Supplementary Information

Silver(I) Carbonyl and Silver(I) Ethylene Complexes of a B-Protected Fluorinated Tris(pyrazolyl)borate Ligand

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Table S1. Selected spectroscopic and X-ray structural data of structurally characterized silver(I) carbonyl complexes

Compound	υ_{CO}(cm^{-1})	δ^{13}C(ppm)	Ag-C(Å)	C-O(Å)	Ag-C-O(deg.)	Ref
[MeB(3-(C_2F_5)Pz)$_3$]AgCO	2153[a]/2151[c]	176.1[e]	2.030(4)	1.117(4)	173.1(3)	this work
[HB(3,5-(CF_3)$_2$Pz)$_3$]AgCO	2178[b]/2162[d]	175[f]	2.037(5)	1.116(7)	175.6(6)	[1, 2]
[AgCO][B($OTeF_5$)$_4$]	2204[b]	174[f]	2.10(1)	1.077(16)	176(1)	[3]
[Ag(CO)$_2$][B($OTeF_5$)$_4$]	2198[b]		2.14(5)[g]	1.08(6)[f]	176(3)[g]	[3]
CO	2143	184[f]	--------	1.12822		[3, 4]

[a]KBr pellet, [b]Nujol mull, [c]CH_2Cl_2, [d]Hexane, [e]$CDCl_3$, [f]CD_2Cl_2, [g]average values for three unique cations

Table S2. Selected spectroscopic and X-ray structural data of structurally characterized silver(I) ethylene complexes

Compound	δ^1H(ppm)	δ^{13}C(ppm)	$^1J_{C-H}$(Hz)	Ag-C(Å)	C=C(Å)	Ref
[MeB(3-(C_2F_5)Pz)$_3$]AgC_2H_4	5.48[a]	105.5[a]	161.1	2.300(2)	1.314(4)	this work
[HB(3,5-(CF_3)$_2$Pz)$_3$]AgC_2H_4	5.52[b]/5.56[c]	104.9[c]	164	2.300(7)	1.298(14)	[1]
[Ag(C_2H_4)$_3$][Al{$OC(CF_3)_3$}$_4$]	5.77[a]	116.4[a]		2.396	1.307	[5]
C_2H_4	5.40[a,b]	123.3[a]	156.4	-------	1.313	[5, 6]

[a]CD_2Cl_2, [b]$CDCl_3$, [c]C_6D_{12}

Experimental:

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres single-station drybox equipped with a -25 ºC refrigerator. Solvents were purchased from commercial sources, purified prior to use. NMR spectra were recorded at 25 ºC on a JEOL Eclipse 500 spectrometer (^{1}H, 500.16 MHz and 300.53 MHz; ^{13}C, 125.78 MHz, and 75.59 MHz; ^{11}B, 160.47 MHz, and 96.42 MHz; ^{19}F, 470.62 MHz, and 282.78 MHz). Proton and carbon chemical shifts are reported in ppm versus Me_4Si. ^{11}B NMR was referenced to external BF_3•Et_2O. ^{19}F NMR was referenced to external $CFCl_3$. IR spectra were recorded on a JASCO FT-IR 410 spectrometer. Raman spectra were recorded with a Spektrum 2000 Perkin-Elmer spectrometer, equipped with a NdYAG-Laser (1060 nm) operating at 100 mW with 100-200 trans and a resolution of 4 cm^{-1}. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Silver (I) triflate were purchased from Aldrich, and CO and ethylene were purchased from Matheson. They were all used as received. Li[$MeBH_3$] was carried out as reported previously.[7]

[MeB(3-(C_2F_5)Pz)$_3$]Li: In a glove box, a sample Li[$MeBH_3$] (0.215 g, 6.00 mmol) kept at -25 ºC in a freezer was added to a Schlenk tube containing 3-(C_2F_5)PzH (3.378 g, 18.19 mmol) at -25 ºC. The resulting mixture was stirred while allowing it to warm to room temperature. After 8hr, the mixture was taken out of the glove box and was heated for 6 hr at 105 ºC under N_2. During this period, some single crystals of the product formed on the wall of the Schlenk tube. The mixture was allowed to cool to room temperature, and the resulting solid was washed by hexane and dried under vacuum to obtain [MeB(3-(C_2F_5)Pz)$_3$]Li as a white solid (1.857g, yield 53% based on Li[$MeBH_3$]). Mp.: 159 ~ 160 ºC. ^{1}H NMR ($CDCl_3$): δ 7.73 (superimposed doublet of triplets, 3H, ^{3}J (H, H) = 2.4Hz, ^{4}J (F, H) = 1.7Hz, Pz-H_4), 6.42 (d, 3H, ^{3}J (H, H) = 2.4Hz, Pz-H_5), 1.08 (s, 3H, BCH_3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.4 (t, ^{2}J (C, F) = 28.8Hz, Pz-C_3), 134.4 (s, Pz-C_5), 119.3 (qt, ^{1}J (C, F) = 285.5Hz, ^{2}J (C, F) = 38.0Hz, CF_3), 110.9 (tq, ^{1}J (C, F) = 248.8Hz, ^{2}J (C, F) = 38.9Hz, CF_2), 104.1 (s, Pz-C_4), 2.5 (br m, BCH_3); ^{19}F NMR ($CDCl_3$):δ -85.7 (s, 9F, CF_3), -114.0 (s, 6F, CF_2); ^{11}B NMR ($CDCl_3$):δ -1.10 (s). IR (KBr, cm^{-1}, resolution: 4cm^{-1}): 3687, 3617, 3571, 3142, 1627, 1490, 1368, 1334, 1172, 1043, 972, 782, 749, 725, 693, 651. Anal. Calcd for $C_{16}H_9BF_{15}N_6Li$: C, 32.68; H, 1.54; N, 14.29. Found: C, 32.26; H, 1.49; N, 13.99.

[MeB(3-(C_2F_5)Pz)$_3$]AgCO: [MeB(3-(C_2F_5)Pz)$_3$]Li (0.295 g, 0.50 mmol) and silver(I) triflate (0.128 g, 0.50 mmol) were mixed in a Schlenk tube covered with aluminum foil. Dichloromethane (30 mL) was

added in this mixture at -78 ºC. Then CO gas was bubbled through the solution for 5 min at -78 ºC and stirred for about 10 hr under CO atmosphere at room temperature. The resulting mixture was filtered and solvent was removed from the filtrate under CO atmosphere to obtain [MeB(3-(C_2F_5)Pz)$_3$]AgCO as a white solid in yield 61%. It was recrystallized from CO saturated hexane at -20 ºC under CO to obtain colorless crystals. Mp.: 276 ~ 277 ºC. ^{1}H NMR ($CDCl_3$): δ 7.70 (superimposed doublet of triplets, 3H, ^3J (H, H) = 2.4Hz, ^4J (F, H) = 1.5Hz, Pz-H$_4$), 6.41 (d, 3H, ^3J (H, H) = 2.4Hz, Pz-H$_5$), 1.01 (s, 3H, BC*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 176.1 (br, *C*O), 141.7 (t, ^2J (C, F) = 27.1Hz, Pz-C$_3$), 135.1 (s, Pz-C$_5$), 118.8 (qt, ^1J (C, F) = 285.6Hz, ^2J (C, F) = 38.7Hz, *C*F$_3$), 111.0 (tq, ^1J (C, F) = 252.9Hz ^2J (C, F) = 39.3Hz, *C*F$_2$), 104.8 (s, Pz-C$_4$), 4.8 (br m, B*C*H$_3$); ^{19}F NMR ($CDCl_3$): δ -85.2 (br m, 9F, C*F*$_3$), -114.0 (br m, 6F, C*F*$_2$); ^{11}B NMR ($CDCl_3$): δ -1.19 (s). IR (KBr, resolution: 1cm^{-1}): 2153 cm^{-1} (CO); IR (KBr, resolution: 4cm^{-1}): 3161, 2962, 2153 (CO), 1488, 1334, 1179, 1045, 970, 920, 749, 722, 700, 650 cm^{-1}. IR (CH_2Cl_2 or Nujol, resolution: 4cm^{-1}): 2151 cm^{-1} (CO); Raman (solid): 3158(m), 3142(m), 2976, 2937, 2876, 2152 (s, CO), 1512(m), 1494, 1384(m), 1368(s), 1335, 1185, 1075, 1047(m), 971, 934, 753(s), 541, 370, 283 cm^{-1};. Anal. Calcd for $C_{17}H_9AgBF_{15}N_6O$: C, 28.48; H, 1.27; N, 11.72. Found: C, 27.92; H, 1.01; N, 12.10.

[MeB(3-(C_2F_5)Pz)$_3$]AgC_2H_4: [MeB(3-(C_2F_5)Pz)$_3$]Li (0.295 g, 0.50 mmol) and silver(I) triflate (0.128 g, 0.50 mmol) were mixed in a Schlenk tube covered with aluminum foil. Dichloromethane (30 mL) was added in this mixture at -78 ºC. Then ethylene was bubbled through the solution for 2 min at -78 ºC, and 10 min at room temperature, and stirred for about 10 hr at room temperature. The resulting mixture was filtered and solvent was removed from the filtrate under ethylene atmosphere to obtain the product as a white solid in yield 76%. It was recrystallized from hexane under ethylene at -20 ºC to obtain colorless crystal of [MeB(3-(C_2F_5)Pz)$_3$]AgC_2H_4. Mp.: 266 ~ 267 ºC. ^{1}H NMR (CD_2Cl_2): δ 7.85 (superimposed doublet of triplets, 3H, ^3J (H, H) = 2.3Hz, ^4J (F, H) = 1.4Hz, Pz-H$_4$), 6.51 (d,3H, ^3J (H, H) = 2.3Hz, Pz-H$_5$), 5.48 (s, 4H, C_2H_4), 1.12 (s, 3H, BC*H*$_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 141.9(t, ^2J (C, F) = 27.1Hz, Pz-C$_3$), 135.8(s, Pz-C$_5$), 119.4 (qt, ^1J (C, F) = 286.0Hz, ^2J (C, F) = 38.5Hz, *C*F$_3$), 111.7 (tq, ^1J (C, F) = 251.2Hz ^2J (C, F) = 39.5Hz, *C*F$_2$), 107.7 (br, C_2H_4),105.2(s, Pz-C$_5$), 6.7 (br m, B*C*H$_3$); ^{13}C NMR (CD_2Cl_2): δ 105.5 (t, ^1J (C, H) = 161.1Hz, C_2H_4); ^{19}F NMR (CD_2Cl_2): δ -85.6 (s, 9F, C*F*$_3$), -113.4 (s, 6F, C*F*$_2$); ^{11}B NMR (CD_2Cl_2): δ -0.81 (s); IR (KBr, resolution: 4cm^{-1}): 3160, 3143, 2975, 1490, 1366, 1334, 1174, 1042, 970, 924, 781, 748, 721, 694, 649 cm^{-1}.Raman (solid): 3158(m), 3141(m), 3018, 2976, 2938, 2875, 1578(C=C, s), 1512, 1494, 1381(m), 1370(s), 1335, 1314(s), 1184, 1073, 1044(m), 978(m), 967, 933, 922, 752(s), 601, 541, 372, 281(w) cm^{-1}. Anal. Calcd for $C_{18}H_{13}AgBF_{15}N_6$: C, 30.15; H, 1.83; N, 11.72. Found: C, 30.00; H, 1.61; N, 11.64.

X-ray data were collected at 100K on a Bruker diffractometer with a SmartApex CCD. X-ray data for **[MeB(3-(C_2F_5)Pz)$_3$]Li;** $C_{16}H_9BF_{15}LiN_6$, Trigonal, Space group $P\bar{3}$; a = 11.8515(4) Å, b = 11.85150(10) Å, c = 9.4723(4) Å, V = 1152.21(6) Å^3, Z = 2, ρ (calc.) = 1.695 Mg/m^3. All nonhydrogen atoms were refined anisotropically. R1, wR2 (I > 2σ(I)) = 0.0571, wR2 = 0.1521. X-ray data for **[MeB(3-(C_2F_5)Pz)$_3$]AgCO**; $C_{17}H_9AgBF_{15}N_6O$, Triclinic, Space group $P\bar{1}$, a = 10.8470(5) Å, b = 11.5748(6) Å, c = 11.6997(6) Å, V = 1231.45(11) Å^3, Z = 2, ρ (calc.) = 1.934 Mg/m^3. All nonhydrogen atoms were refined anisotropically, R1, wR2 (I > 2σ(I)) = 0.0288, 0.0693. X-ray data for **[MeB(3-(C_2F_5)Pz)$_3$]AgC_2H_4;** $C_{18}H_{13}AgBF_{15}N_6$, Monoclinic, Space group $C2/c$, a = 20.0180(8) Å, b = 11.8825(5) Å, c = 21.2546(8) Å, V = 5000.7(3) Å^3, Z = 8, ρ (calc.) = 1.905 Mg/m^3. All nonhydrogen atoms were refined anisotropically, R1, wR2 (I > 2σ(I)) = 0.0260, 0.0666. The CCDC 271567–271569 contain the supplementary crystallographic data for this paper. 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).

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