Supplementary Material (ESI) for Dalton Transactions

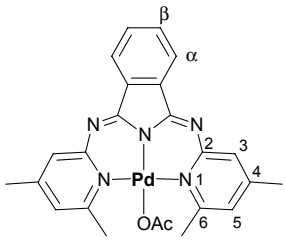
Cyclometalation vs. Werner-type coordination of sterically enforced palladium(II)-1,3-bis(pyridyl-2-imino)isoindolines (Pd-BPIs)

Martin Bröring,* Christian Kleeberg

Supplementary information

1. Preparation, analyses and spectroscopic data for **3** and **5**
2. NOESY and HMBC spectra for **5**

*Numbering scheme for **3**:*



The numbering of equivalent positions of **5** is according to the one shown here for **3**.

1. Preparation, analyses and spectroscopic data for 3 and 5

*(4,6-Me_2BPI)PdOAc (**3**):*

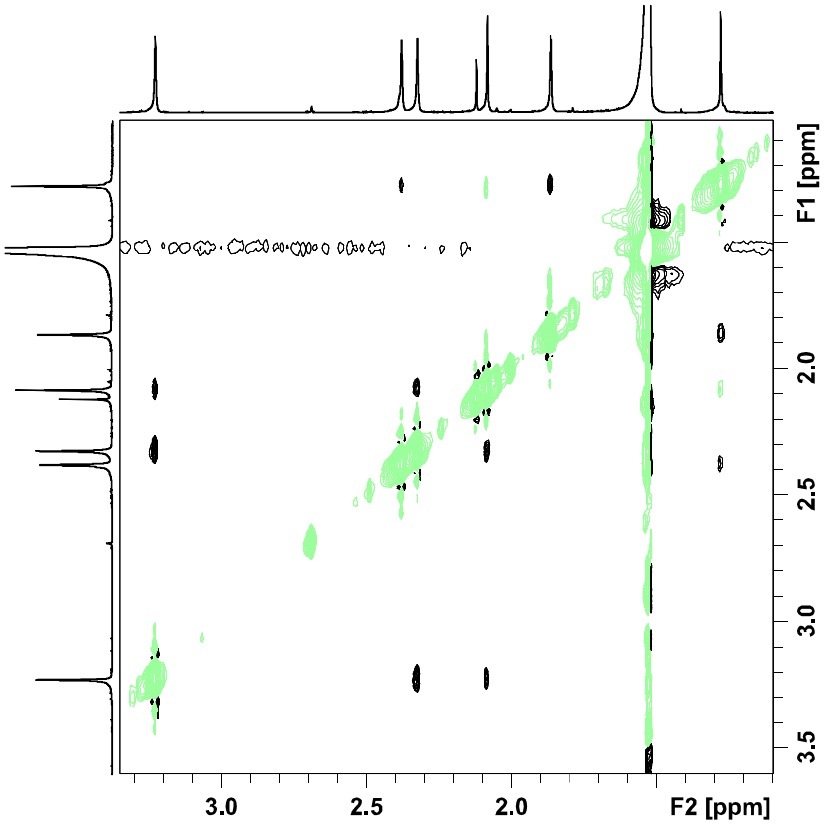
H-4,6-Me_2BPI **4** (100 mg, 0.28 mmol) and palladium acetate (65.1 mg, 0.29 mmol) are suspended in methanol (6.5 ml) and stirred at room temperature under a blanket of argon for 16 h. The mixture is then filtered through celite and the solvent removed in vacuo. The title compound is obtained after recrystallization from dichloromethane/*n*-hexane as fine, intensely red needles. Yield: 132 mg (93%). Mp.: 180°C (decomp.). Anal. calc. ($C_{24}H_{23}N_5PdO_2$): C 55.45, H 4.46, N 13.47; found: C 55.52, H 4.28, N 13.42 %. HRMS (ESI): m/z 460.0753, calc. for ([M-OAc]$^+$): 460.0748, Δ = 0.5 mmu. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 8.21 – 8.13 (m, 2 H, α-CH), 7.88 - 7.85 (m, 2 H, β-CH), 7.16 (s, 2 H, *3*-CH_{Ar}), 6.80 (s, 6 H, *5*-CH_{Ar}), 2.69 (s, 6 H, *6*-Me), 2.37 (s, 6 H, *4*-Me), 1.91 (s, 3 H, OAc). ^{13}C-NMR (100 MHz, CD_2Cl_2): 177.7, 160.7, 155.3, 153.3, 151.4, 137.6, 131.0, 123.5, 122.6, 122.1, 26.6, 22.9, 20.5.

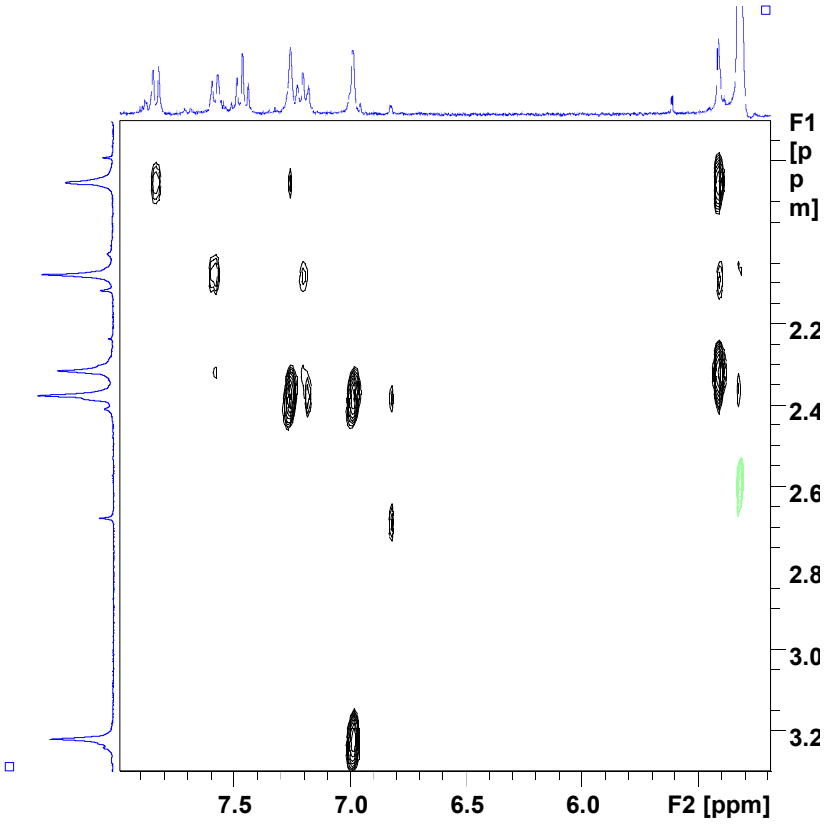
*(4,6-Me_2BPI)$_2$Pd$_4$(OAc)$_4$ (**5**):*

H-4,6-Me_2BPI **4** (50 mg, 0.14 mmol) and palladium acetate (62.9 mg, 0.28 mmol) are suspended in methanol (3 ml) and stirred at room temperature under a blanket of argon for 16 h. A solid separates, which is collected by filtration and washed extensively with methanol. The title compound remains as an orange-yellow solid. Yield: 45 mg (47%). Mp.: > 200°C. Anal. calc. ($C_{52}H_{50}N_{10}Pd_4O_8$): C 45.63, H 3.68, N 10.23; found: C 45.22, H 3.80, N 10.00%. HRMS (ESI): m/z 460.0744, calc. for ([BPI-Pd]$^+$): 460.0748, Δ = 0.4 mmu. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 7.84 (d, *J* = 7.2 Hz, 1 H, α-CH), 7.58 (d, *J* = 7.6 Hz, 1 H, α-CH), 7.50 - 7.42 (m, 1 H, β-CH), 7.26 (s, 1 H, CH_{Ar}), 7.23 - 7.17 (m, 1 H, β-CH), 6.98 (s, 1 H, CH_{Ar}), 5.42 (s, 1 H, CH_{Ar}), 3.22 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 1.86 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3).

2. NOESY and HMBC spectra for 5

H,H-NOESY spectra (CD_2Cl_2, 400 MHz; top: aliphatic area; bottom: aliphatic/aromatic cross section)





H,C-HMBC spectra (CD_2Cl_2, 400 MHz; $H_{aliphatic}$-$C_{aromatic}$ cross section)