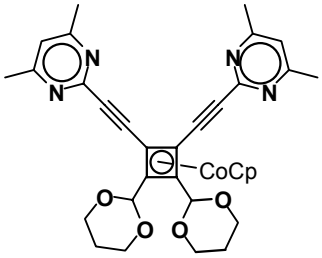
A supramolecular organometallic-metalorganic square

Matthew Laskosi,[b] Jason G. M. Morton,[b] Mark D. Smith,[b] and Uwe H. F. Bunz,[a]*

[a] *School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA. Fax: 1(404)894-7452; Tel: 1(404)385-1795; E-mail: uwe.bunz@chemistry.gatech.edu*

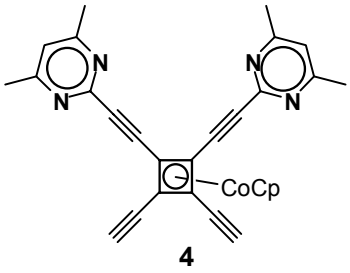
[b] *USC NanoCenter, The University of South Carolina, Columbia, South Carolina, 29208, USA.*

SUPPLEMENTARY INFORMATION



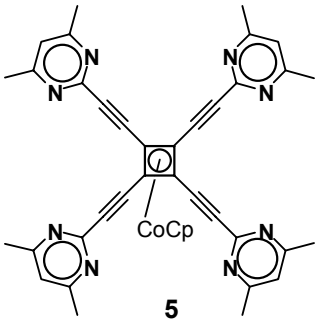
2

(2). In a 25 mL Schlenk flask, **1** (235 mg, 0.593 mmol), 1-iodo-4,6-dimethylpyrimidine (320 mg, 1.37 mmol), $(PPh_3)_2PdCl_2$ (9 mg, 0.0129 mmol) and CuI (5 mg, 0.0263 mmol) were dissolved in THF (1 mL) and NEt_3 (2 mL) and reacted at room temperature for 24h under dry nitrogen. Aqueous workup is followed by column chromatography (SiO_2; hexanes/CH_2Cl_2, 1:1 + 10 % NEt_3) furnished **2** (289 mg, 86 %) as a red-yellow oil. IR (Neat): ν [cm^{-1}]: 2966, 2850, 2206, 1581, 1346, 1107,1006, 729. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.88 (s, 1H, pyrimidine-H), 5.22 (s, 2H, acetal-CH), 5.08 (s, 5H, Cp-H), 4.20-4.12 (m, 2H, acetal-CH_2), 3.87-3.77 (m, 2H, acetal-CH_2), 2.45 (s, 12H, -CH_3), 2.16-2.04 (m, 2H, acetal-CH_2), 1.24-1.22 (m, 2H, acetal-CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.47, 152.55, 118.12, 97.38, 91.42, 83.39, 82.51, 78.27, 66.65, 53.88, 45.93, 25.93, 23.54, 11.34. MS (EI) *m/z* Calc. For M^+ ($C_{33}H_{33}CoN_4O_4$) 608.2, Found 608.



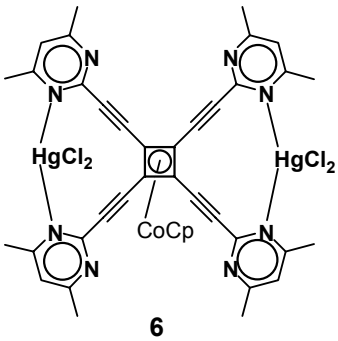
4

(4). A 50 mL round bottom flask was charged with **2** (90 mg, 0.149 mmol), *p*-toluenesulfonic acid (100 mg, 0.526 mmol), THF (5 mL) and H_2O (1 mL). The resulting solution was stirred at ambient temperature for 6 h before being quenched with water and dichlormethane. The water layer was separated and extracted with dichloromethane (250 mL). The combined organic layers were dried over $MgSO_4$ and the solvent removed *in vacuo* to yield a dark red oil. The oil was placed in a 100 mL Schlenk flask and reacted with K_2CO_3 (0.128 g, 0.928 mmol) and diazophosphonate **3** (0.128 g, 6.67 mmol) in dry THF (2 mL) and dry methanol (3 mL) were added at 0^{o}C. After removal of the ice bath the reaction mixture is stirred for 16h at ambient temperature. Aqueous workup and column chromatography (SiO_2; hexanes/CH_2Cl_2, 3:1 +10 % NEt_3) furnishes **4** (43 mg, 61 %) as a orange oil. IR (Neat): ν [cm^{-1}]: 2926, 2206, 1585, 1523, 1342, 783. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (s, 1H, pyrimidine-H), 5.09 (s, 5H, Cp-H), 3.28 (s, 2H, alkyne-H), 2.47 (s, 12H, -CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.03, 152.47, 118.86, 115.34, 92.51, 84.25, 82.68, 81.63, 61.48, 59.08, 31.55. MS (EI) *m/z* Calc. For M^+ ($C_{29}H_{21}CoN_4$) 484.1, Found 484.



5

(5). In a 25 mL Schlenk flask, **4** (42 mg, 0.0870 mmol), 2-iodo-4,6-dimethylpyrimidine (45 mg, 0.193 mmol), $(PPh_3)_2PdCl_2$ (1 mg, 0.001 mmol) and CuI (0.8 mg, 0.004 mmol) were dissolved in THF (1 mL) and NEt_3 (1 mL) and reacted at room temperature for 24h under dry nitrogen. Aqueous workup followed by column chromatography (SiO_2; hexanes/CH_2Cl_2, 1:1 + 10 % NEt_3) furnished **5** (54 mg, 90 %) as an orange solid, which was crystallized by slow evaporation of a dichloromethane solution. Mp: 220 °C (turned dark). IR (Neat): ν [cm^{-1}]: 2923, 2206, 1585, 1531, 1447, 1299, 783. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93 (s, 4H, pyrimidine-H), 5.21 (s, 5H, Cp-H), 2.47 (s, 24H, -CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.88, 152.35, 118.80, 92.98, 84.39, 81.42, 60.85, 23.78. MS (EI) *m/z* Calc. For M^+ ($C_{41}H_{33}CoN_8$) 696.2, Found 696.



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(**6**). Compound **5** (20 mg, 0.029 mmol) was dissolved in 3 mL dichloromethane and placed in a vial. A solution of $HgCl_2$ (20 mg, 0.074 mmol) dissolved in 5 mL of acetonitrile was carefully layered atop the dichloromethane solution. The vial was capped and placed in the dark, and after 3 days red, block-like crystals appeared at the interface. Crystals of **6** (14 mg, 45 %) were collected by vacuum filtration.