Cp₂Fe(PR₂)₂PdCl₂ (R = *i*-Pr, *t*-Bu) Complexes as Air-Stable Catalysts in Challenging Suzuki Coupling Reactions

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Experimental: All the reactions were carried out in inert atmosphere in conjunction with Schlenk-line/Vacuum atmosphere glove box. Solvents were purchased from Alfa-Asear/Aldrich and used without further purification. All the catalysts employed in the study were commercially available through Johnson Matthey. Since **1a** and **1b** are only briefly mentioned in the literature¹⁷ their characterization details are listed below.

Synthesis and characterization of di-isopppfPdCl₂ (1a) and di-tbpfPdCl₂ (1b): These complexes were isolated as orange yellow and orange reddish brown solids, respectively in over 95 % yield using the internal method. However these catalysts are now available in gram to multi-kilogram quantities through Johnson Matthey, Catalysis and Chiral Technology, 2001 Nolte Drive, West Deptford, NJ 08066.

Characterization:

1a: ³¹P{¹H} NMR (400 MHz, Brüker) in CD₂Cl₂ : (δ): 64.07 PPM (reported value: 65.8 PPM in C₆D₆)^{17b}. Anal. Calc. (%): C, 44.36; H = 6.09; Cl = 11.9. Found: C, 44.66, H = 5.92, Cl, 12.11 (Robertson Microlit Lab, NJ-07940 – sample ID: 2043-65).

1b: $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz, Brüker) in CD_2Cl_2 : (δ): 68.71 PPM. Anal. Calc. (%): C, 47.91; H, 6.80; Cl, 10.88. Found: C, 47.92, H = 6.82, Cl = 10.84 (Robertson Microlit Lab, NJ-07940 – sample ID: 2043-69).

Screening: Radley's high throughput screening carousel or Chemspeed machine were employed in the study. In a typical experiment the reaction tubes were charged with K_2CO_3 (276 mg, 2 mmol), $\text{PhB}(\text{OH})_2$ (122 mg, 1 mmol), aryl halide (1 mmol) and dtbpfPdCl_2 (7 mg, 0.01 mmol). To this was added 5 mL DMF that was degassed prior to use. The reaction mixture was heated to 120 °C for 15 hours. After cooling to room temperature, the reaction mixture was extracted with 5 mL TBDME and washed with 5mL H_2O . A sample of the reaction mixture was filtered through a 5 μm filter. 10 μL of this filtrate was taken and diluted to 1 mL with ACN. The sample was analyzed by HPLC equipped with an auto-sampler. The products were analyzed by comparing the respective peaks of the coupled products and starting material (halide) to the analytical standards. HPLC method: Column; Agilent Zorbax 3.5 μm , SB-C8, 2.1 mm x 50 mm; UV: 225 nm and 254 nm; flow: 0.5 mL/min; Solvent: 95% H_2O /0.01% TFA, 5% ACN/0.01% TFA. The following formulas were used for calculations: %Wt analysis = $(\text{Impurity Ave PA})(\text{Std mg/mL})(\text{Std \% purity})/(\text{Std Ave PA})(\text{Sample mg/mL}) \times 100$ and %Yield = $\text{\%WtProd}/(\text{\%WtProd} + \text{\%WtSM})$. The HPLC/MS traces are submitted only for review, however details on calculations are attached.