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Facile intramolecular C(sp^3)-H bond activation with Pd^{II}

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*Preparation and characterization of ligand **3*** (4-tBuBTI)*:*

1,3-Diiminoisoindoline (1.67 g, 11.5 mmol) and 2-amino-4-*tert*-butylthiazole (3.77 g, 24.2 mmol) are mixed in ethanol (30 mL) and heated to reflux for 14h. After cooling the solvent is removed *in vacuo* and the residue is purified by chromatography on silica with pentane/ethyl acetate (15:1) as the eluent. The first orange-yellow fraction contains the title compound and is obtained as orange solid after evaporation of the solvent (690 mg; 14%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.95 (s br, 1 H, NH), 8.08 – 8.05 (m, 2 H, α-CH), 7.68-7.65 (m, 2 H, β-CH), 6.80 (s, 2 H, CH_{Th}), 1.36 (s, 18 H, $C(CH_3)_3$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.4, 165.1, 152.8, 134.8, 132.5, 132.3, 108.8, 35.2, 30.1. HRMS (ESI, MeOH): calc. for $[C_{22}H_{26}N_5S_2]^+$: 424.1624, found: 424.1628.

*Preparation and characterization of complex **4*** [(4-tBuBTI*)Pd]*:*

HtBuBTI **3** (30 mg, 70 μmol) and palladiumacetate (47.2 mg, 210 μmol) are dissolved in dichloromethane (3 mL) and stirred at ambient temperature for 48h. The mixture is then reduced to 0.5 mL, filtered over alumina and eluted with dichloromethane. The title compound remains as a brilliant red solid after removal of the solvent (25.9 mg, 78%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.01 – 7.98 (m, 1 H, α/α'-CH), 7.88 – 7.85 (m, 1 H, α/α'-CH), 7.57 – 7.48 (m, 2 H, β,β'-CH), 6.54 (s, 1 H, CH_{Th}), 6.51 (s, 1 H, $CH_{Th'}$), 2.14 (s, 2 H, CH_2), 1.40 (s, 9 H, $(CH_3)_3$), 1.35 (s, 6 H, $(CH_3)_2$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 168.0, 167.7, 165.7, 165.5, 161.5, 138.7, 138.4, 131.7, 131.2, 123.3, 122.1, 106.2, 103.0, 44.0, 36.0, 35.3, 30.7, 29.4. HRMS (ESI, MeOH): calc. for $[(C_{22}H_{24}N_5S_2Pd]^+$: 528.0502, found: 528.0498. Combustion analysis: calc. for $C_{22}H_{23}N_5PdS_2$: C 50.04, H 4.39, N 13.26%, found: C 50.29, H 4.34, N 12.82%.

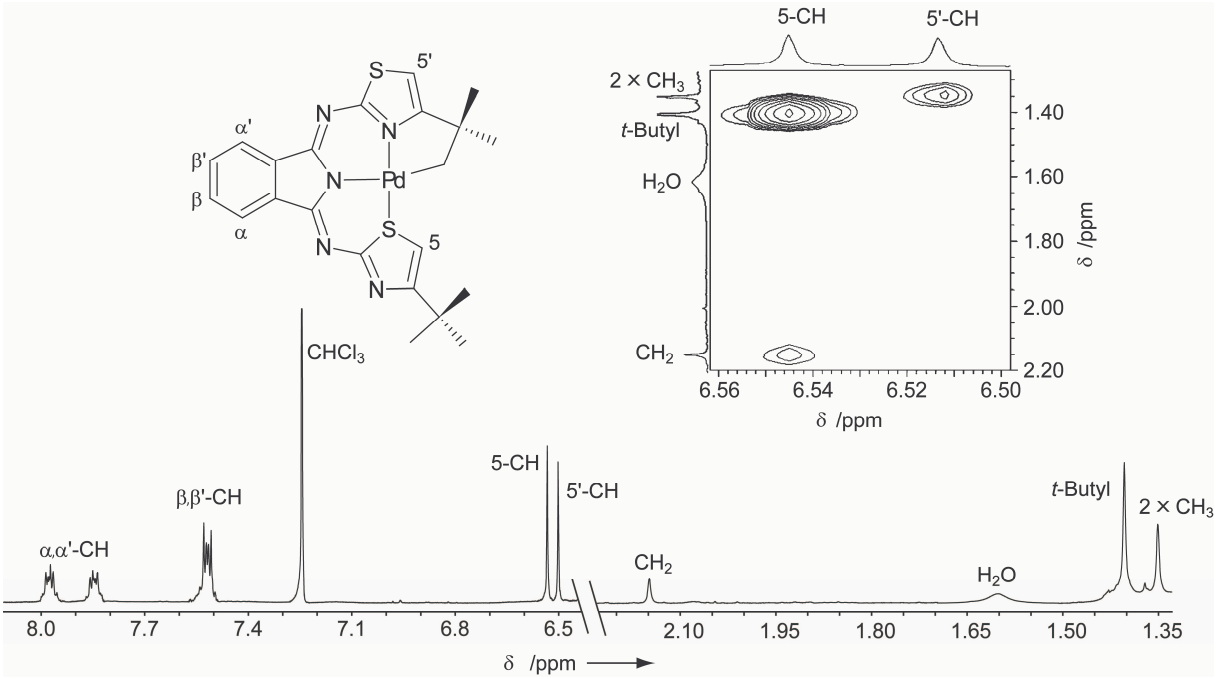


Fig. E1: Details from the ^{1}H and NOESY NMR spectra of **4** ($CDCl_3$, 400 MHz) with signal assignments.

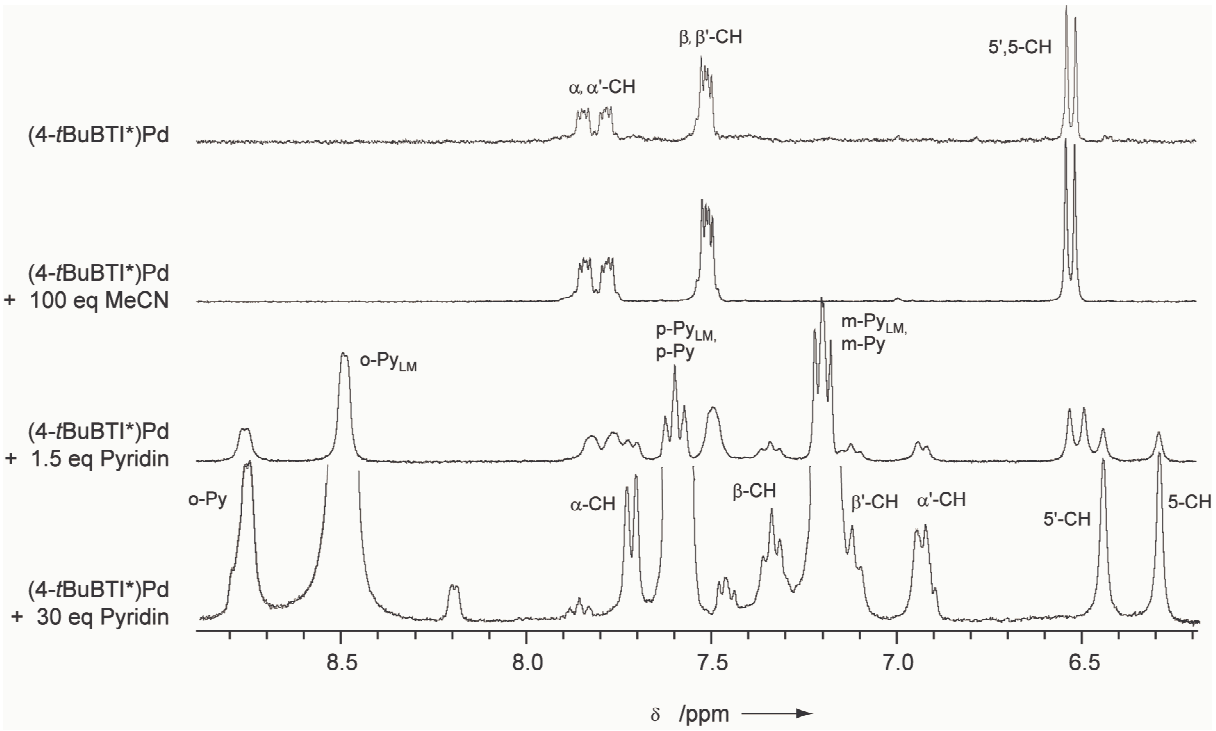
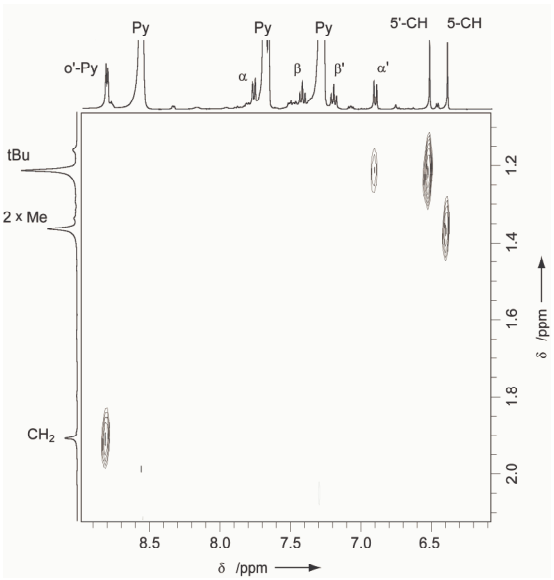


Fig. E2: Details from the ^{1}H NMR spectra of **4** (CD_2Cl_2, 300 MHz) in the presence of differing amounts of donor solvents. Unassigned signals are excess solvent peaks and satellite peaks thereof.

Preparation and characterization of complex ***5*** ([(4-tBuBTI)*Pd(py)])*:*

[(4-tBuBTI)*Pd] **4** (27 mg, 51 µmol) are dissolved in pyridine (0.5 mL) and layered with *n*-hexane (6 mL). The mixture is kept at –20°C for 16h and then at ambient temperature until crystallization of the title compound occurs (19 mg, 61%).

^{1}H-NMR (400 MHz, CD_2Cl_2, C_5H_5N, 240 K): δ = 8.81 (d, J = 4.9 Hz, 2 H, 2-CH_{Py}), 7.77 (d, J = 7.4 Hz, 1 H, α-CH), 7.42 (t, J = 7.5 Hz, 1 H, β-CH), 7.20 (t, J = 7.6 Hz, 1 H, β'-CH), 6.91 (d, J = 7.7 Hz, 1 H, α'-CH), 6.52 (s, 1 H, $CH_{Th'}$), 6.40 (s, 1 H, CH_{Th}), 1.91 (s, 2 H, CH_2), 1.37 (s, 6 H, CHC($C\underline{H}_3$)$_2$), 1.22 (s, 9 H, C($C\underline{H}_3$)$_3$). The missing signals are underneath the pyridine derived peaks. MS (MALDI-TOF, no matrix): 629 $[M+Na]^+$, 527 $[M–C_5H_5N]^+$. Combustion analysis: calc. for $C_{27}H_{28}N_6PdS_2$: C 53.42, H 4.65, N 13.84%, found: C 53.30, H 4.64, N 13.86%.



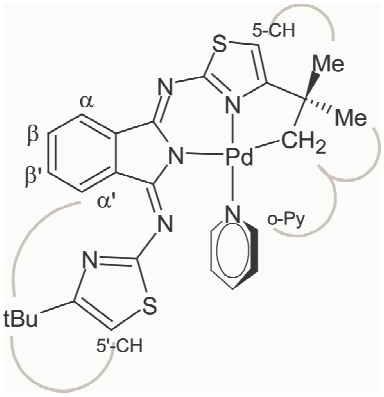


Fig. E3: Details from the NOESY spectrum of **5** (CD_2Cl_2 + 30 eq pyridine, 400 MHz, 240 K) with signal assignments.