

Supplementary Information

Neutral Cu₄N₁₂ and Ag₄N₁₂ metallacycles with a *para*-cyclophane framework assembled from copper(I) and silver(I) pyrazolates and pyridazine

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Experimental

General procedures. All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were purchased from commercial sources, distilled from conventional drying agents and degassed by the freeze-pump-thaw method twice prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at 25 °C on a JEOL Eclipse 500 spectrometer (¹H, 500.16 MHz, ¹³C, 125.78 MHz, ¹⁹F, 470.62 MHz). Proton and carbon chemical shifts are reported in ppm versus Me₄Si. ¹⁹F NMR chemical shifts were referenced relative to external CFCl₃. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed using a Perkin Elmer Model 2400 CHN analyzer.

Synthesis of [{3,5-(CF₃)₂Pz}₄Cu₄(C₄H₄N₂)₂]

{[3,5-(CF₃)₂Pz]Cu}₃ (0.50 g, 0.63 mmol) and C₄H₄N₂ (pyridazine) (0.01 g, 0.94 mmol) were mixed in degassed benzene (15.0 mL). The mixture was warmed (50 °C) and stirred overnight under nitrogen. The solvent was removed under reduced pressure to obtain the product as a yellow solid (0.52 g, 90%). X-ray quality, golden yellow crystals were grown from hexane at 6 °C. Mp: 127-128 °C; ¹H NMR (CDCl₃): δ 9.10 (br s, H_{3',6'}, 4H); 7.65 (br s, H_{4',5'}, 4H); δ 6.87 (s, Pz-H, 4H); ¹³C {¹H} NMR (CDCl₃): δ 103.3 (C₄); 120.4 (q, ¹J_{CF} = 274 Hz, CF₃); 126.7 (C_{4',5'}); 143.1 (q, ²J_{CF} = 34 Hz, CCF₃); 152.6 (C_{3',6'});

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^{19}F NMR (CDCl_3): δ -60.4 (s, CF_3); Anal. Calc. for $\text{C}_{28}\text{H}_{12}\text{N}_{12}\text{F}_{24}\text{Cu}_4$: C, 27.42; H, 0.99; N, 13.70. Found: C, 27.97; H, 0.92; N, 13.45.

Synthesis of $[\{3,5\text{-(CF}_3)_2\text{Pz}\}_4\text{Ag}_4(\text{C}_4\text{H}_4\text{N}_2)_2]$

$\{[3,5\text{-(CF}_3)_2\text{Pz}]\text{Ag}\}_3$ (0.50 g, 0.53 mmol) and $\text{C}_4\text{H}_4\text{N}_2$ (pyridazine) (0.06 g, 0.80 mmol) were mixed in degassed benzene (15.0 mL). The resulting mixture was protected from light using aluminum foil, and stirred overnight under nitrogen at room temperature. The solvent was removed under reduced pressure to obtain the product as a white solid (0.53 g, 95%). X-ray quality, colorless crystals were grown from hexane at 6 °C. Mp: 124-125 °C; ^1H NMR (CDCl_3): δ 9.02 (t, $^3J_{\text{HH}} = 3.6$ Hz, $\text{H}_{3',6'}$, 4H); 7.52 (t, $^3J_{\text{HH}} = 3.6$ Hz, $\text{H}_{4',5'}$, 4H); δ 6.95 (s, Pz-H, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 102.8 (C_4); 120.5 (q, $^1J_{\text{CF}} = 271$ Hz, CF_3); 127.6 ($\text{C}_{4',5'}$); 144.1 (q, $^2J_{\text{CF}} = 37$ Hz, CCF_3); 152.0 ($\text{C}_{3',6'}$); ^{19}F NMR (CDCl_3): δ -60.9 (s, CF_3); Anal. Calc. for $\text{C}_{28}\text{H}_{12}\text{N}_{12}\text{F}_{24}\text{Ag}_4$: C, 23.95; H, 0.86; N, 11.97. Found: C, 32.84; H, 0.66; N, 12.13.

Synthesis of $[\{3,5\text{-(CF}_3)_2\text{PzCu}\}_3(\text{C}_{12}\text{H}_8\text{N}_2)]$

Mixture of $\{[3,5\text{-(CF}_3)_2\text{Pz}]\text{Cu}\}_3$ (0.50 g, 0.63 mmol) and $\text{C}_{12}\text{H}_8\text{N}_2$ (benzo[*c*]cinnoline) (0.13 g, 0.63 mmol) in degassed tetrahydrofuran (20.0 mL) and toluene (30.0 mL) was stirred at 40 °C for 6 h. The solution turned into red immediately after mixing. After cooling, the solvent was removed under reduced pressure and a reddish brown powder was obtained (0.54 g, 95%). X-ray quality crystals were grown from CH_2Cl_2 at -25 °C. Mp: 219-222 °C, ^1H NMR (CDCl_3): δ 6.94 (s, Pz-H, 3H), 7.88 (apparent td, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, $\text{H}_{5',8'}$, 2H), 7.95 (apparent td, $^3J_{\text{HH}} = 8.0$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, $\text{H}_{4',9'}$, 2H), 8.53 (d, $^3J_{\text{HH}} = 8.5$ Hz, $\text{H}_{6',7'}$, 2H), 8.58 (d, $^3J_{\text{HH}} = 8.0$ Hz, $\text{H}_{3',10'}$, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 103.9 (C_4), 121.6, 130.0, 130.2, 132.5, 145.1, other peaks could not be unambiguously identified; ^{19}F NMR (CDCl_3): δ -60.6 (s, CF_3); Anal. Calc. for $\text{C}_{27}\text{H}_{11}\text{Cu}_3\text{F}_{18}\text{N}_8$: C, 33.09; H, 1.13; N, 11.43. Found: C, 32.85; H, 1.09; N, 11.29.

The same product was obtained when $\{[3,5\text{-(CF}_3)_2\text{Pz}]\text{Cu}\}_3$ was treated with $\text{C}_{12}\text{H}_8\text{N}_2$ (benzo[*c*]cinnoline) at 1: 1.5 molar ratio in degassed toluene or THF/toluene mixture.

X-ray Structure Determination. A suitable crystal covered with a layer of hydrocarbon oil was selected and mounted with paratone-N oil on a cryo-loop, and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data were measured on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series Cryostream cooler, a graphite monochromator, and a Mo K α fine-focus sealed tube ($\lambda = 0.710\ 73\ \text{\AA}$). The detector was placed at a distance of 5.995 cm from the crystal. The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using Bruker SHELXTL (Version 6.14) software package. Structural details are given in CIF files.