

Supporting Information for:

**Short Metal–Metal Separations in a Highly Luminescent Trimetallic Ag(I)
Complex Stabilized by Bridging NHC Ligands.**

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Preparation of $[(\text{pyCH}_2)_2\text{im}]_2\text{AgCl}$, $1\bullet\text{Cl}$. Method A: A 100 mL round bottom flask was charged with 2.51 g (8.75 mmol) of $[\text{H}(\text{pyCH}_2)_2\text{im}]\text{Cl}$, 1.01 g (4.38 mmol) of Ag_2O and 50 mL of CH_2Cl_2 . The flask was removed from light and stirred at room temperature for 4 hours. The mixture was then filtered through Celite, reduced in volume and precipitated with Et_2O leaving 0.66 g (1.02 mmol) of $1\bullet\text{Cl}$ as a beige powder (23%).

Method B: A 50 mL round bottom flask was charged with 1.00 g (3.49 mmol) of $[\text{H}(\text{pyCH}_2)_2\text{im}]\text{Cl}$, a catalytic amount of $[\text{Bu}_4\text{N}]\text{Cl}$, and 15 mL of CH_2Cl_2 . The flask was then charged with a mixture of 15 mL of 1 M NaOH and 0.202 g (0.872 mmol) of Ag_2O . The flask was removed from light and stirred at room temperature for 4 hours. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were combined, filtered through Celite, reduced in volume and precipitated with Et_2O leaving 0.47 g of $1\bullet\text{Cl}$ as a beige powder (38%).

Preparation of $1\bullet\text{BF}_4$. Method A: A 50 mL round bottom flask was charged with 0.50 (0.78 mmol) of $1\bullet\text{Cl}$ and excess NaBF_4 . To this was added 20 mL of CH_2Cl_2 and 5 mL of MeOH. This mixture was placed in an ultrasonic cleaner for 5 minutes. The volatiles were then removed with a rotary evaporator. To the remaining brown residue was added 15 mL CH_2Cl_2 of and this mixture was then filtered through Celite. The remaining light brown solution was reduced in volume and precipitated with Et_2O affording 0.48 g (0.69 mmol) of $1\bullet\text{BF}_4$ as a beige powder (89%). Method B: A 100 mL round bottom flask was charged with 1.66 g (4.85 mmol) of $[\text{H}(\text{pyCH}_2)_2\text{im}](\text{BF}_4)$, a catalytic amount of $[\text{Bu}_4\text{N}](\text{BF}_4)$, and 30 mL CH_2Cl_2 . To this was added a mixture of 20 mL of 1 M NaOH and 0.282 g (1.22 mmol) of Ag_2O . The flask was removed from light and the mixture stirred at room temperature for 4 hours. The organic layer was separated and the

aqueous layer extracted with CH₂Cl₂ (3 x 20 mL). The organic layers were combined, filtered through Celite, reduced in volume and precipitated with Et₂O affording 1.34 g (1.93 mmol) of **1**•BF₄ as a beige solid (79%). Anal. Calcd (C₃₀H₂₈N₈AgBF₄): C, 51.83; H, 4.06; N, 16.12. Found: C, 51.60; H, 3.97; N, 15.86. ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 8.46 (m), 7.65 (m), 7.30 (m), 7.21 (s), 7.19 (m), 5.41 (s). ¹³C{¹H} NMR (75 MHz, CDCl₃, 25°C): δ = ??? (m), 155.5, 149.8, 137.7, 123.6, 122.8, 122.6, 57.1. UV (CH₃CN) λ_{max}, nm (ε): 243 (14123), 249 (14868), 254 (15463), 260 (13774), 266 (sh, 9614), 360 (905).

Preparation of [((pyCH₂)₂im)₃Ag₃](BF₄)₃, **2.** Method A: A 50 mL round bottom flask was charged with 1.00 g (2.92 mmol) of [H(pyCH₂)₂im](BF₄) and 3.38 g (14.6 mmol) of Ag₂O in 30 mL of CH₃CN. The mixture was removed from light and brought to reflux overnight. The mixture was cooled, filtered through Celite, reduced in volume and precipitated with Et₂O affording 1.04 g (0.779 mmol) of **2** as an off-white powder (79%). Method B: A 100 mL round bottom flask was charged with 2.66 g (3.83 mmol) of **1**•BF₄, 1.49 g (7.65 mmol) of AgBF₄ and 50 mL of CH₃CN. This mixture was removed from light and brought to reflux for 6 hours. The mixture was cooled, filtered through Celite, reduced in volume and precipitated with Et₂O affording 0.981 g (0.735 mmol) of **2** as an off-white powder (51%). Anal. Calcd (C₄₅H₄₂N₁₂Ag₃B₃F₁₂): C, 40.49; H, 3.17; N, 12.59. Found: C, 40.69; H, 3.09; N, 12.55. ¹H NMR (300 MHz, CD₃CN, 25°C): δ = 7.95 (m), 7.66 (m), 7.63 (s), 7.32-7.26 (m), 5.20 (s). ¹³C{¹H} NMR (126 MHz, CD₃CN, 25°C): δ = 175.4 (m), 154.0, 151.2, 140.8, 126.5, 126.2, 125.8, 56.5. UV (CH₃CN) λ_{max}, nm (ε): 254 (28353), 260 (27282), 266 (21436), 296 (sh, 4422).

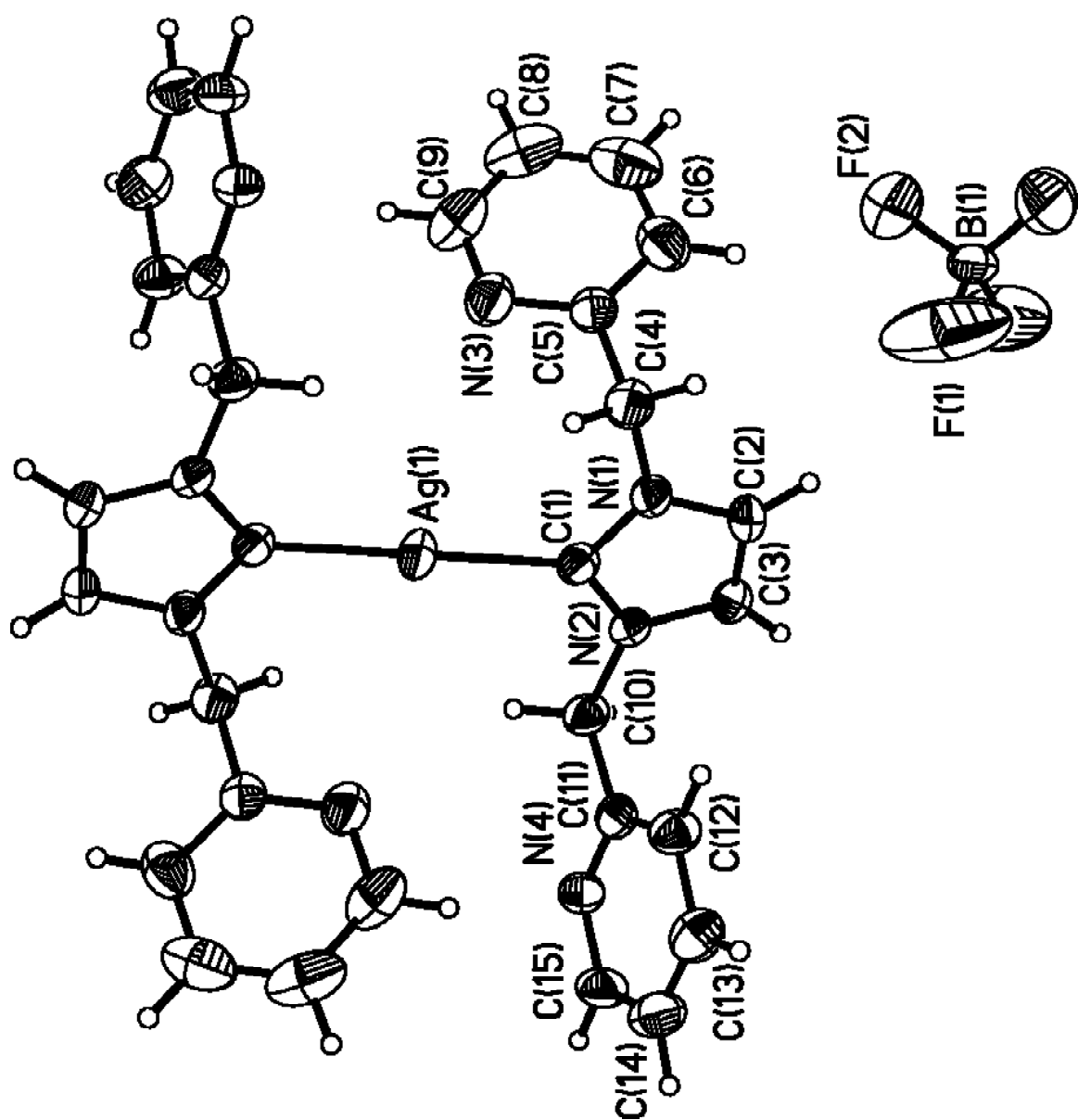


Figure S1. Thermal ellipsoid plot of $[(\text{pyCH}_2)_2\text{im}]_2\text{Ag}^+\text{BF}_4^-$ drawn at 40%. The nearest $\text{Ag}\cdots\text{Ag}$ interaction is over 8.45 Å.

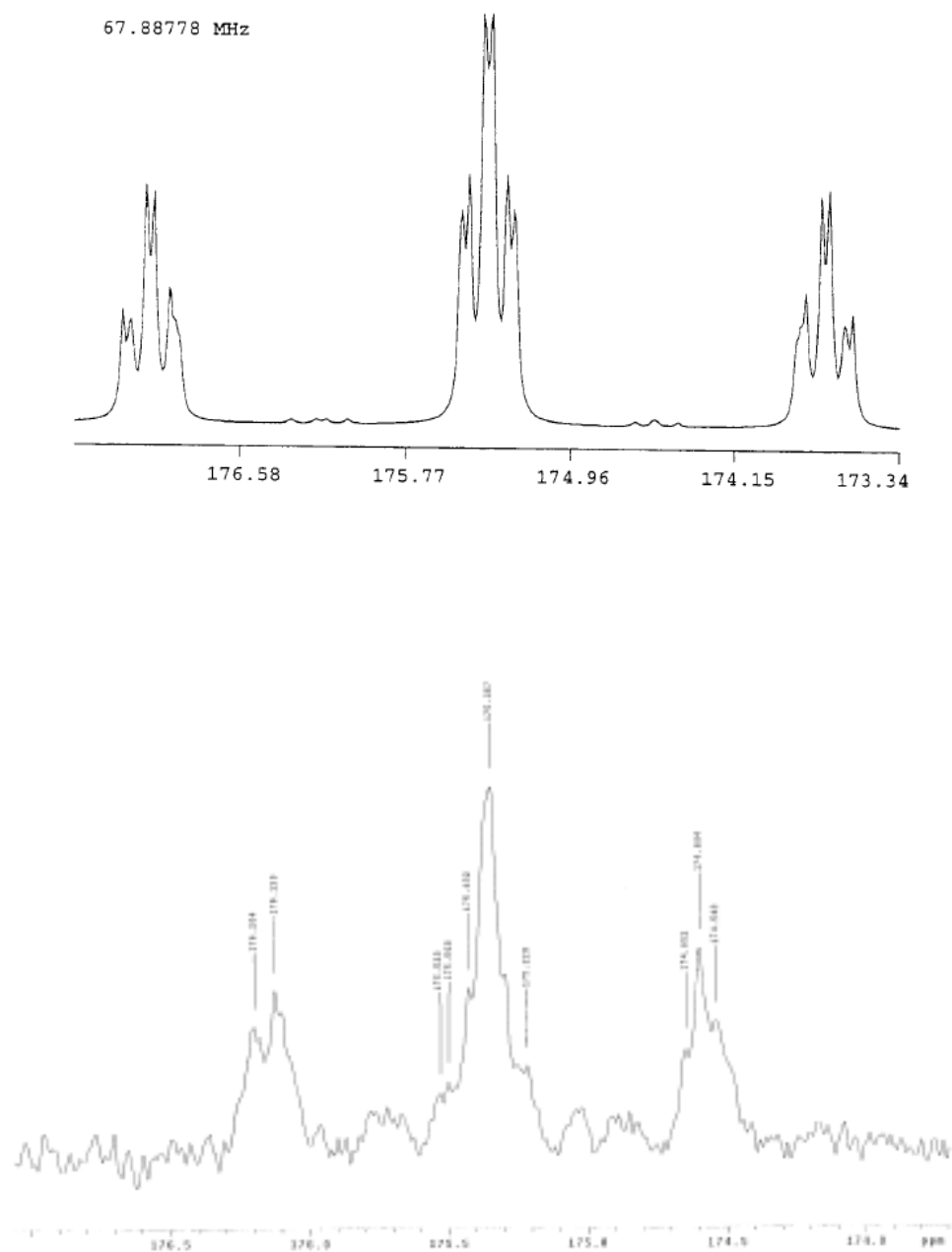


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of carbene region for **2** (bottom) and simulated spectrum (top) using $^1J_{\text{Ag-C}} = 104.5$ Hz, $^2J_{\text{Ag-C}} = 8.0$ Hz and $^3J_{\text{Ag-C}} = 3.0$ Hz.