain virtually unchanged upon coordination to silver(I). $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCNBu^t$ has a relatively strong Ag−C bond. The isocyanide carbon resonance appears at δ 137.4 in the ^{13}C NMR spectrum. The υ_{CN} band appears at 2214 cm^{-1}, which is about 76 cm^{-1} higher than that for free $CNBu^t$. The Ag−C and C−N distances are 2.059(4) and 1.139(5) Å, respectively. The isocyanide group is slightly bent with a Ag−C−N angle of 173.7(4)° and a C−N−C angle of 176.2(4)°. Structural features of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgNCBu^t$ are very similar to those of the $CNBu^t$ analogue. The υ_{NC} band appears at 2277 cm^{-1}. All these complexes show pseudo-tetrahedral silver centers with pyrazolyl N−Ag distances ranging from 2.297 to 2.447 Å. The stability of these silver adducts may be primarily attributed to the unique electronic properties of the $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand.

Introduction

Tris(pyrazolyl)borate ligands have been used extensively in inorganic, bioinorganic, and organometallic chemistry.[1−6] However, the vast majority of these studies are either limited to the use of parent ligand $[HB(Pz)_3]^-$ (1) or ligands with hydrocarbon substituents such as $-CH_3$, $-C_3H_7$, $-C_4H_9$, and $-C_6H_5$. Despite the importance and growing interest of fluoro ligands, very little is known about the tris(pyrazolyl)borates containing perfluorinated substituents.[1,4,7] Recently, we reported the synthesis and chemistry of several such systems bearing $-CF_3$, $-C_2F_5$, and $-C_3F_7$ groups on the pyrazolyl ring 3- or 3,5-positions, e.g., $[HB(3\text{-}(CF_3)Pz)_3]^-$, $[HB(3\text{-}(C_2F_5)Pz)_3]^-$, $[HB(3\text{-}(C_3F_7)Pz)_3]^-$, and $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (**2**).[8−10] Studies of their metal complexes indicate that fluoro substituents on the pyrazolyl rings exert a significant effect on the electronic properties of the metal center.[11,12] For example, the carbonyl stretching frequency of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ (where $[HB(3,5\text{-}(CF_3)_2Pz)_3]$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate) is the highest observed for a [tris(pyrazolyl)borato]copper(I) complex, and it is about 71 cm^{-1} higher than that of $[HB(3,5\text{-}(CH_3)_2Pz)_3]CuCO$.[11] Copper complexes of the $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand also show relatively high oxidation potentials.[12]



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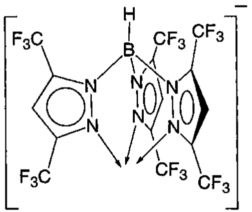

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An area of research focus in this laboratory is the chemistry of silver tris(pyrazolyl)borates. We are particularly interested in investigating the role that fluorinated tris(pyrazolyl)borate ligands such as **2** may play in stabilizing silver(I) complexes of small unsaturated molecules. Tris(pyrazolyl)borate ligands (although mainly non-fluorinated versions) have been used successfully for similar applications in copper chemistry.[1,4,10−16]

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For example, the first stable copper carbonyl and nitrosyl derivatives were obtained using $[HB(Pz)_3]^-$ and $[HB(3\text{-}(Bu^t)\text{-}Pz)_3]^-$ ligands.[13−15] However, in contrast to copper, silver tris(pyrazolyl)borates have received very little attention.[1,17] The first examples of this type were reported by Bruce and co-workers.[18,19] They reported the isolation of $[HB(Pz)_3]Ag$, $[HB(3,5\text{-}(CH_3)_2Pz)_3]Ag$, and a number of their derivatives which mainly contain phosphine donors. Then, in 1995, we communicated the successful use of fluorinated tris(pyrazolyl)borates in silver carbonyl chemistry,[20] and McCleverty, et al. described the synthesis of a trinuclear silver cluster using $[HB(3\text{-}(2\text{-}pyridyl)Pz)_3]^-$ ligand.[21] Shortly thereafter, the ligand transfer ability of silver tris(pyrazolyl)borates[22] and the syntheses of phosphine adducts $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgPPh_3$ and $[HB(3\text{-}(CF_3)Pz)_3]AgPPh_3$ were reported.[9] It is also noteworthy that, except for the latest publication,[9] all of the previous reports on this subject were short communications.[18−22] Silver complexes of tris(triazolyl)borate[23] and tris(pyrazolyl)methane ligands[24] have also attracted some current interest.

The scarcity of information on silver tris(pyrazolyl)borates and the interesting preliminary results we obtained using $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ prompted us to explore the silver chemistry of these fluoro ligands in more detail. Here we present full details of the synthesis and spectroscopic and structural characterization of [hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borato]silver(I) complexes containing donor ligands tetrahydrofuran (THF), toluene, CO, $H_2C{=}CH_2$, $HC{\equiv}CH$, $HC{\equiv}CPh$, $CNBu^t$, and $NCBu^t$. Some details of the THF, CO, and $CNBu^t$ adducts have appeared in two preliminary reports.[20,22]

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen either with standard Schlenk techniques or in a Vacuum Atmospheres single station drybox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources, distilled from conventional drying agents, and degassed twice prior to use.[25] Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded at 25 °C on a Bruker MSL-300 spectrometer (^1H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.36 MHz) or Nicolet NT-200 spectrometer (^1H, 200.06 MHz; ^{13}C, 50.31 MHz). Chemical shifts for ^1H and ^{13}C NMR spectra are referenced either to internal tetramethylsilane or to the solvent peak. ^{19}F NMR chemical shifts were referenced relative to an external $CFCl_3$. Infrared spectra were recorded on a BioRad 40S spectrometer operating at 2 cm^{-1} spectral resolution. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed using a Perkin-Elmer Model 2400 instrument. AgOTf, CO, $H_2C{=}CH_2$, $HC{\equiv}CH$, $HC{\equiv}CPh$, $CNBu^t$, and $NCBu^t$ were purchased from commercial sources. The syntheses of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ (**3**) were carried out as reported previously.[9,22]

$[DB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$. This was prepared in a manner similar to that of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ using $[DB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$ instead of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$. ^{19}F NMR (C_6D_6): δ −58.5 (s), −61.2. IR (Nujol mull, cm^{-1}): 1959, 1920 (BD).

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ (4). $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$ (800 mg, 0.1 mmol) in THF (30 mL) was slowly added to silver(I) triflate (287 mg, 0.11 mmol) in THF (10 mL) at 0 °C. After the addition, the mixture was stirred overnight at room temperature. The solvent was removed from the solution under reduced pressure to obtain a solid. It was dissolved in toluene and concentrated to obtain $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ as a white solid (92%). The colorless crystals were grown from *n*-hexane at −25 °C; mp, 94.5−96 °C. ^1H NMR (C_6D_{12}): δ 2.50 (s, 3H, CH_3), 6.84 (s, 3H, CH), 7.50−7.64 (m, 5H, CH). ^{19}F NMR (C_6D_{12}): δ −59.6 (d, ^5J(F,H) = 3.1 Hz), −62.4. $^{13}C\{^1H\}$ NMR (C_6D_{12}): δ 21.5 (s, CH_3), 106.5 (s, CH), 118.0 (s), 119.9 (q, ^1J(C,F) = 271 Hz, CF_3), 121.2 (q, ^1J(C,F) = 269 Hz, CF_3), 124.2 (s), 130.6 (s), 140.8 (br m, CCF_3), 142.0 (s, CCH_3), 144.3 (q, ^2J(C,F) = 38.1 Hz, CCF_3). IR (KBr, cm^{-1}): 2608 (BH). Anal. Calcd for $C_{22}H_{12}N_6F_{18}BAg$: C, 32.18; H, 1.47; N, 10.24. Found: C, 32.17; H, 1.03; N, 10.50.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ (5). The CO (1 atm) was bubbled through a hexane solution of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(toluene)$ at room temperature. The resulting mixture was kept in a −25 °C freezer to obtain colorless crystals of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ in quantitative yield; mp, dec around 74 °C. ^1H NMR (CD_2Cl_2): δ 6.96. ^{19}F NMR (CD_2Cl_2): δ −59.1 (d, ^5J(F,H) = 3.5 Hz), −62.1. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 106.8 (s, CH), 119.8 (q, ^1J(C,F) = 271 Hz, CF_3), 120.9 (q, ^1J(C,F) = 269 Hz, CF_3), 141.2 (q, ^2J(C,F) = 42.7 Hz, CCF_3), 144.2 (q, ^2J(C,F) = 38.2 Hz, CCF_3), 175.5 (s, CO). IR (hexane, cm^{-1}): 2162 (CO), 2612 (BH). IR (Nujol mull, cm^{-1}): 3167, 2616 (BH), 2178 (CO), 2163 sh (CO), 2128 (^{13}CO), 1559, 1498, 1461, 1376, 1366, 1267, 1254, 1079, 1040, 993, 829, 779, 736, 700. Anal. Calcd for $C_{16}H_4N_6F_{18}BAgO$: C, 25.39; H, 0.53; N, 11.1. Found: C, 25.29; H, 0.29; N, 11.24.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(H_2C{=}CH_2)$ (6). $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ (400 mg, 0.05 mmol) was dissolved in *n*-hexane (15 mL) and treated with ethylene gas (1 atm) at room temperature. The mixture was kept at −25 °C to obtain colorless crystals of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(H_2C{=}CH_2)$ in quantitative yield; mp, crystals became opaque around 90 °C and melted at 107 °C. ^1H NMR ($CDCl_3$): δ 5.52 (s, 4H, CH_2), 6.85 (s, 3H, CH). ^{19}F NMR ($CDCl_3$): δ −59.3 (d, ^5J(F,H) = 3.5 Hz), −62.1. ^1H NMR (C_6D_{12}): δ 5.56 (s, 4H, CH_2), 6.79 (s, 3H, CH). ^{19}F NMR (C_6D_{12}): δ −59.5 (d, ^5J(F,H) = 3.2 Hz), −62.5. ^{13}C NMR (C_6D_{12}): δ 104.9 (t, ^1J(C,H) = 164 Hz, CH_2), 106.5 (d, ^1J(C,H) = 185 Hz, CH), 119.9 (q, ^1J(C,F) = 271 Hz, CF_3), 121.2 (q, ^1J(C,F) = 270 Hz, CF_3), 141.7 (m, CCF_3), 144.3 (q, ^2J(C,F) = 37 Hz, CCF_3). IR (Nujol mull, cm^{-1}): 2634 (BH). Anal. Calcd for $C_{17}H_8N_6BF_{18}Ag$: C, 26.98; H, 1.07; N, 11.10. Found: C, 26.83; H, 0.74; N, 11.31.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ (7). Purified acetylene[25] (1 atm) was gently bubbled through a hexane solution of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(toluene)$ (300 mg, 0.37 mmol) for 2 min at room temperature. This mixture was cooled to −25 °C to obtain colorless crystals of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ in 88% yield; mp, dec around 95 °C. ^1H NMR ($CDCl_3$): δ 3.48 (s, 2H, $HC{\equiv}$), 6.92 (s, 3H, CH). ^{19}F NMR ($CDCl_3$): δ −59.0 (d, ^5J(F,H) = 3.3 Hz), −61.6. ^{13}C NMR ($CDCl_3$): δ 66.3 (dd, ^1J(C,H) = 256 Hz, ^2J(C,H) = 49.2 Hz, $HC{\equiv}$), 106.3 (d, ^1J(C,H) = 185 Hz, CH), 119.1 (q, ^1J(C,F) = 271 Hz, CF_3), 120.3 (q, ^1J(C,F) = 269 Hz, CF_3), 140.5 (m, CCF_3), 143.3 (q, ^2J(C,F) = 38.5 Hz, CCF_3). Anal. Calcd for $C_{17}H_6N_6BF_{18}Ag$: C, 27.05; H, 0.80; N, 11.13. Found: C, 27.66; H, 0.75; N, 10.75.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CPh)$ (8). $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(toluene)$ (300 mg, 0.37 mmol) was dissolved in hexane (10 mL) and treated with phenylacetylene (40 mg, 0.37 mmol) at room temperature. The mixture was stirred for 2 h, and the solution was concentrated and cooled to −25 °C to obtain colorless crystals of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CPh)$ in quantitative yield; mp, 97−98 °C. ^1H NMR ($CDCl_3$): δ 4.33 (s, H, $HC{\equiv}$), 6.88 (s, 3H, CH), 7.36 (m, Ph), 7.46

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Table 1. Crystal Data and Summary of Data Collection and Refinement for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgL

	3 (L = THF)	**4** (L = toluene)	**5** (L = CO)	**6** (L = H$_2$C=CH$_2$)	**7** (L = HC≡CH)	**8** (L = HC≡CPh)	**9** (L = CNBu^t)	**10** (L = NCBu^t)
formula	$C_{19}H_{12}AgBF_{18}N_6O$	$C_{22}H_{12}AgBF_{18}N_6$	$C_{16}H_4AgBF_{18}N_6O$	$C_{17}H_8AgBF_{18}N_6$	$C_{17}H_6AgBF_{18}N_6$	$C_{23}H_{10}AgBF_{18}N_6$	$C_{20}H_{13}AgBF_{18}N_7$	$C_{20}H_{13}AgBF_{18}N_7$
fw	801.0	821.06	756.9	756.97	754.96	831.05	812.1	812.05
space group	$C2/c$	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$	$Pnma$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	16.236(2)	12.440(2)	8.1794(5)	8.2544(10)	19.849(3)	14.919(1)	11.911(2)	11.938(1)
b, Å	21.658(2)	14.707(3)	15.230(1)	15.077(2)	15.015(3)	11.275(1)	23.758(4)	23.730(3)
c, Å	17.180(2)	17.230(4)	19.311(1)	19.906(2)	8.2106(11)	18.336(2)	10.752(2)	10.7606(9)
α, deg	90	84.41(2)	90	90	90	90	90	90
β, deg	114.710(6)	82.930(9)	90	90	90	112.236(6)	104.118(14)	103.761(6)
γ, deg	90	66.150(14)	90	90	90	90	90	90
vol, Å^3	5488.4(11)	2857.3(11)	2405.69(25)	2477.4(6)	2447.0(6)	2855.0(4)	2950.7(8)	2960.8(6)
Z	8	4	4	4	4	4	4	4
ρ_{calc}, g/cm^3	1.939	1.909	2.090	2.029	2.049	1.933	1.828	1.822
μ, mm^{-1}	0.885	0.850	1.003	0.971	0.982	0.852	0.823	0.820
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T, °C	−80(2)	−80(2)	−90(2)	−90(2)	−90(2)	−90(2)	−80(2)	−80(2)
R_1, R_{w2}^{a}		0.0300, 0.0758		0.0298, 0.0683	0.0354, 0.0770	0.0349, 0.0824		0.0363, 0.0817
R, R_w^{b}	0.0384, 0.0422		0.0315, 0.0409				0.0406, 0.0596	

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_{w2} = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. ^{b} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(m, Ph), 7.63 (m, Ph). ^{19}F NMR (CDCl$_3$): δ −58.9 (d, ^5J(F,H) = 3.4 Hz), −61.7 (d, J = 1.3 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 66.5 (s, HC≡), 86.7 (s, C-Ph), 106.3 (s, CH), 118.3 (s), 119.2 (q, ^1J(C,F) = 270 Hz, CF$_3$), 120.2 (q, ^1J(C,F) = 270 Hz, CF$_3$), 128.6 (s), 130.8 (s), 133.2 (s), 140.5 (q, ^2J(C,F) = 45.3 Hz, *C*CF$_3$), 143.5 (q, ^2J(C,F) = 38.1 Hz, *C*CF$_3$). ^{13}C NMR (CDCl$_3$): selected δ 66.5 (d, ^1J(C,H) = 255 Hz, HC≡), 86.7 (d, ^2J(C,H) = 49.6 Hz, C−Ph), 106.3 (d, ^1J(C,H) = 185 Hz, CH). IR (Nujol mull, cm^{-1}): 2041 (C≡C), 2636 (BH), 3264 (HC≡). Anal. Calcd for $C_{23}H_{10}N_6BF_{18}Ag$: C, 33.24; H, 1.21; N, 10.11. Found: C, 33.61; H, 1.43; N, 10.31.

[HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgCNBu^t (9). [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(toluene) (300 mg, 0.37 mmol) was treated with *tert*-butylisonitrile (14.3 mg/mL in toluene, 2.4 mL, 1.1 equiv). The resulting mixture was stirred overnight, and the volatiles were removed under reduced pressure to yield [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgCNBu^t as a white solid in quantitative yield. This was recrystallized from toluene−hexane at −25 °C; mp, 170−172 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.83 (s, 9H, CH$_3$), 6.30 (s, 3H, CH). ^{19}F NMR (C$_6$D$_6$): δ −58.3 (d, ^5J(F,H) = 3.0 Hz), −61.2. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 29.2 (s, CH$_3$), 57.3 (s, CMe$_3$), 106.6 (s, CH), 119.9 (q, ^1J(C,F) = 270 Hz, CF$_3$), 121.0 (q, ^1J(C,F) = 269 Hz, CF$_3$), 137.4 (s, CN), 140.2 (q, ^2J(C,F) = 42.2 Hz, *C*CF$_3$), 143.7 (q, ^2J(C,F) = 38.8 Hz, *C*CF$_3$). IR (Nujol mull, cm^{-1}): 2214 (CN), 2607 (BH). Anal. Calcd. for $C_{20}H_{13}F_{18}N_7BAg$: C, 29.58; H, 1.61; N, 12.07. Found: C, 29.83; H, 1.11; N, 12.26.

[HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgNCBu^t (10). [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) (150 mg, 0.187 mmol) in THF (10 mL) was treated with pivalonitrile (15.6 mg) in 10 mL of THF at room temperature. The solution was stirred for 3 h and concentrated to obtain [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgNCBu^t as a pale yellow solid in quantitative yield. X-ray quality crystals were grown from the NMR sample (C$_6$D$_6$) at 10 °C; mp, dec around 130 °C; ^{1}H NMR (C$_6$D$_6$): δ 0.79 (s, 9H, CH$_3$) 6.36 (s, 3H, CH). ^{19}F NMR (C$_6$D$_6$): δ −58.4 (d, ^5J(F,H) = 3.4 Hz), −61.5 (d, J = 2.1 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 27.2 (s, CH$_3$), 28.6 (s, CMe$_3$), 106.5 (s, CH), 119.9 (q, ^1J(C,F) = 271 Hz, CF$_3$), 121.1 (q, ^1J(C,F) = 269 Hz, CF$_3$), 140.5 (m, *C*CF$_3$), 143.6 (q, ^2J(C,F) = 38 Hz, *C*CF$_3$). IR (Nujol mull, cm^{-1}): 2277 (NC), 2604 (BH). Anal. Calcd for $C_{20}H_{13}N_7F_{18}AgB$: C, 29.58; H, 1.61; N, 12.07. Found: C, 29.53; H, 1.42; N, 11.74.

X-ray Data Collection and Solution and Refinement of Structures. General Procedures. A suitable crystal covered with a layer of hydrocarbon oil was selected and mounted on a glass fiber with a small amount of Paratone-N oil/grease and immediately placed in the low-temperature nitrogen stream.[26] Data collections were carried out on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz, polarization, and absorption (using ψ scans) effects. All of the structures were solved by direct methods. Software programs and the sources of scattering factors are contained in the SHELXTL (PC version 4.2 or 5.03) software package provided by Siemens Analytical X-ray Instruments, Inc.[27,28] Some details of data collection and refinements are given in Table 1. Selected bond distances and angles are given in Tables 2−9. Further details of the crystal structures are presented in the Supporting Information.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF)

Ag−O	2.234(4)	Ag−N12	2.381(4)
Ag−N22	2.344(4)	Ag−N32	2.365(5)
N12−Ag−N22	81.0(1)	N12−Ag−N32	80.2(1)
N22−Ag−N32	82.2(2)	N12−Ag−O	131.7(1)
N22−Ag−O	134.6(2)	N32−Ag−O	127.4(2)
C1−O−C4	109.5(5)	Ag−O−C1	121.4(4)
Ag−O−C4	124.2(4)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [HB(3,5−(CF$_3$)$_2$Pz)$_3$]Ag(η^2−toluene)

Ag1−N22	2.351(2)	Ag2−N42	2.359(2)
Ag1−N32	2.384(2)	Ag2−N62	2.375(2)
Ag1−N12	2.423(2)	Ag2−N52	2.447(3)
Ag1−C4A	2.392(4)	Ag2−C4B	2.414(4)
Ag1−C3A	2.480(4)	Ag2−C3B	2.506(4)
C1A−C6A	1.379(6)	C1B−C2B	1.361(6)
C1A−C2A	1.377(5)	C1B−C6B	1.376(6)
C1A−C7A	1.509(6)	C1B−C7B	1.512(5)
C2A−C3A	1.375(6)	C2B−C3B	1.397(7)
C3A−C4A	1.370(7)	C3B−C4B	1.381(7)
C4A−C5A	1.372(7)	C4B−C5B	1.385(6)
C5A−C6A	1.362(7)	C5B−C6B	1.366(6)
N22−Ag1−N32	81.18(8)	N42−Ag2−N62	80.16(8)
N22−Ag1−C4A	150.82(13)	N42−Ag2−C4B	152.6(2)
N32−Ag1−C4A	118.9(2)	N62−Ag2−C4B	123.9(2)
N22−Ag1−N12	81.04(8)	N42−Ag2−N52	79.65(8)
N32−Ag1−N12	79.14(8)	N62−Ag2−N52	79.16(8)
C4A−Ag1−N12	121.47(14)	C4B−Ag2−N52	115.15(13)
N22−Ag1−C3A	125.67(14)	N42−Ag2−C3B	120.9(2)
N32−Ag1−C3A	151.36(14)	N62−Ag2−C3B	154.79(13)
C4A−Ag1−C3A	32.6(2)	C4B−Ag2−C3B	32.5(2)
N12−Ag1−C3A	111.94(11)	N52−Ag2−C3B	116.01(14)

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[HB(3,5-(CF_3)_2Pz)_3]AgCO$

Ag−C	2.037(5)	C−O	1.116(7)
Ag−N12	2.297(4)	Ag−N22	2.320(4)
Ag−N32	2.366(4)		
Ag−C−O	175.6(6)	N12−Ag−N22	80.6(1)
N12−Ag−N32	83.0(1)	N22−Ag−N32	81.2(1)
C−Ag−N12	127.0(2)	C−Ag−N22	135.4(2)
C−Ag−N32	130.4(2)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[HB(3,5-(CF_3)_2Pz)_3]Ag(H_2C{=}CH_2)$

Ag−C1	2.294(7)	Ag−C2	2.307(7)
Ag−N32	2.333(4)	Ag−N12	2.345(4)
Ag−N22	2.395(3)	C1−C2	1.298(14)
C1−Ag−C2	32.8(3)	C1−Ag−N32	119.4(3)
C2−Ag−N32	51.0(3)	C1−Ag−N12	150.7(3)
C2−Ag−N12	21.5(4)	N32−Ag−N12	81.57(13)
C1−Ag−N22	20.5(3)	C2−Ag−N22	118.1(3)
N32−Ag−N22	80.23(14)	N12−Ag−N22	81.00(14)
C1−C2−Ag	73.1(5)	C2−C1−Ag	74.1(5)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[HB(3,5-(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$

Ag−C1A	2.293(4)	Ag−C1	2.293(4)
Ag−N12	2.347(3)	Ag−N12A	2.347(3)
Ag−N22	2.364(4)	C1−C1A	1.143(14)
C1A−Ag−C1	28.9(4)	C1A−Ag−N12	148.6(2)
C1−Ag−N12	121.9(2)	C1A−Ag−N12A	121.9(2)
C1−Ag−N12A	148.6(2)	N12−Ag−N12A	81.1(2)
C1A−Ag−N22	120.8(2)	C1−Ag−N22	120.8(2)
N12−Ag−N22	80.99(11)	N12A−Ag−N22	80.99(11)
C1A−C1−Ag	75.6(2)		

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $[HB(3,5-(CF_3)_2Pz)_3]Ag(HC{\equiv}CPh)$

Ag−C1	2.263(5)	Ag−N32	2.312(4)
Ag−N12	2.364(3)	Ag−C2	2.407(5)
Ag−N22	2.436(3)	C1−C2	1.189(8)
C2−C(3)	1.450(7)	C(3)−C(8)	1.382(7)
C(3)−C(4)	1.396(7)	C(4)−C(5)	1.386(8)
C(5)−C(6)	1.371(8)	C(6)−C(7)	1.369(8)
C(7)−C(8)	1.383(7)		
C1−Ag−N32	155.0(2)	C1−Ag−N12	117.8(2)
N32−Ag−N12	81.34(12)	C1−Ag−C2	29.3(2)
N32−Ag−C2	126.8(2)	N12−Ag−C2	144.1(2)
C1−Ag−N22	116.6(2)	N32−Ag−N22	81.34(12)
N12−Ag−N22	78.82(12)	C2−Ag−N22	122.8(2)
C(3)−C2−Ag	118.1(3)	C2−C1−Ag	82.1(4)
C1−C2−C(3)	173.3(5)	C1−C2−Ag	68.6(3)

Table 8. Selected Bond Lengths (Å) and Angles (deg) for $[HB(3,5-(CF_3)_2Pz)_3]AgCNBu^t$

Ag−C1	2.059(4)	C1−N	1.139(5)
N−C2	1.472(5)	Ag−N12	2.349(3)
Ag−N22	2.390(3)	Ag−N32	2.387(3)
Ag−C1−N	173.7(4)	C1−N−C(2)	176.2(4)
N12−Ag−N22	81.4(1)	N12−Ag−N32	81.8(1)
N22−Ag−N32	77.1(1)	C1−Ag−N12	134.8(1)
C1−Ag−N22	133.7(1)	C1−Ag−N32	126.9(1)

Table 9. Selected Bond Lengths (Å) and Angles (deg) for $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$

Ag−N	2.120(4)	Ag−N12	2.382(3)
Ag−N22	2.385(3)	Ag−N32	2.351(3)
N−C1	1.139(6)	C1−C2	1.468(7)
N−Ag−N32	132.7(2)	N−Ag−N12	133.5(2)
N−Ag−N22	127.9(2)	N32−Ag−N12	82.41(11)
N32−Ag−N22	82.43(11)	N12−Ag−N22	77.77(11)
N−C1−C2	178.3(6)	C1−N−Ag	169.6(4)

Results and Discussion

One of the major goals of this study was to investigate the chemistry of *neutral* silver complexes containing carbon based σ- and π-donors. Metal complexes of small unsaturated molecules such as CO, $H_2C{=}CH_2$, and $HC{\equiv}CH$ have attracted considerable interest due to their importance in various organometallic processes.[29−32] The silver(I) chemistry of these ligands has also been investigated for many years.[33] However, stable, well-defined silver complexes containing these ligands are still fairly limited.[17,31,33] For example, there are only a very few structurally characterized silver carbonyl complexes in the literature.[34−36] They include $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$. Silver olefin compounds are often unstable toward loss of the olefin ligand.[31,33,37−39] Most of the relatively stable complexes are based on ionic silver salts (e.g., AgX, where X is usually an anion like OTf^-, NO_3^-, BF_4^-, or ClO_4^-) and substituted olefins or polyenes (e.g., COD).[31,40−51] Silver alkynes are less investigated compared to the olefin adducts.[39,52−54] They also suffer from weak Ag−ligand interaction.[55] Unsubstituted alkynes are also known to undergo further reactions with silver ions leading to explosive silver acetylides.[33] During the course of our studies on fluorinated poly(pyrazolyl)borates,[8−12,20,22,56−58] we found that the highly fluorinated $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand is an excellent choice for obtaining a variety of important silver adducts, including those of CO, $H_2C{=}CH_2$, and $HC{\equiv}CH$ (Scheme 1). Details of the synthesis

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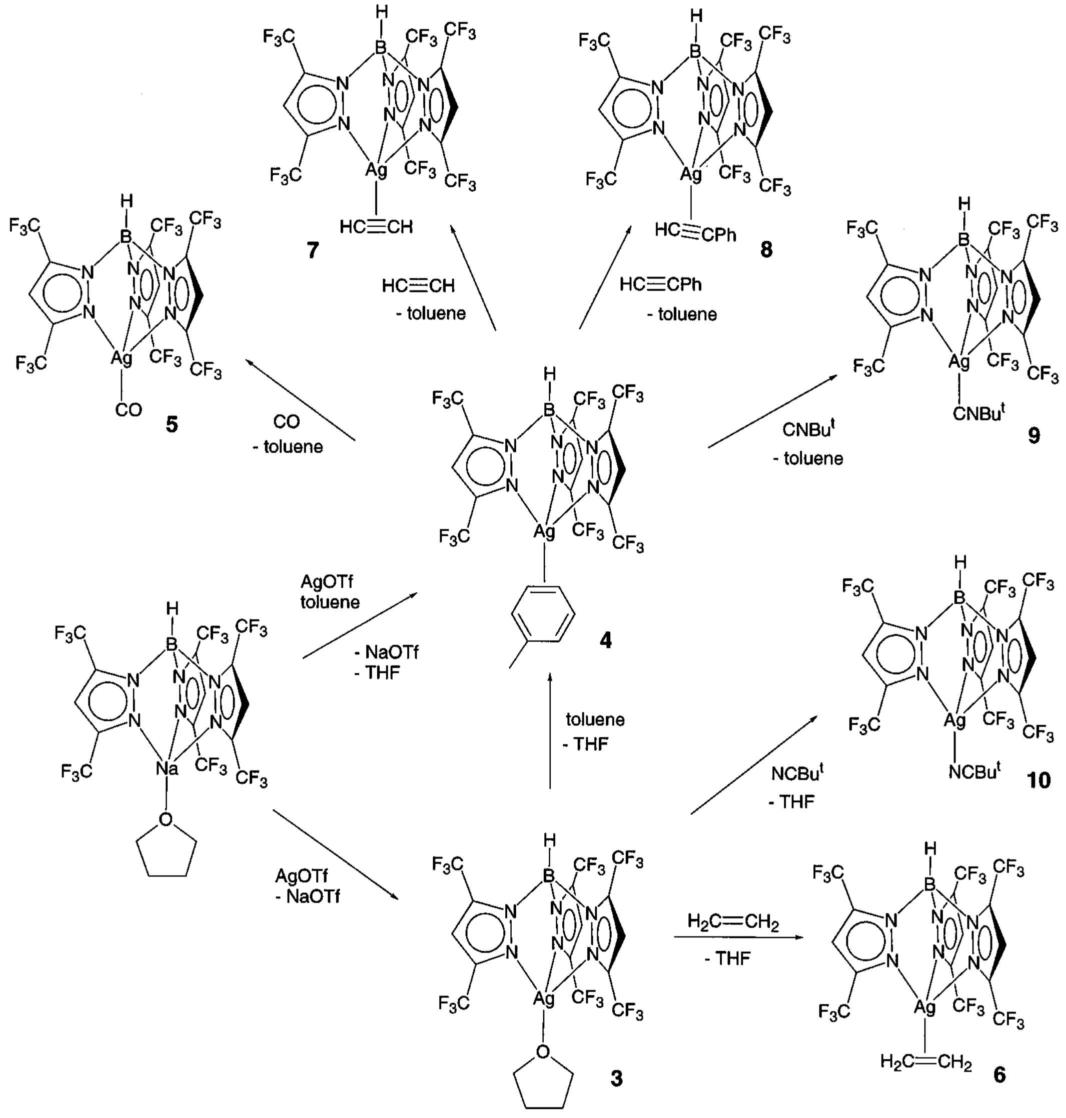
Scheme 1. Formation of Complexes **3**−**10**^{a}



and the spectroscopic, structural, and physical properties are described below for each silver complex.

[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF). The THF adduct of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag was prepared from [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Na and AgOTf in tetrahydrofuran. This compound shows good solubility in common organic solvents. The presence of coordinated THF in [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) was clearly evident from the elemental analysis and NMR spectroscopic data. This tendency to form adducts with neutral oxygen donors has not been observed in the corresponding non-fluorinated analogues. For example, [HB(Pz)$_3$]Ag, [HB(3,5-(CH$_3$)$_2$Pz)$_3$]Ag, and [HB-(3-(2-pyridyl)Pz)$_3$]$_2$Ag$_3$ClO$_4$ have been isolated as solids free of any coordinated solvent, although their syntheses were performed in solvents such as H$_2$O and MeOH.[19,21] The ^{19}F NMR spectrum of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) in C$_6$D$_6$ shows two signals as expected for the CF$_3$ groups on the 3- and 5-positions of the pyrazole ring. One of the peaks, which corresponds to the trifluoromethyl groups on the pyrazole ring 5-position, appears as a doublet. Similar splitting was observed for most of the metal complexes derived from the [HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$ ligand.[9] This is believed to be due to long-range coupling to the hydrogen atom on boron. In fact, the ^{19}F NMR spectrum of the deuterated analogue [DB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag-(THF) displayed only a singlet for the trifluoromethyl groups on the 5-position (peaks were not sharp enough to observe D−F coupling, which was estimated to be about 0.5 Hz using $J_{DF}/J_{HF} = 0.154$).[59]

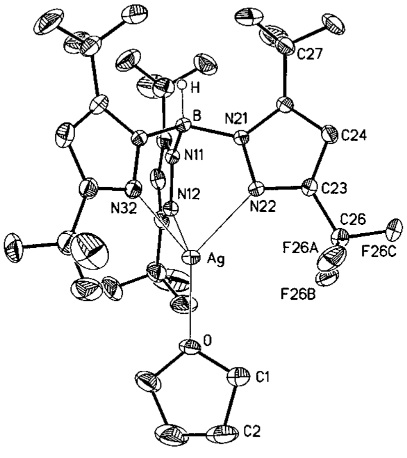


Figure 1. Molecular structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF).

The X-ray crystal structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) is illustrated in Figure 1. It features a pseudo-tetrahedral silver ion with the oxygen atom of THF occupying one of the sites.

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The $[HB(3,5-(CF_3)_2Pz)_3]Ag$ moiety is essentially trigonally symmetric around the Ag···B axis. The Ag−O bond distance is 2.234(4) Å. Structurally characterized complexes of silver with oxygen donors have not been reported in the poly(pyrazolyl)borate family. However, this Ag−O distance is comparable to the corresponding distances in $BaAg[OC(CF_3)_3]_3(THF)_4$ (2.209(12) Å)[60] and [bis(phosphonio)isophosphindolide]-silver complexes (2.238(4) and 2.203(8) Å).[61] The geometry at the oxygen in the THF ligand is very close to planar (sum of the bond angles, 355°).

$[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene). This silver−toluene adduct is an air-stable solid with very good solubility in hydrocarbon solvents such as hexane and benzene. The silver ion coordinated to the $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand, which contains six powerful electron-withdrawing $-CF_3$ groups, would be very electrophilic. This is reflected in the ease of arene adduct formation as in $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene). In general, only silver salts of strong acids (or very weakly coordinating anions) form easily isolable adducts with arene ligands such as benzene or toluene.[62−76]

In order to establish the structural features of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene) in the solid state, an X-ray diffraction experiment was performed and the outcome is shown in Figure 2. There are two chemically identical but crystallographically different molecules in the asymmetric unit. The relative orientation of toluene ligands in these two molecules is shown in Figure 2b,c. The silver ion binds to meta and para carbons of the toluene molecule in η^2-fashion. The $[HB(3,5-(CF_3)_2Pz)_3]Ag$ moiety basically adopts C_{3v} symmetry. Silver atoms show distorted pseudo-tetrahedral geometry. The Ag−C distances for Ag(1) are 2.392(4) and 2.480(4) Å and for Ag(2) are 2.414(4) and 2.506(4) Å. This type of unsymmetric η^2-arene coordination (one long and one short Ag−C) is not unusual in silver chemistry.[64,66,71,73] There are even examples of η^1-bonded silver arene complexes.[74] The Ag−C distances of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene) can be compared to those of $[Ag(\textit{closo}\text{-}6,7,8,9,10\text{-}Br_5CB_9H_5)(\eta^2\text{-toluene})]$ (Ag−C = 2.618(36), 2.642(38) Å),[73] $[AgOTeF_5(toluene)]_2$ (Ag−C = 2.485(5), 2.697(6) Å),[71] $[Ag(\eta^2\text{-benzene})_2(12\text{-}CB_{11}H_{11}F)]$ (Ag−C = 2.462(9), 2.729(10), 2.527(9), 2.585(9) Å),[75] and $[Ag(\eta^1\text{-benzene})(B_{11}CH_{12})]$ (Ag−C = 2.400(7) Å).[74]

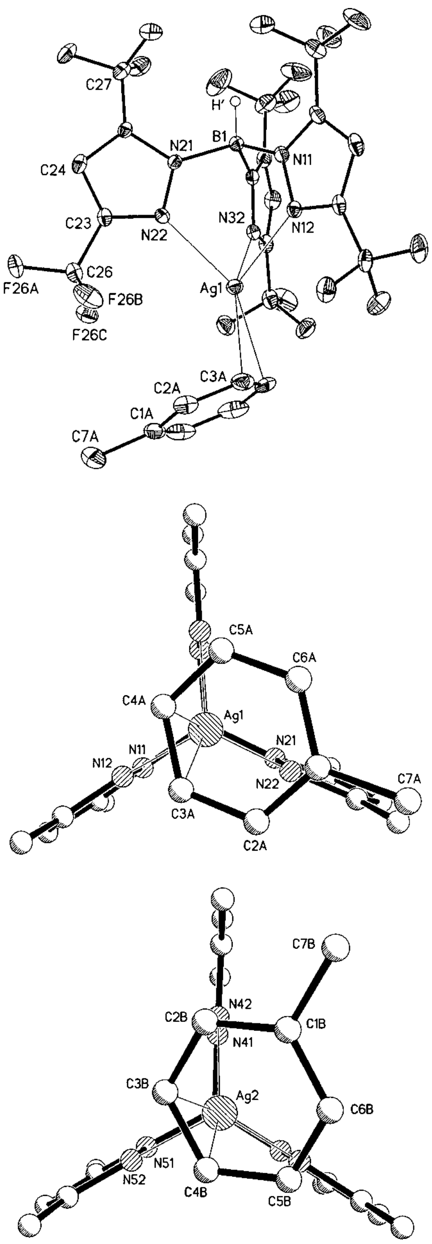

Figure 2. Molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene): (a, top) ORTEP drawing with atom numbering scheme; (b, middle) view of molecule 1 down the Ag1···B axis with hydrogens and fluorines removed; (c, bottom) view of molecule 2 down the Ag2···B axis with hydrogens and fluorines removed.

The room temperature ^{13}C NMR spectrum of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene) in cyclohexane-d_{12} displayed four sharp signals for the aromatic ring carbons, indicating the presence of a fluxional toluene ligand. The fluorine NMR spectrum shows a singlet and a doublet consistent with the C_{3v} symmetry of the $[HB(3,5-(CF_3)_2Pz)_3]Ag$ moiety.

$[HB(3,5-(CF_3)_2Pz)_3]AgCO$. This was synthesized by treating $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene) with CO. Although $[HB(3,5-(CF_3)_2Pz)_3]AgCO$ is a stable solid at room temperature, it very slowly loses CO under reduced pressure. In solution, $[HB(3,5-(CF_3)_2Pz)_3]AgCO$ easily loses CO to competing ligands. For example, the evolution of gas was evident when $[HB(3,5-(CF_3)_2Pz)_3]AgCO$ was dissolved even in a weakly coordinating solvent such as C_6D_6. However, upon exposure to CO, $[HB(3,5-(CF_3)_2Pz)_3]Ag$ readily coordinates CO and reverts back to $[HB(3,5-(CF_3)_2Pz)_3]AgCO$. The nucleophilicity of solvents such as $CHCl_3$ and CH_2Cl_2 is not sufficient to displace CO from $[HB(3,5-(CF_3)_2Pz)_3]AgCO$. For example, a CH_2Cl_2 solution of

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$[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ displayed an absorption band at 2164 cm^{-1} corresponding to the carbonyl stretching frequency. In hexane, the v_{CO} band of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ appears at 2162 cm^{-1}. The solid state spectrum of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ consisted of a band at 2178 cm^{-1} (^{13}CO side band at 2128 cm^{-1}). Surprisingly, a small shoulder was noticed (around 2163 cm^{-1}) on the main peak. This shoulder appears only in solid samples (i.e., solution samples show only a single sharp band for CO), and its intensity seems to depend on the sample preparation and/or crystallization method. The peak splitting in solid state samples has been observed previously.[77−80] Several factors can lead to such split peaks in the solid state, including different crystal forms, correlation field effects, and Fermi coupling.[80−82] Therefore, without the results from more detailed studies, it is difficult to provide a definitive explanation for this observation.

Stable silver carbon monoxide complexes are exceedingly rare and only a very few compounds available for any comparisons.[34−36,83,84] The structurally characterized Ag−CO species are limited only to $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$.[34−36] Interestingly, the Ag−CO interaction in these solid compounds is very weak, and as a result, they lose CO under a vacuum or in the presence of even weakly coordinating solvents (e.g., toluene, CH_2Cl_2). The v_{CO} values of $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$ are 2204 and 2198 cm^{-1}, respectively. These compounds show virtually no metal-to-CO π-back-bonding.[36,83] They are generally classified as nonclassical metal carbonyl complexes.[36,83,85] The v_{CO} of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ is much smaller compared to these values. However, it is also significantly higher than that of the free CO ($v_{CO} = 2143\ cm^{-1}$),[82] suggesting mainly a σ-type Ag−CO interaction with little π-back-bonding. Classical carbonyl complexes (in which the π-back-bonding component is of significant importance) show carbonyl stretching frequencies significantly lower than that of the free CO; e.g., v_{CO} of $Cr(CO)_6 = 1984\ cm^{-1}$.[30,82,86] The v_{CO} of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ can also be compared to the corresponding bands in σ-type CO adducts $BH_3{\cdot}CO$ (2165 cm^{-1}),[87] HCO^+ (2184 cm^{-1}),[88,89] and CH_3CO^+ (2295 cm^{-1}).[90] The closely related copper and gold complexes of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ show v_{CO} bands at 2137 and 2144 cm^{-1}, respectively.[11,58]

The $^{13}C\{^1H\}$ NMR spectrum of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ in CD_2Cl_2 exhibited a resonance at 175.5 ppm which could be assigned to the CO carbon. This value is very close to that observed for $[Ag(CO)][OTeF_5]$ (δ 172.8 (solid state)).[36] It is also in the typical range where ^{13}C NMR resonance of the CO carbon of nonclassical metal carbonyls appear.[84] For comparison, the corresponding signal of the free CO appears at 184 ppm, whereas the classical metal carbon monoxide complexes such as $Cr(CO)_6$ or $Fe(CO)_5$ show much higher values (δ 212.3 and 211.9, respectively).[36,91,92] Therefore, on the basis of the IR and NMR data, $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ can be classified as a nonclassical metal carbon monoxide complex, i.e., CO mainly acting as a σ-donor. Since carbon monoxide is a very weak base and Ag(I) is a poor π-donor, a highly electrophilic silver site is crucial for the isolation of species which contain Ag−CO bonds. The weakly coordinating $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand is certainly a good candidate to support a silver center with such features. Furthermore, it also provides some steric protection to the Ag−CO moiety. Ligands such as $[(C_5H_5)Co\{P(OEt)_2O\}_3]^-$ and $[HC(3\text{-}(Bu^t)Pz)_3]$ have thus far come fairly close to supporting isolable molecules which contain a Ag−CO unit.[24,93]

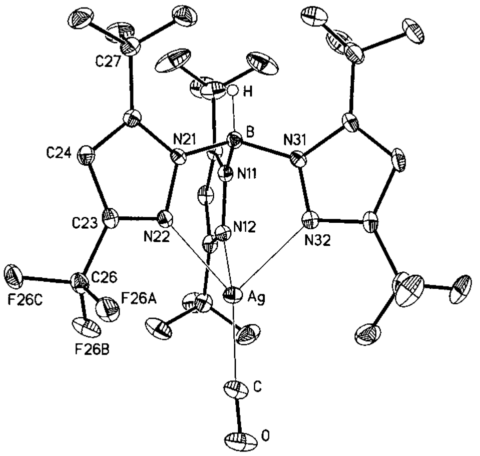

Figure 3. Molecular structure of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$.

The X-ray crystal structure of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ is shown in Figure 3. The silver atom adopts a pseudo-tetrahedral geometry. The Ag−C bond distance of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ (2.037(5) Å) is marginally shorter than the Ag−C separation of 2.10(1) Å for $[Ag(CO)][B(OTeF_5)_4]$ or 2.06(5)−2.20(4) Å for $[Ag(CO)_2][B(OTeF_5)_4]$.[34−36] It is higher than the metal−C distances of 1.808(4) Å in $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$[11] and 1.862(9) Å in $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$.[58] In this closely related series of isoleptic coinage metal carbonyl complexes $[HB(3,5\text{-}(CF_3)_2Pz)_3]MCO$ (where M = Cu, Ag, and Au), the Cu−CO distance is shorter than the Ag−CO distance, as expected on the basis of the atomic radii of Cu and Ag atoms. There is, however, some conflicting information regarding the relative sizes of monovalent Ag and Au ions. The most recent theoretical and experiment data point to a significant reduction in size going from silver to gold.[94,95] The Ag−C and Au−C bond distances of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$ are in excellent agreement with these findings. The C−O distance of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ (1.116(7) Å) is in the expected region.[96] For comparison, the C−O bond distance in free CO is 1.12822(7) Å.[97]

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(CH_2{=}CH_2)$. This ethylene adduct is an air-stable, colorless solid. Unlike the typical Ag−olefin

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complexes,[31,33,37−39] $[HB(3,5-(CF_3)_2Pz)_3]Ag(CH_2{=}CH_2)$ does not lose ethylene under reduced pressure. It was characterized by NMR (^1H, ^{13}C, and ^{19}F) spectroscopy and by X-ray diffraction. The ^1H NMR spectrum in $CDCl_3$ exhibited a resonance at 5.56 ppm which could be assigned to the protons of the ethylene moiety. The signal due to free ethylene appears at 5.28 ppm,[98] whereas, in the closely related copper adducts $[HB(3,5-(CF_3)_2Pz)_3]Cu(CH_2{=}CH_2)$[99] and $[HB(3,5-(CH_3)_2Pz)_3]Cu(CH_2{=}CH_2)$,[16] this peak appears at δ 4.98 and 4.41, respectively. This opposite shift of vinyl protons in Ag and Cu systems (compared to that in free ethylene) is believed to be due to the difference in Ag(I)−olefin and Cu(I)−olefin bonding.[91,100−103] The σ-bonding predominates in silver systems. This results in an overall electron density reduction in the ethylene moiety. However, in the copper systems, the π-back-bonding is relatively more significant, causing a net shielding effect. Alternative explanations such as changes in excitation energy have also been proposed to account for Ag−olefin NMR spectroscopic data.[91,100]

The proton coupled ^{13}C NMR spectrum displayed a triplet at δ 104.9. This can be assigned to the vinyl carbons of the ethylene moiety. The corresponding peak in free ethylene appears at much lower frequency (δ 123.5).[98] The $^1J_{C-H}$ coupling constant of ethylene does not change very much upon coordination (156.4 Hz in free ligand vs 164 Hz in $[HB(3,5-(CF_3)_2Pz)_3]Ag(CH_2{=}CH_2)$). This is consistent with previous observations.[91] We could not observe the $\upsilon_{C=C}$ stretching band in the IR spectrum.

The solid state structure of $[HB(3,5-(CF_3)_2Pz)_3]Ag(CH_2{=}CH_2)$ shows a pseudo-tetrahedral silver ion coordinated to three pyrazole nitrogens and to the ethylene molecule. The $[HB(3,5-(CF_3)_2Pz)_3]Ag$ moiety shows the common C_{3v} symmetry. As seen from Figure 4, the ethylene molecule occupies a site slightly off centered from the 3-fold axis. However, unlike in the toluene adduct, the ethylene molecule binds symmetrically to the silver atom. A search of the Cambridge database did not provide any examples of structurally characterized silver complexes containing $H_2C{=}CH_2$.[40] However, X-ray structures of copper(I) ethylene adducts[16,104,105] and silver complexes containing various substituted olefins are known. Most of the silver adducts are of the ionic type containing weakly coordinating anions such as BF_4^-, ClO_4^-, or NO_3^-.[40] A few neutral silver olefin complexes (mainly containing hexafluoroacetylacetonate ligand) have also been reported.[106,107] The Ag−C distances of $[HB(3,5-(CF_3)_2Pz)_3]Ag(CH_2{=}CH_2)$ are on the short end of the values typically observed for silver(I) alkene and arene complexes (2.31−2.84 Å).[53] The C−C bond distance of the coordinated ethylene (1.298(14) Å) is essentially the same as that for the free molecule (1.3371(2) Å.[108] This is indicative of a poor Ag(I)-to-olefin π-back-bonding interaction. It is noteworthy that the related copper(I) analogue $[HB(3,5-(CH_3)_2Pz)_3]Cu(CH_2{=}CH_2)$ is a useful catalyst for carbene and nitrene transfer reactions.[109] It has also been investigated as a useful model for the ethylene binding site of plants.[16]

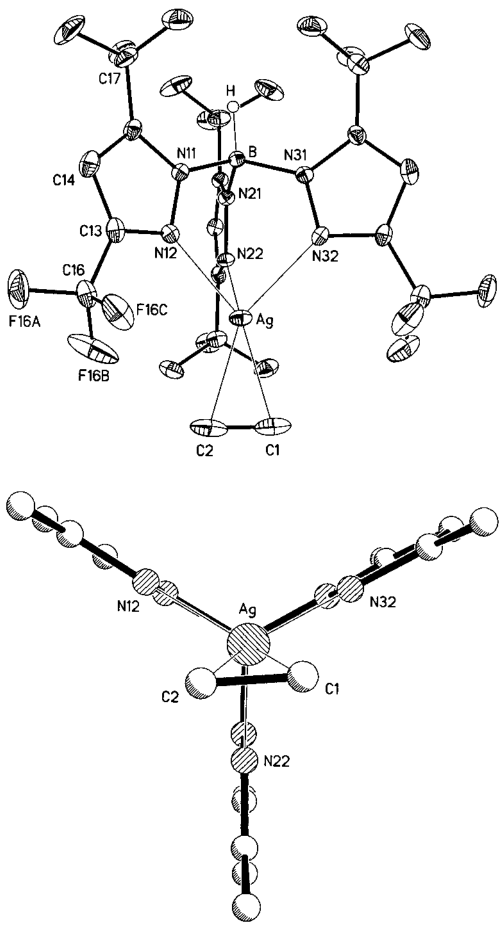

Figure 4. Molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]Ag(H_2C{=}CH_2)$: (a, top) ORTEP drawing with atom numbering scheme; (b, bottom) view down the Ag···B axis with hydrogens and fluorines removed.

$[HB(3,5-(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$. This acetylene complex could be prepared conveniently by displacing toluene from $[HB(3,5-(CF_3)_2Pz)_3]Ag(toluene)$. The ^1H NMR spectrum taken in $CDCl_3$ shows a singlet at δ 3.48. It can be assigned to the protons of the acetylene unit. Bubbling excess acetylene into a solution of $[HB(3,5-(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ resulted in the disappearance of this δ 3.48 peak and the appearance of a broad new signal at a chemical shift value much closer to that of the free $HC{\equiv}CH$ (δ 2.36).[98] This indicates the presence of a labile acetylene ligand. We could not observe the signal due to acetylene when the NMR spectrum was taken in C_6D_6. This is perhaps due to the displacement of acetylene by benzene molecules. The ^{13}C signal due to coordinated acetylene was observed at δ 66.3 (compared with free acetylene at δ 71.9).[98] This peak appears as a doublet of doublet in the proton coupled ^{13}C NMR spectrum. The $^1J_{C-H}$ and $^2J_{C-H}$ values are 256 and 49.2 Hz, respectively. These changes are very minor compared to those of 249.0 and 49.6 Hz for free acetylene ligand.[98] We could not observe the $\upsilon_{C\equiv C}$ stretching band in the IR spectrum. However, a broad band was observed at 3246 cm^{-1} which may be assigned to the C−H stretching frequency of the coordinated acetylene.

The X-ray crystal structure of $[HB(3,5-(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ is shown in Figure 5. Overall structural features are very similar to those of the ethylene analogue. The silver ion adopts a pseudo-tetrahedral symmetry. The Ag−C distances

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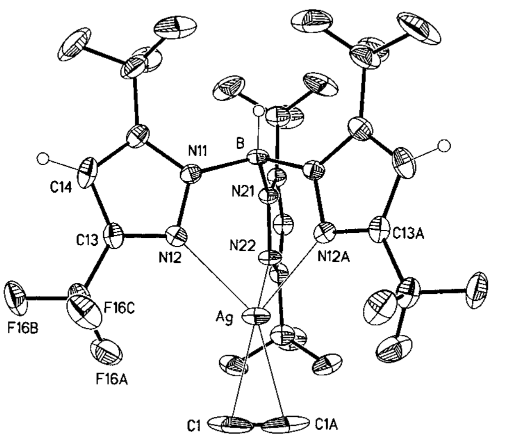

Figure 5. Molecular structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CH).

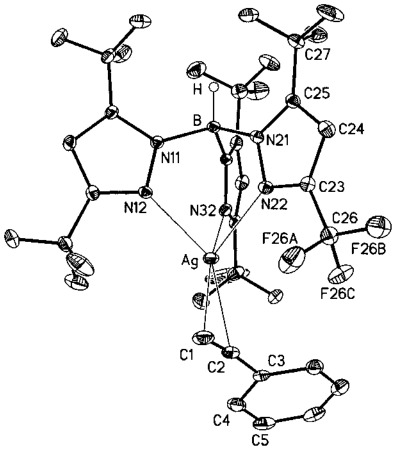

Figure 6. Molecular structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh).

are essentially identical to the corresponding distances in [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(H$_2$C=CH$_2$). Unfortunately, the acetylene moiety shows some disorder as evident from the relatively large thermal parameters along the C−C axis. Therefore, it is unwise to interpret the structural parameters of the acetylene unit in great detail. On the basis of the data from [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh) (see below) and copper complexes [(phen)Cu(HC≡CH)]ClO$_4$ (C−C = 1.190(7) Å)[110] and [(NH(py)$_2$Cu(HC≡CH)]BF$_4$ (C−C = 1.188(11) Å),[104] one would expect to see virtually no lengthening in the C−C distance upon coordination.

Structurally characterized silver alkynes are rare,[40,52−54] perhaps as a result of weak Ag−alkyne interaction. Further difficulty may be the secondary reactions of acetylene and terminal alkynes with silver ions leading to the formation of insoluble, sometimes explosive, silver acetylides.[33,39] Relatively stable adducts generally contain polyalkyne ligands and/or ionic silver salts.[53,54]

[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh). The alkyne complex [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh) was obtained by the treatment of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(toluene) with phenylacetylene. The ^{1}H NMR spectrum displayed a resonance at 4.33 ppm due to the alkyne proton of the coordinated phenylacetylene (cf. the free ligand at 3.05 ppm).[108] The ^{13}C NMR spectrum exhibited resonances at δ 66.5 and 86.7 which correspond to the H−*C* and *C*−Ph carbons of the alkyne unit. The corresponding resonances of the free ligand were observed at δ 77.6 and 83.9, respectively.[108] The one- and two-bond C−H coupling constants were essentially identical to those of the acetylene analogue.

The $\nu_{C\equiv C}$ stretching band of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh) was observed at 2041 cm^{-1}. This value is about 69 cm^{-1} lower than the $\nu_{C\equiv C}$ band for the free HC≡CPh ligand (2110 cm^{-1}). Both the 2041 cm^{-1} value and the relatively small lowering of $\nu_{C\equiv C}$ suggest a very weak metal−alkyne interaction. Typically, complexes which contain weak metal−alkyne bonds show C≡C stretching bands in the 1950−2120 cm^{-1} region.[31] They are also characterized by relatively small lowering of the $\nu_{C\equiv C}$ frequency (150−250 cm^{-1}).[31] The IR band observed at 3264 cm^{-1} may be assigned to $\nu_{C_{sp}-H}$. This corresponds to a small lowering relative to that for the free ligand (3292 cm^{-1}). These data are consistent with the previous observations of silver−alkyne adducts.[39] Relatively large lowerings were observed in copper adducts. For example, these data of can be compared to the $\nu_{C\equiv C}$ (1977 cm^{-1}) and $\nu_{C_{sp}-H}$ (3172 cm^{-1}) values of ClCu(HC≡CPh)[111] and $\nu_{C\equiv C}$ (1921 cm^{-1}) of [(phen)Cu(HC≡CPh)]ClO$_4$ [110] (phen = 1,10-phenanthroline).

The X-ray crystal structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh) is depicted in Figure 6. Interestingly, the HC≡CPh coordinates to the silver atom in an asymmetric manner with one short Ag−C bond length (2.263(5) Å) and one long Ag−C distance (2.407(5) Å). Similar asymmetric bonding of HC≡CPh, but to a significantly lesser extent, has been observed in copper systems. For example, the Cu−C separations in ClCu(HC≡CPh)[111] and [(phen)Cu(HC≡CPh)]ClO$_4$ are 1.999(4), 2.066(3) Å and 1.922(12), 1.995(10) Å, respectively. Relatively large asymmetry in [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh) is perhaps due to unfavorable steric interactions between the phenyl group and the CF$_3$ substituents at the pyrazolyl ring 3-position. The X-ray crystal structure also shows the coordination of silver ion to the alkyne unit as opposed to the π-system in the phenyl group. The average Ag−C distance is similar to the corresponding distances in the ethylene or acetylene complexes. The C≡C bond distance shows virtually no effect as a result of silver ion coordination. This is consistent with the IR data which show only a minor change in the $\nu_{C\equiv C}$ stretching frequency. The C≡C−C angle is 173.3(5)°. This corresponds to only about 6.7° bending-back angle. There is a good linear relationship between $\Delta\nu_{C\equiv C}$ ($\Delta\nu = \nu_{\text{free}} - \nu_{\text{complex}}$) and the bending-back angle of transition metal acetylenic complexes.[110,112] Smaller $\Delta\nu_{C\equiv C}$ values generally correspond to smaller bending-back angles. The small $\Delta\nu_{C\equiv C}$ of 69 cm^{-1} observed for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(HC≡CPh) is in excellent agreement with the relatively small bending-back angle of 6.7°. The hydrogen atom on the alkyne was located from the difference map during refinement. The Ag···H1 separation is about 2.68 Å, and the C2−C1−H1 angle is 173°. Overall, spectroscopic and structural data indicate only a very weak silver-to-alkyne back-donation.

[HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgCNBu^t. Unlike the CO adduct, [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgCNBu^t is stable both in solution and as a pure solid, and donors such as benzene or toluene do not displace CNBu^t from the silver ion. This indicates the presence of a much stronger Ag−C interaction in [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgCNBu^t. Metal isocyanides have often been compared to metal carbonyls, perhaps due to the isoelectronic relationship between CNH and CO.[30,113] However, compared to CO, isocyanide ligands display stronger σ-donor character and weaker π-acceptor character.[29,30] As a result, they form relatively stable complexes with metal ions in high oxidation

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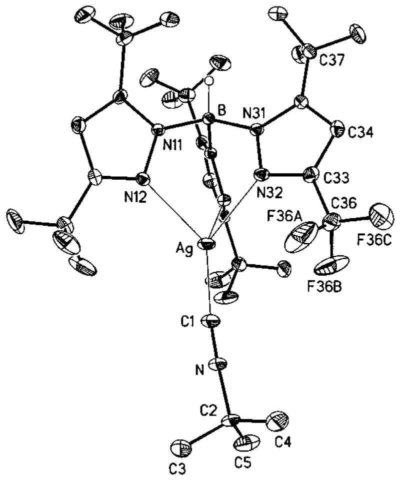

Figure 7. Molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]AgCNBu^t$.

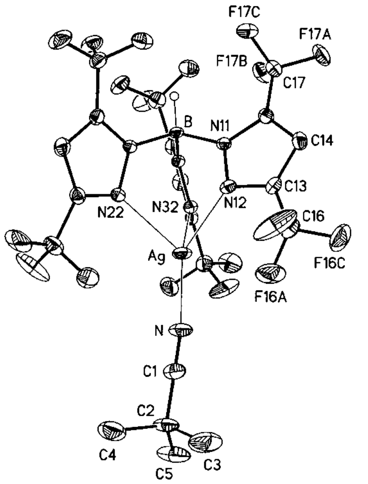

Figure 8. Molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$.

states where π-back-bonding is of little significance.[29,113,114] This is true also for silver(I) as evident from the relative stability of $[HB(3,5-(CF_3)_2Pz)_3]AgCNBu^t$ and $[HB(3,5-(CF_3)_2Pz)_3]AgCO$.

The resonance observed at δ 137.4 in the ^{13}C NMR spectrum of $[HB(3,5-(CF_3)_2Pz)_3]AgCNBu^t$ can be assigned to the isocyanide carbon.[115,116] This is very similar to that observed for $[Ag_2L'_2](ClO_4)_2$ (δ 139.39, where $L' = 2,5$-dimethyl-2,5-diisocyanohexane).[115] The infrared stretching band corresponding to the CN moiety of $[HB(3,5-(CF_3)_2Pz)_3]AgCNBu^t$ appears at 2214 cm^{-1}. It is significantly higher than the ν_{CN} value observed for free $CNBu^t$ ($\nu_{CN} = 2138\ cm^{-1}$), indicating predominantly σ-type Ag−$CNBu^t$ interaction.[117,118] The corresponding values in silver complexes such as $[B(Pz)_4]AgCNBu^t$,[18] $\{[HC(3-Bu^tPz)_3]AgCNBu^t\}OTf$,[24] and $[(C_5H_5)Co\{P(OEt)_2O\}_3]AgCNBu^t$ [93] are 2185, 2202, and 2187 cm^{-1}, respectively. The relatively higher ν_{CN} for $[HB(3,5-(CF_3)_2Pz)_3]AgCNBu^t$ may be a direct result of increased Lewis acidity of the silver center due to the presence of the highly electron deficient tris(pyrazolyl)borate ligand. The copper and gold analogues, $[HB(3,5-(CF_3)_2Pz)_3]CuCNBu^t$ ($\nu_{CN} = 2196\ cm^{-1}$)[57] and $[HB(3,5-(CF_3)_2Pz)_3]AuCNBu^t$ ($\nu_{CN} = 2248\ cm^{-1}$),[58] show relatively lower and higher ν_{CN} values compared to that of the silver adduct.

The X-ray crystal structure of $[HB(3,5-(CF_3)_2Pz)_3]AgCNBu^t$ is illustrated in Figure 7. It features a pseudo-tetrahedral silver ion with $CNBu^t$ occupying one of the sites. The Ag−C and C−N distances are 2.059(4) and 1.139(5) Å, respectively. The isocyanide group is slightly bent with a Ag−C−N angle of 173.7(4)° and a C−N−C angle of 176.2(4)°. These features are similar to those of the somewhat related tris(pyrazolyl)methane complex $\{[HC(3-Bu^tPz)_3]AgCNBu^t\}OTf$.[24]

$[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$. In order to see whether there are any major differences between silver(I) complexes of the two isomers $NCBu^t$ and $CNBu^t$, we carried out the synthesis of $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$. The treatment of $[HB(3,5-(CF_3)_2Pz)_3]Ag(THF)$ with pivalonitrile ($NCBu^t$) led quantitatively to the related $NCBu^t$ adduct. The ^1H NMR chemical shifts of the two isomers are essentially identical. However, ^{13}C and ^{19}F NMR spectra showed clear differences. The ^{13}C NMR signal due to CMe_3 of $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$ (δ 28.6) appeared at a significantly higher frequency than that of the $[HB(3,5-(CF_3)_2Pz)_3]AgCNBu^t$ (δ 57.3). We did not detect the resonance corresponding to the N*C* carbon. Although the ^{19}F NMR chemical shift values and the peaks centered at −58 ppm were similar for the two complexes, the upfield resonance in $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$ appeared as a doublet. This is perhaps due to long-range Ag−F coupling. We have observed such coupling in the $[HB(3,5-(CF_3)_2Pz)_3]AgPPh_3$ complex.[9] The ν_{NC} band of $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$ appears at 2277 cm^{-1}. It is about 43 cm^{-1} higher than the NC stretching frequency of free $NCBu^t$ ($\nu_{CN} = 2234\ cm^{-1}$). The corresponding shift in the $CNBu^t$ analogue is about 76 cm^{-1}.

The X-ray crystal structure of $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$ is illustrated in Figure 8. General structural features are very similar between the two isomers. For example, the symmetry of the $[HB(3,5-(CF_3)_2Pz)_3]Ag$ moiety in both $NCBu^t$ and $CNBu^t$ complexes may be described as C_3 due to the tilting of pyrazolyl rings with respect to the Ag···B axis. However, the structural parameters of the $AgNCBu^t$ unit are different. The Ag−N bond distance in $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$ (2.120(4) Å) is much larger than the Ag−C distance of the $CNBu^t$ analogue. This and the smaller increase in ν_{NC} suggest a relatively weak Ag−ligand interaction in the N-bonded species. The N−C distance (1.139(6) Å) is in the range typically observed for metal nitriles.[96] Interestingly, the Ag−N and N−C distances of this four-coordinate silver adduct $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$ are not very different from the corresponding distances in two coordinate species $(CF_3)_2CFAgNCCH_3$ (2.083(7), and 1.124(11) Å).[119] The Ag−N−C−C moiety is not linear. The Ag−N−C and N−C−C angles are 169.6(4) and 178.3(6)°, respectively.

General Features of $[HB(3,5-(CF_3)_2Pz)_3]Ag$ Adducts 3−10. Silver complexes of $[HB(3,5-(CF_3)_2Pz)_3]^-$ are colorless solids at room temperature. They show good solubility in hydrocarbon solvents such as hexane. Non-fluorinated species like $[HB(Pz)_3]Ag$ and $[HB(3,5-(CH_3)_2Pz)_3]Ag$ show very poor solubility in most organic solvents.[19] Compounds **3−10** can be handled in air for short periods without any significant decomposition. However, prolonged storage at room temperature under visible light leads to slow discoloration and/or decomposition. Therefore, these silver adducts are best stored under nitrogen in a low-temperature freezer. These silver adducts are also soluble in chlorinated solvents, but, due to slow decomposition over a

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period of several hours, those solvents should be avoided as a medium for storage. We have used $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ or $[HB(3,5-(CF_3)_2Pz)_3]Ag(THF)$ as the $[HB(3,5-(CF_3)_2Pz)_3]Ag$ donor (Scheme 1). These complexes also serve as convenient starting material for various other [tris(pyrazolyl)borato]metal derivatives. For example, $[HB(3,5-(CF_3)_2Pz)_3]Ag(THF)$ was used as the ligand transfer agent in the synthesis of $[HB(3,5-(CF_3)_2Pz)_3]In$, $[HB(3,5-(CF_3)_2Pz)_3]AuCO$, and $[HB(3,5-(CF_3)_2Pz)_3]Mn(CO)_3$.[12,22,58] The ^{19}F and ^{13}C NMR chemical shift values of the $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand do not depend significantly on the secondary ligand on silver. The ^1H NMR resonance of the pyrazolyl ring protons usually shows up in the 6.3−7.0 ppm range. The infrared absorption band corresponding to B−H appears at 2620 ± 16 cm^{-1}. Silver adducts of non-fluorinated $[HB(Pz)_3]^-$ and $[HB(3,5-(CH_3)_2Pz)_3]^-$ ligands exhibit this band at a relatively lower frequency; e.g., the υ_{BH} band of $[HB(Pz)_3]^-$ appears around 2450 cm^{-1}.

The $[HB(3,5-(CF_3)_2Pz)_3]Ag$ complexes described in this paper easily afford clear, X-ray quality crystals from hydrocarbon solvents at low temperatures. Solid state structures show the $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand bonded to silver ion in a tripodal fashion with pyrazolyl nitrogen to silver distances ranging from 2.297 to 2.447 Å. Interestingly, these values are very similar to Ag−N separations of silver adducts derived from non-fluorinated $[HB(3-(2\text{-pyridyl})Pz)_3]^-$, $[HC(3\text{-}Bu^tPz)_3]$, and $[HB(1,2,4\text{-triazolyl})_3]^-$ ligands.[21,23,24]

Summary and Conclusion

We have described the synthesis, properties, and X-ray crystal structures of $[HB(3,5-(CF_3)_2Pz)_3]AgL$, where L = THF, toluene, CO, $H_2C{=}CH_2$, $HC{\equiv}CH$, $HC{\equiv}CPh$, $CNBu^t$, and $NCBu^t$. Despite the wide use of tris(pyrazolyl)borates, very few groups have investigated their silver derivatives. Compounds described in this paper represent a major addition to that family. The majority of the silver complexes of L are typically those of ionic silver salts (e.g., AgX, where X is usually an anion like OTf^-, NO_3^-, BF_4^-, or ClO_4^-). Neutral molecules like compounds **3**−**8** are not very common in silver chemistry. Their stability may be attributed mainly to the unique electronic properties of the $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand. The main difficulty in obtaining stable silver adducts containing ligands such as CO, $H_2C{=}CH_2$, and $HC{\equiv}CH$ is the inherently weak silver−L interaction. Silver(I) is a poor donor of electrons to π-acid ligands. This is reflected in the spectroscopic and structural data of compounds **5**−**9**. As a result, a strong σ-bonding component is very important to their stability. The $[HB(3,5-(CF_3)_2Pz)_3]^-$ is a powerful electron-withdrawing ligand as demonstrated by our previous studies of its copper and manganese derivatives.[10−12] Thus, the coordination of silver(I) ion to $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand may not significantly reduce the electrophilic character at the silver site. This allows the formation of a relatively strong Ag−L σ-bond. The steric protection afforded by $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand to the Ag−L moiety further enhances the stability of $[HB(3,5-(CF_3)_2Pz)_3]AgL$ species.

Ligand steric and electronic properties of tris(pyrazolyl)borate ligands can be modulated by changing substituents on the pyrazolyl rings and on boron.[1,4] Such studies are not possible with ionic $[Ag{-}L]^+X^-$ type adducts. We are currently investigating the effects of ligand properties on the chemical reactivity of Ag−L adducts, as well as the reactivity of some of the $[HB(3,5-(CF_3)_2Pz)_3]AgL$ complexes.

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Supporting Information Available: Text giving additional information about the structure solution and refinements and views down the Ag···B axis for **5**, **8**, and **10** (6 pages). X-ray crystallographic files, in CIF format, for the structure determinations of **4**, **6**, **7**, **8**, and **10** are available on the Internet only. Ordering and access information is given on any current masthead page.

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