Silver(I) Complex [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH$_3$ Supported by a Partially-fluorinated Scorpionate

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Supporting information

Experimental

All manipulations were carried out under an atmosphere of purified dry nitrogen using standard Schlenk techniques. Solvents were purchased from commercial sources, purified by distilling over conventional drying agents and degassed by the freeze-pump-thaw method prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded on a JEOL Eclipse 500. Proton and carbon chemical shifts are reported in ppm, and referenced using the residual proton or carbon signals of the deuterated solvent. ^{19}F NMR chemical shifts were referenced relative to $CFCl_3$ (external). Elemental analyses were performed at Intertek Pharmaceutical Services, Whitehouse, NJ. CF_3SO_3Ag was purchased from Sigma Aldrich and used without further purification. The compound [HB(3-(CF_3),5-(CH_3)Pz)$_3$]Na was prepared by a reported procedure (Bucher *et al.*, 1995).

Synthesis of [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH$_3$

[HB(3-(CF_3),5-(Me)Pz)$_3$]Na **(**0.165 g, 0.34 mmol) and CF_3SO_3Ag (0.09g, 0.34 mmol) were placed in a Schlenk flask under nitrogen atmosphere. To this mixture, dichloromethane (10

mL) was at the room temperature and stirred for a few minutes. Then, CH_3CN (1 mL) was added to the solution and stirred for additional 2h. Thereafter, the mixture was filtered and the resulting clear filtrate was placed in a freezer maintained at -20 ^oC overnight. [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH_3 was obtained as a colourless crystalline solid in 85% yield. It is stable under vacuum and can be handled in open air for short periods. Longer exposure to light and air causes decomposition. ^{1}H NMR ($CDCl_3$, 500.16 MHZ, 298 K): δ 6.21 (s, 3H, Pz-*H*), 2.43 (s, 9H, C*H*$_3$Pz), 2.14 (s, 3H, C*H*$_3$CN).^{13}C{^{1}H} NMR ($CDCl_3$, 125.76 MHz, 298 K): δ 145.5 (Pz), 142.1 (Pz, J_{C-F} = 34.7 Hz), 121.7 (*C*F$_3$, J_{C-F} = 269.8 Hz), 117.2 (CH_3*C*N), 103.5 (Pz), 13.1 (*C*H$_3$Pz), 2.1 (*C*H$_3$CN). ^{19}F NMR ($CDCl_3$, 470.62 MHz, 298 K): δ -61.55. Analysis Calcd. for $C_{17}H_{16}AgBF_9N_7$: C, 33.58; H, 2.65; N, 16.13%. Found. C, 33.42; H, 2.43; N, 16.63%.

A suitable crystal of [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH_3 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 were measured at 100(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 Kα fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed using the Bruker ApexII program suite. Absorption corrections were applied by using SADABS. 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.(Sheldrick, 2008) All the non-hydrogen atoms were refined anisotropically. The hydrogen atom on boron was located from a difference Fourier map and refined (x,y,z and U_{iso}). The remaining hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(C) for the methyl groups and U_{iso}(H) = 1.2U_{eq}(C) for the pyrazolyl ring protons. X-ray structural figures were generated using Olex2. (Dolomanov *et al.*, 2009) (Dolomanov *et al.*, 2009) (Dolomanov *et al.*, 2009) Further details are given below.

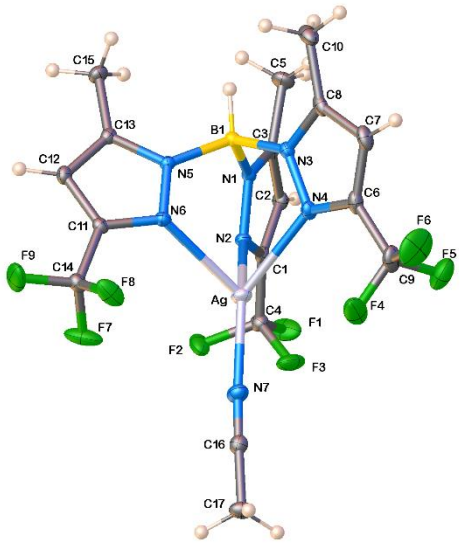

Figure S1 Molecular structure of [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH$_3$ showing atom labelling scheme

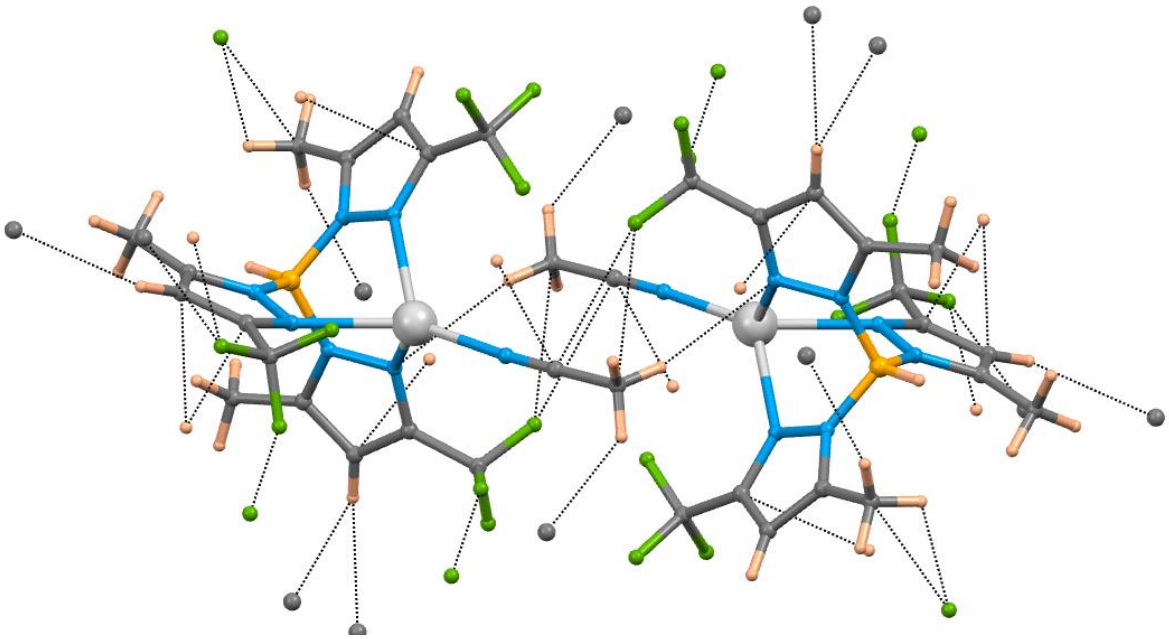

Figure S2 A view showing various types of inter-molecular contacts observed in [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH$_3$

Table S1 Crystal data and structure refinement for $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]AgNCCH_3$.

Identification code	rad269_0m_a
Empirical formula	$C_{17}H_{16}AgBF_9N_7$
Formula weight	608.05
Temperature/K	99.96
Crystal system	triclinic
Space group	P-1
a/Å	8.9547(7)
b/Å	11.3267(8)
c/Å	11.8011(9)
α/°	102.9190(10)
β/°	103.5640(10)
γ/°	96.9010(10)
Volume/Å^3	1115.14(15)
Z	2
ρ_{calc}g/cm^3	1.811
μ/mm^{-1}	0.999
F(000)	600.0
Crystal size/mm^3	0.22 × 0.21 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.61 to 53.994
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	11629
Independent reflections	4790 [R_{int} = 0.0096, R_{sigma} = 0.0118]
Data/restraints/parameters	4790/0/324
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0210, wR_2 = 0.0545
Final R indexes [all data]	R_1 = 0.0214, wR_2 = 0.0548
Largest diff. peak/hole / e Å^{-3}	0.57/-0.49

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]AgNCCH_3$. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ag	7925.3(2)	7346.3(2)	3546.2(2)	17.43(5)
F1	8494.3(15)	3217.6(13)	1182.6(12)	33.2(3)
F2	8885.0(14)	3948.5(12)	3088.5(11)	28.1(3)
F3	9407.1(13)	5144.7(12)	2011.0(13)	30.4(3)
F4	8472.8(17)	9788.6(16)	2570.7(14)	47.4(4)
F5	7557.2(18)	9261.2(13)	644.4(13)	39.3(3)
F6	7019(2)	10865.9(12)	1678.7(16)	49.4(4)
F7	8906.7(14)	7728.5(12)	6719.2(13)	36.0(3)
F8	7946.3(15)	9362.8(10)	6740.2(12)	30.7(3)
F9	7484.0(16)	8256.7(14)	7910.1(11)	36.7(3)
N1	4877.0(16)	5359.4(12)	2106.3(12)	10.4(3)
N2	6449.6(16)	5422.5(13)	2494.5(13)	11.8(3)
N3	4424.0(17)	7545.2(13)	2228.1(12)	12.5(3)
N4	5914.1(17)	8026.6(13)	2274.2(13)	14.6(3)
N5	4660.8(16)	6697.2(12)	4083.2(12)	10.7(3)
N6	6058.1(16)	7448.2(13)	4702.7(13)	12.2(3)
N7	10340.6(18)	8191.7(15)	4355.8(14)	19.9(3)
C1	6748.5(19)	4425.9(15)	1798.4(15)	12.3(3)
C2	5399(2)	3711.0(16)	958.0(15)	14.2(3)
C3	4216(2)	4339.1(15)	1178.5(14)	12.7(3)
C4	8375(2)	4185.8(17)	2020.2(16)	16.1(3)
C5	2508(2)	4013.4(17)	555.9(17)	19.4(4)
C6	5790(2)	8983.2(16)	1796.5(15)	17.4(3)
C7	4245(2)	9133.7(17)	1434.4(16)	19.5(4)
C8	3391(2)	8193.0(16)	1717.5(15)	15.8(3)
C9	7215(3)	9718.8(18)	1682.3(18)	24.6(4)
C10	1667(2)	7885.0(19)	1520.0(17)	21.5(4)
C11	6199.1(19)	7471.1(15)	5859.2(15)	12.3(3)
C12	4927(2)	6749.2(15)	6011.2(15)	13.8(3)
C13	3958.4(19)	6258.5(15)	4850.7(15)	12.1(3)
C14	7632(2)	8197.7(16)	6799.2(16)	15.7(3)
C15	2415(2)	5411.9(16)	4445.6(16)	16.6(3)
C16	11605(2)	8679.6(16)	4745.0(16)	15.8(3)
C17	13233(2)	9285.1(17)	5202.5(18)	19.6(4)
B1	4069(2)	6386.0(17)	2683.0(16)	11.5(3)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $[HB(3\text{-}(CF_3),5\text{-}(CH_3)Pz)_3]AgNCCH_3$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ag	12.23(7)	18.20(8)	19.16(8)	3.02(5)	3.09(5)	-1.70(5)
F1	24.5(6)	38.0(7)	30.0(7)	-10.7(5)	8.2(5)	13.9(5)
F2	24.9(6)	44.9(7)	23.3(6)	17.4(5)	8.2(5)	20.1(5)
F3	12.7(5)	33.6(7)	47.4(8)	18.8(6)	6.8(5)	0.9(5)
F4	32.0(7)	63.1(10)	40.4(8)	31.6(7)	-5.2(6)	-21.0(7)
F5	46.0(8)	40.6(8)	34.7(7)	9.5(6)	23.1(6)	-2.5(6)
F6	67.5(11)	18.2(6)	72.1(11)	20.6(7)	31.7(9)	1.3(7)
F7	15.9(6)	30.2(7)	45.9(8)	-10.1(6)	-5.9(5)	9.2(5)
F8	34.6(7)	13.6(5)	32.0(6)	5.4(5)	-8.9(5)	-4.4(5)
F9	38.1(7)	50.3(8)	12.0(5)	5.6(5)	-0.4(5)	-10.0(6)
N1	9.7(6)	10.4(6)	10.1(6)	2.6(5)	1.4(5)	0.6(5)
N2	10.0(6)	12.2(6)	12.7(6)	3.2(5)	2.6(5)	1.2(5)
N3	14.3(7)	12.5(6)	10.7(6)	3.2(5)	2.5(5)	3.5(5)
N4	16.7(7)	12.5(7)	13.3(7)	4.5(5)	2.2(5)	-0.3(5)
N5	10.2(6)	9.9(6)	11.7(6)	2.3(5)	2.9(5)	1.5(5)
N6	10.5(6)	11.8(6)	12.8(7)	2.2(5)	2.0(5)	1.4(5)
N7	16.4(8)	20.3(8)	20.4(8)	2.3(6)	5.0(6)	-1.3(6)
C1	13.6(8)	13.5(7)	11.0(7)	3.8(6)	5.3(6)	2.2(6)
C2	17.2(8)	13.3(8)	10.7(7)	0.9(6)	4.0(6)	1.9(6)
C3	14.9(8)	12.3(7)	9.6(7)	3.1(6)	1.7(6)	0.3(6)
C4	15.9(8)	17.9(8)	15.1(8)	2.8(7)	5.6(6)	4.6(7)
C5	14.5(8)	18.8(8)	18.5(8)	-0.2(7)	-1.9(7)	0.1(7)
C6	27.2(9)	12.1(8)	11.7(8)	3.3(6)	3.9(7)	1.7(7)
C7	31.8(10)	14.4(8)	13.3(8)	5.2(6)	4.4(7)	9.4(7)
C8	22.7(9)	16.5(8)	8.5(7)	1.6(6)	3.2(6)	9.6(7)
C9	35.1(11)	18.2(9)	20.9(9)	9.5(7)	6.9(8)	-1.3(8)
C10	20.8(9)	29(1)	16.4(8)	6.0(7)	3.7(7)	13.5(8)
C11	13.5(8)	10.8(7)	12.5(7)	2.9(6)	2.3(6)	4.3(6)
C12	17.4(8)	12.6(7)	13.1(8)	4.8(6)	5.0(6)	4.1(6)
C13	13.5(8)	10.3(7)	14.6(8)	4.6(6)	5.4(6)	4.0(6)
C14	17.7(8)	13.5(8)	14.1(8)	2.8(6)	1.3(6)	3.2(6)
C15	15.3(8)	15.1(8)	19.7(8)	5.2(7)	5.9(7)	0.0(6)
C16	19.1(9)	13.0(8)	16.2(8)	2.9(6)	6.5(7)	4.2(7)
C17	13.9(8)	14.4(8)	26.1(9)	0.9(7)	1.8(7)	1.2(6)
B1	11.3(8)	11.8(8)	10.9(8)	2.5(7)	2.1(6)	2.4(6)

Table S4 Bond Lengths for [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag	N2	2.3161(14)	N4	C6	1.333(2)
Ag	N4	2.3818(15)	N5	N6	1.3641(19)
Ag	N6	2.3913(14)	N5	C13	1.363(2)
Ag	N7	2.1521(16)	N5	B1	1.555(2)
F1	C4	1.336(2)	N6	C11	1.335(2)
F2	C4	1.335(2)	N7	C16	1.136(2)
F3	C4	1.343(2)	C1	C2	1.394(2)
F4	C9	1.327(3)	C1	C4	1.487(2)
F5	C9	1.339(2)	C2	C3	1.387(2)
F6	C9	1.333(2)	C3	C5	1.494(2)
F7	C14	1.329(2)	C6	C7	1.392(3)
F8	C14	1.337(2)	C6	C9	1.488(3)
F9	C14	1.336(2)	C7	C8	1.384(3)
N1	N2	1.3626(19)	C8	C10	1.492(3)
N1	C3	1.360(2)	C11	C12	1.391(2)
N1	B1	1.555(2)	C11	C14	1.492(2)
N2	C1	1.335(2)	C12	C13	1.387(2)
N3	N4	1.363(2)	C13	C15	1.491(2)
N3	C8	1.362(2)	C16	C17	1.453(2)
N3	B1	1.552(2)			

Table S5 Bond Angles for [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Ag	N4	82.63(5)	F2	C4	F1	106.78(15)
N2	Ag	N6	85.05(5)	F2	C4	F3	105.93(15)
N4	Ag	N6	79.66(5)	F2	C4	C1	112.65(14)
N7	Ag	N2	138.88(6)	F3	C4	C1	112.71(15)
N7	Ag	N4	129.54(6)	N4	C6	C7	111.91(16)
N7	Ag	N6	121.30(5)	N4	C6	C9	119.77(17)
N2	N1	B1	121.00(13)	C7	C6	C9	128.31(17)
C3	N1	N2	110.71(13)	C8	C7	C6	104.73(16)
C3	N1	B1	128.26(14)	N3	C8	C7	107.30(16)
N1	N2	Ag	116.54(10)	N3	C8	C10	123.86(16)
C1	N2	Ag	133.46(11)	C7	C8	C10	128.85(17)
C1	N2	N1	105.30(13)	F4	C9	F5	107.06(19)
N4	N3	B1	121.09(13)	F4	C9	F6	107.57(18)
C8	N3	N4	110.78(14)	F4	C9	C6	112.80(16)
C8	N3	B1	128.10(15)	F5	C9	C6	112.46(16)
N3	N4	Ag	115.62(10)	F6	C9	F5	105.47(16)
C6	N4	Ag	136.66(12)	F6	C9	C6	111.05(18)
C6	N4	N3	105.29(14)	N6	C11	C12	112.26(15)
N6	N5	B1	121.73(13)	N6	C11	C14	119.47(15)
C13	N5	N6	110.72(13)	C12	C11	C14	128.25(16)
C13	N5	B1	127.50(14)	C13	C12	C11	104.36(15)
N5	N6	Ag	112.24(10)	N5	C13	C12	107.54(14)
C11	N6	Ag	131.37(11)	N5	C13	C15	123.51(15)
C11	N6	N5	105.13(13)	C12	C13	C15	128.95(15)
C16	N7	Ag	176.36(16)	F7	C14	F8	106.10(15)
N2	C1	C2	112.04(15)	F7	C14	F9	107.20(15)
N2	C1	C4	119.19(15)	F7	C14	C11	112.92(14)
C2	C1	C4	128.72(15)	F8	C14	C11	112.77(14)
C3	C2	C1	104.31(14)	F9	C14	F8	106.12(15)
N1	C3	C2	107.63(14)	F9	C14	C11	111.29(15)
N1	C3	C5	123.52(15)	N7	C16	C17	178.0(2)
C2	C3	C5	128.86(15)	N1	B1	N5	109.83(13)
F1	C4	F3	106.90(15)	N3	B1	N1	109.35(13)
F1	C4	C1	111.43(15)	N3	B1	N5	110.68(13)

Table S6 Torsion Angles for [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ag	N2	C1	C2	-153.68(12)	C2	C1	C4	F2	-111.9(2)
Ag	N2	C1	C4	28.6(2)	C2	C1	C4	F3	128.32(19)
Ag	N4	C6	C7	-160.73(13)	C3	N1	N2	Ag	158.75(10)
Ag	N4	C6	C9	20.6(3)	C3	N1	N2	C1	-0.27(17)
Ag	N6	C11	C12	-139.35(13)	C3	N1	B1	N3	-103.21(18)
Ag	N6	C11	C14	39.2(2)	C3	N1	B1	N5	135.16(16)
N1	N2	C1	C2	0.13(18)	C4	C1	C2	C3	177.53(16)
N1	N2	C1	C4	-177.62(14)	C6	C7	C8	N3	0.43(19)
N2	N1	C3	C2	0.31(18)	C6	C7	C8	C10	-179.16(17)
N2	N1	C3	C5	-179.86(15)	C7	C6	C9	F4	148.4(2)
N2	N1	B1	N3	74.80(18)	C7	C6	C9	F5	-90.4(2)
N2	N1	B1	N5	-46.84(19)	C7	C6	C9	F6	27.5(3)
N2	C1	C2	C3	0.05(19)	C8	N3	N4	Ag	165.79(10)
N2	C1	C4	F1	-174.55(15)	C8	N3	N4	C6	0.51(18)
N2	C1	C4	F2	65.5(2)	C8	N3	B1	N1	127.72(16)
N2	C1	C4	F3	-54.4(2)	C8	N3	B1	N5	-111.15(18)
N3	N4	C6	C7	-0.22(19)	C9	C6	C7	C8	178.36(18)
N3	N4	C6	C9	-178.85(15)	C11	C12	C13	N5	-0.35(18)
N4	N3	C8	C7	-0.60(19)	C11	C12	C13	C15	-179.90(16)
N4	N3	C8	C10	179.02(15)	C12	C11	C14	F7	110.4(2)
N4	N3	B1	N1	-50.19(19)	C12	C11	C14	F8	-129.37(19)
N4	N3	B1	N5	70.94(18)	C12	C11	C14	F9	-10.2(3)
N4	C6	C7	C8	-0.1(2)	C13	N5	N6	Ag	147.85(11)
N4	C6	C9	F4	-33.2(3)	C13	N5	N6	C11	-0.39(17)
N4	C6	C9	F5	88.0(2)	C13	N5	B1	N1	-97.08(18)
N4	C6	C9	F6	-154.09(17)	C13	N5	B1	N3	142.08(16)
N5	N6	C11	C12	0.16(18)	C14	C11	C12	C13	-178.32(16)
N5	N6	C11	C14	178.75(14)	B1	N1	N2	Ag	-19.58(18)
N6	N5	C13	C12	0.47(18)	B1	N1	N2	C1	-178.60(14)
N6	N5	C13	C15	-179.95(15)	B1	N1	C3	C2	178.49(15)
N6	N5	B1	N1	80.07(18)	B1	N1	C3	C5	-1.7(3)
N6	N5	B1	N3	-40.8(2)	B1	N3	N4	Ag	-15.96(18)
N6	C11	C12	C13	0.11(19)	B1	N3	N4	C6	178.75(14)
N6	C11	C14	F7	-68.0(2)	B1	N3	C8	C7	-178.68(15)
N6	C11	C14	F8	52.3(2)	B1	N3	C8	C10	0.9(3)
N6	C11	C14	F9	171.42(15)	B1	N5	N6	Ag	-29.73(17)
C1	C2	C3	N1	-0.22(18)	B1	N5	N6	C11	-177.97(14)
C1	C2	C3	C5	179.97(17)	B1	N5	C13	C12	177.88(15)
C2	C1	C4	F1	8.1(3)	B1	N5	C13	C15	-2.5(3)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for [HB(3-(CF_3),5-(CH_3)Pz)$_3$]AgNCCH_3.

Atom	***x***	***y***	***z***	**U(eq)**
H2	5310	2963	368	17
H5A	1936	3767	1104	29
H5B	2319	3330	-166	29
H5C	2148	4730	321	29
H7	3862	9747	1073	23
H10A	1279	7037	1022	32
H10B	1158	8451	1108	32
H10C	1430	7965	2301	32
H12	4760	6621	6744	17
H15A	1579	5881	4261	25
H15B	2278	5027	5089	25
H15C	2375	4772	3721	25
H17A	13766	9085	4567	29
H17B	13737	9000	5898	29
H17C	13292	10179	5451	29
H1	2840(30)	6090(20)	2417(19)	13(5)