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# Supporting Information

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# Quantitative Formation of Sandwich-Shaped Trinuclear Silver(I) Complexes and Dynamic Feature of Their (*P*)⇄(*M*) Flip Motion in Solution

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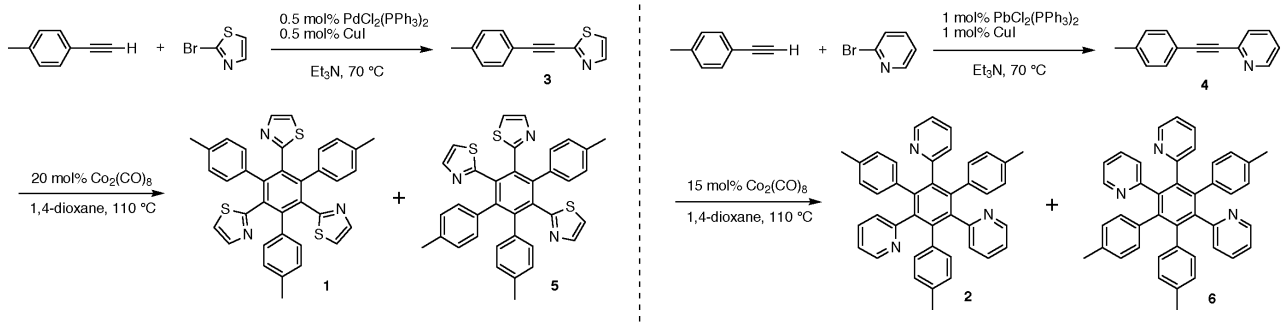
**Contents**

**Preparation of Tridentate Ligands 1 and 2**

Disk-shaped tridentate ligands **1** and **2** were synthesized by a cobalt-catalyzed trimerization of alkynes **3** and **4**, respectively (Scheme S1). The Pd-catalyzed Sonogashira coupling reaction of ethynyltoluene with 2-bromothiazole in the presence of 0.5 mol% $PdCl_2(PPh_3)_2$ and 0.5 mol% CuI in $Et_3N$ afforded alkyne **3** in 77% yield. Trimerization of alkyne **3** in the presence of 20 mol% $Co_2(CO)_8$ yielded **1** and its regio-isomer **5** in 28% and 33% yields, respectively.

A similar strategy was applied for 2-pyridine-type ligand **2**. The sonogashira coupling reaction of ethynyltoluene with 2-bromopyridine in the presence of 1 mol% $PdCl_2(PPh_3)_2$ and 1 mol% CuI in $Et_3N$ provided alkyne **4** in 68% yield. The cobalt-catalyzed trimerization of **4** afforded symmetrical **2** and its 1,2,4-tris-2-pyridyl isomer **6** in 21% and 25% yields, respectively.

Scheme S1. Preparation of disk-shaped tridentate ligands **1** and **2**.




**2-Thiazolyl-*p*-tolyl-ethyne 3.** To a solution of CuI (29 mg, 0.15 mmol, 0.5 mol%), $PdCl_2(PPh_3)_2$ (104 mg, 0.15 mmol, 0.5 mol%), and 2-bromothiazole (2.9 mL, 32 mmol) in $Et_3N$ (44 mL) was added ethynyltoluene (3.9 mL, 31 mmol). The mixture was degassed and heated at 65 °C for 10 h under an $N_2$-gas atmosphere. The resulting dark brown mixture was filtered and the solvent was removed in vacuo. Purification by silica gel chromatography was performed (*n*-hexane/AcOEt (7:1 - 4:1)) to obtain the desired coupling product **3** (4.74 g) in 77% yield as a pale yellow solid: Mp 76.0–76.5 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 3.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 3.0 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 2.38 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 149.0, 143.5, 139.9, 131.8, 129.2, 120.5, 118.3, 94.2, 81.7, 21.6; IR (KBr) ν 3100, 2200, 1500, 1460, 1270, 1090, 1040, 820, 740 cm$^{-1}$. Anal. calcd for $C_{12}H_9NS$: C, 72.33; H, 4.55; N, 7.03. Found: C, 72.51; H, 4.82; N, 6.85.

**Cobalt-Catalyzed Trimerization of 3**. $Co_2(CO)_8$ (169 mg, 0.49 mmol, 20 mol%), **3** (500 mg, 2.5 mmol), and 1,4-dioxane (5 mL) were placed in a sealed tube flask. The mixture was then degassed and heated at 110 °C for 4 h. The solvent was removed in vacuo. Purification by silica gel column chromatography ($CHCl_3$/AcOEt (4:1)) afforded the desired **1** (140 mg, 28%) and its regio isomer **5** (163 mg, 33%) as a pale yellow solid.

**1,3,5-Tris(2-thiazolyl)-2,4,6-tris(*p*-tolyl)benzene 1.** Mp 255.0-255.5 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 3.5 Hz, 3H), 7.03 (d, *J* = 3.5 Hz, 3H), 6.94 (d, *J* = 7.8 Hz, 6H), 6.79 (d, *J* = 7.8 Hz, 6H). 2.15 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.3, 144.5, 141.5, 136.1, 135.1, 133.4, 130.0, 127.7, 120.7, 21.1; IR (KBr) ν 3000, 2910, 1510, 1090, 810 cm$^{-1}$. Anal. calcd for $C_{36}H_{27}N_3S_3$: C, 72.33; H, 4.55; N, 7.03. Found: C, 72.21; H, 4.68; N, 6.84.

**1,2,4-Tris(2-thiazolyl)-3,5,6-tris(*p*-tolyl)benzene 5.** Mp 338 °C (dec); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 3.5 Hz, 1H), 7.41 (d, *J* = 3.5 Hz, 1H), 7.39 (d, *J* = 3.0 Hz, 1H), 7.05 (m, 2H), 6.95 (dd, *J* = 1.5, 3.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2 H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 2.14 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.61, 165.40, 165.14, 143.90. 142.46, 141.89, 141.46, 141.42, 141.35, 136.17, 135.85, 135.75, 135.62, 135.54, 135.32, 135.30, 135.02, 133.92, 130.62, 130.35, 130.20, 127.76, 127.85, 127.69, 120.97, 120.63, 21.11; IR (KBr) ν 3025, 2925, 1520, 1080, 820, 730 cm$^{-1}$. MS (ESI-TOF) *m/z* exact mass $[M + Na]^+$ 620.1248, $C_{36}H_{27}N_3S_3Na$ requires 620.1265.

**2-Pyridyl-*p*-tolyl-ethyne 4.** Ethynyltoluene (1.27 mL, 10.0 mmol) was added to a solution of CuI (19 mg, 0.10 mmol, 1 mol%), $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol, 1 mol%), and 2-bromopyridine (0.96 mL, 10.0 mmol) in $Et_3N$ (4 mL) and THF (16 mL). The mixture was degassed and heated at 65 °C for 64 h under an $N_2$-gas atmosphere. The resulting dark brown mixture was filtered and the solvent was removed in vacuo. The crude material was purified by silica gel chromatography (*n*-hexane/AcOEt (9:1)) to obtain the desired coupling product **4** (1.32 g) in 68% yield as a colorless solid: Mp 76.5–77.5 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.8 Hz, 1H), 7.68 (ddd, *J* = 1.7, 7.7, 7.6 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.23 (dd, *J* = 4.8, 7.6 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 2.38 (s, 3H, $CH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 149.9, 143.5, 139.2, 136.1, 131.9, 129.1, 127.0, 122.5, 119.1, 89.4, 88.0, 21.5. IR (KBr) ν 3050, 3030, 2930, 2230, 1580, 1560, 1510, 1460, 1430, 1280, 1160, 995, 830, 780 cm$^{-1}$. Anal. calcd for $C_4H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.96; H, 5.91; N, 7.01.

**Cobalt-Catalyzed Trimerization of 4.** $Co_2(CO)_8$ (27 mg, 80 μmol, 15 mol%) and **3** (100 mg, 0.52 mmol) in 1,4-dioxane (2.5 mL) were placed in a sealed tube flask. The mixture was then degassed and heated at 110 °C for 36 h. The solvent was removed in vacuo. Purification by silica gel column chromatography ($CHCl_3$/$CH_3OH$ (30:1)) afforded the desired **2** (21 mg, 21%) and its regio isomer **6** (25 mg, 25%), and **6** was further purified by recrystallization from toluene to obtain a pale yellow solid.

**1,3,5-Tris(2-pyridyl)-2,4,6-tris(*p*-tolyl)benzene 2.** Mp 305 °C (dec); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.5 Hz, 3H), 7.18 (ddd, *J* = 1.8, 8.0, 8.0 Hz, 3H), 6.84 (d, *J* = 7.0 Hz, 6H), 6.76 - 6.74 (m, 6H), 6.64 (d, *J* = 7.0 Hz, 6H), 2.06 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.3, 147.9, 140.5, 139.7, 136.6, 134.7, 134.3, 130.8, 127.3, 126.7, 120.2, 21.0; IR (KBr) ν 3020, 2930, 1585, 1560, 1515, 1475, 1400, 1155, 1020, 1000, 825, 780, 750, 740 cm$^{-1}$. Anal. calcd for $C_{42}H_{33}N_3$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.16; H, 5.89; N, 7.30.

**1,2,4-Tris(2-pyridyl)-3,5,6-tris(*p*-tolyl)benzene 6**. Mp 309 °C (dec); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.7 Hz, 1H), 8.13 - 8.12 (m, 2H), 7.20 - 7.17 (m, 3H), 6.94 - 6.65 (m, 18H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.5, 159.3, 159.1, 147.8, 147.7, 147.6, 140.9, 140.6, 140.3, 140.0, 139.5, 139.4, 136.8, 136.6, 136.5, 134.8, 134.7, 134.5, 134.3, 131.3, 131.0, 130.4, 127.5, 126.8, 126.6, 120.1, 120.1, 120.0, 21.0, 21.0; IR (KBr) ν 3020, 2930, 1590, 1560, 1520, 1480, 1410, 1170, 1150, 1040, 1020, 990, 820, 790, 750 cm$^{-1}$. Anal. calcd for $C_{42}H_{33}N_3$·(toluene): C, 87.59; H, 6.15; N, 6.25. Found: C, 87.45; H, 6.28; N, 6.16.

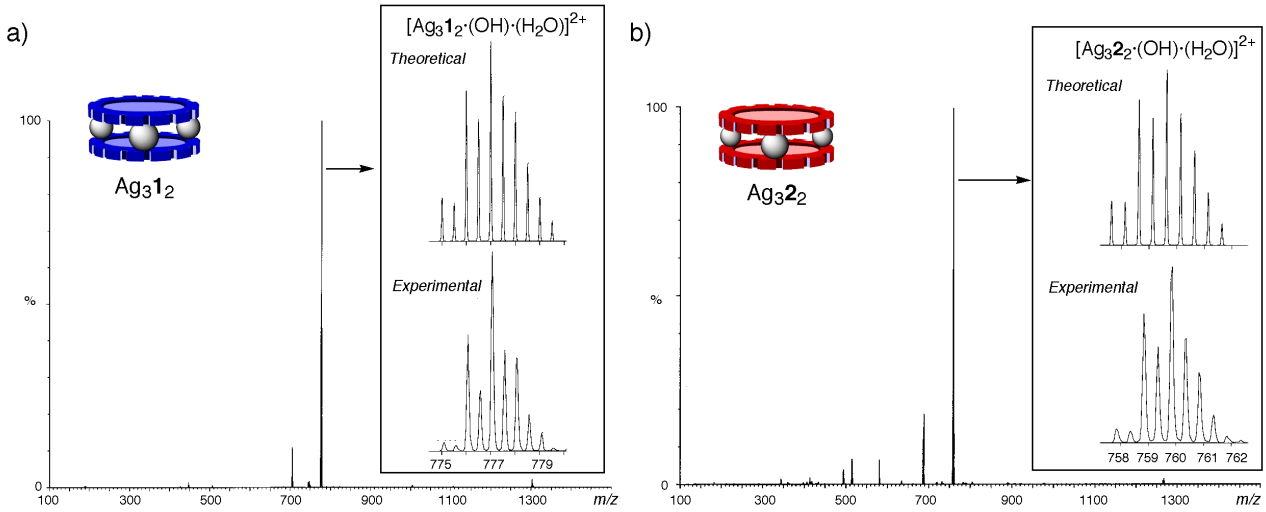



Figure S1. ESI-TOF mass spectra of a) $Ag_3\mathbf{1}_2$ and b) $Ag_3\mathbf{2}_2$.