

## SUPPORTING INFORMATION FOR

A  $\sigma^4$ ,  $\lambda^5$ -Phosphinine Palladium Complex: A New Type of Phosphorus Ligand and Catalyst.  
Application to the Pd-Catalyzed Formation of Arylboronic Esters.

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### **General procedure:**

All reactions were performed under an inert atmosphere of dry nitrogen by using Schlenk techniques and dry deoxygenated solvents. Pinacol borane and iodoaryl were used as received by the suppliers. The first step consists in weighing the appropriate amount of catalyst **3**. Due to the low-loading of catalyst complex **4** (10 mg) was first dissolved in dichloromethane (10 mL). Then 100  $\mu$ l of this solution were preleved with a syringe and transferred in a second schlenck tube. After evaporation of the solvent, the isoaryl (1.0 mmol), pinacolborane (1.5 mmol, solution 1M in THF), triethylamine (3.0 mmol), and dioxane (4 mL) were successively added. The resulting mixture was then heated at 80°C and the reaction was monitored by GC. In the case of iodobenzene and 4-iodotoluene, reactions were completed in 15 h and 48 hours respectively. For the other couplings, reactions were deliberately stopped after 5 days. The mixture were cooled to room temperature and the solvent was evaporated. Ether (10 mL) was added to allow the separation of Et<sub>3</sub>NHI by filtration. Dry celite (0.5 g) was added to the ether solution collected and the mixture obtained was evaporated to dryness yielding a yellow powder which was deposited onto the top of a column of silicagel for chromatography (Note that prior to the chromatographic separation, a solution of hexane/Et<sub>3</sub>N was eluted in order to remove any traces of acid). The arylboronic esters were purified using hexane as eluent. Characterizations were achieved by NMR techniques (<sup>1</sup>H and <sup>13</sup>C) and by comparison with reported data.

4,4,5,5-Tetramethyl-2-phenyl-[1,3,2]-dioxaborolane : see ref. 1.

4,4,5,5-Tetramethyl-2-p-tolyl-[1,3,2]-dioxaborolane : see ref. 1.

4,4,5,5-Tetramethyl-2-o-tolyl-[1,3,2]-dioxaborolane : see ref. 1

4,4,5,5-Tetramethyl-2-thiophene-2-yl-[1,3,2]-dioxaborolane : see ref. 1.

4,4,5,5-Tetramethyl-2-naphthalen-2-yl-[1,3,2]-dioxaborolane : see ref. 1.

2-(4-bromophenyl)-4,4,5,5-Tetramethyl-[1,3,2]-dioxaborolane : see ref. 2.

2-(4-methoxy-phenyl)-4,4,5,5-Tetramethyl-[1,3,2]-dioxaborolane : see ref. 3.

### References:

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- 2) T. Ishiyama, M. Murata, N. Miyaoura, *J. Org. Chem.*, 1995, **60**, 7508.
- 3) T. Ishiyama, I. Itoh, T. Kitano, *Tetrahedron Lett.*, 1997, **38**, 3447.