

## SUPPLEMENTARY INFORMATION

# A new insight into *ortho*-(dimesitylboryl)diphenylphosphines: applications in Pd-catalyzed Suzuki-Miyaura couplings and evidence for secondary $\pi$ -interaction

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## Experimental Section

### General

All reactions were carried out under an argon atmosphere in oven-dried glassware using standard Schlenk techniques. Toluene was distilled under argon from molten sodium. Unless stated otherwise, commercially compounds were used without further purification. Ligands **1-2** (T. W. Hudnall, Y.-M. Kim, M. W. P. Bebbington, D. Bourissou and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2008, **130**, 10890) and **3** (T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 4685) as well as precursor [Pd(nbd)(ma)] (K. Itoh, F. Ueda, K. Hirai and Y. Ishii, *Chem. Lett.*, 1977, **6**, 877) were prepared according to procedures previously described. NMR spectra were recorded on Bruker Avance 300 or 500 spectrometers. GC analyses were carried out on an Agilent GC6890 with a flame ionization detector, using a SGE BPX5 column composed by 5% of phenylmethylsiloxane.

### Synthesis of complex 1-Pd

*o*-Ph<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)BMes<sub>2</sub> (255 mg, 0.5 mmol) and [Pd(nbd)(ma)] (148 mg, 0.5 mmol) were dissolved in THF (20 mL) under argon and the solution was stirred at 60 °C for 1h. The reaction mixture was filtered and the solvent was removed under vacuum. After washing with pentane (10 mL), complex **1-Pd** was isolated as an orange powder (305 mg, 86% yield). Crystals suitable for XRD analysis were obtained by slow evaporation from a dichloromethane solution at room temperature. Elemental analysis: % calculated: C 67.23, H 5.32; found: C 67.47, H 5.36.; mp 265-267 °C; <sup>11</sup>B NMR (160.5 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 69.4; <sup>31</sup>P NMR analysis shows the presence of two isomers at room temperature; <sup>1</sup>H and <sup>13</sup>C NMR signals corresponding to the *o*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub> are observed but they are too overlapped to allow precise assignment; thanks to 2D HMQC and HMBC experiments, the signals for the maleic anhydride and the BMes<sub>2</sub> fragment could be attributed.

**Isomer A:** <sup>31</sup>P NMR (202.5 MHz, CDCl<sub>3</sub>):  $\delta$  31.1; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.17 (s, 1H, mMes), 6.86 (s, 1H, mMes), 6.69 (s, 1H, mMes), 6.52 (s, 1H, mMes), 4.55 (pseudot, 1H, CH-am,  $J_{HH}$ =4.2Hz,  $J_{HP}$ =4.6Hz), 3.70 (dd, 1H, CH-am,  $J_{HH}$ =4.2Hz,  $J_{HP}$ =9.2Hz), 2.61 (s, 3H, Me), 2.20 (s, 3H, Me), 1.80 (s, 3H, Me), 1.52 (s, 3H, Me), 1.49 (s, 3H, Me), 1.13 (s, 3H, Me); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$  169.05 (s, CO), 166.78 (d,  $J_{CP}$  = 4.1Hz, CO), 144.68 (s, C<sub>quat</sub> Mes), 144.28 (s, C<sub>quat</sub> Mes), 143.61 (s, C<sub>quat</sub> Mes), 140.38 (s, C<sub>quat</sub> Mes), 138.72 (s, C<sub>quat</sub> Mes), 138.16 (s, C<sub>quat</sub> Mes), 134.10 (s, C<sub>quat</sub> Mes), 131.14 (s, CH, mMes), 129.50 (s, CH, mMes) 127.80 (s, CH, mMes), 127.67 (s, CH, mMes), 104.66 (s, C<sub>quat</sub> Mes), 61.99 (d,  $J_{CP}$  = 22.7Hz, CH-am), 59.80 (d,  $J_{CP}$  = 3.1Hz, CH-am), 27.40 (s, CH<sub>3</sub>) 25.40 (s, CH<sub>3</sub>), 23.13 (s, CH<sub>3</sub>), 21.69 (s, CH<sub>3</sub>), 21.37 (s, CH<sub>3</sub>), 20.93 (s, CH<sub>3</sub>).

**Isomer B:**  $^{31}\text{P}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.6;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (s, 1H, mMes), 6.97 (s, 1H, mMes), 6.77 (s, 1H, mMes), 6.64 (s, 1H, mMes), 3.77 (pseudo-t, 1H, CH-am,  $J_{\text{HH}}=4\text{Hz}$ ,  $J_{\text{HP}}=4.3\text{Hz}$ ), 2.46 (s, 3H, Me), 2.32 (dd, 1H, CH-am,  $J_{\text{HH}}=4\text{Hz}$ ,  $J_{\text{HP}}=9.1\text{Hz}$ ), 2.24 (s, 3H, Me), 1.73 (s, 6H, Me), 1.72 (s, 6H, Me);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.07 (s, CO), 168.27 (d,  $J_{\text{CP}}=4.5\text{Hz}$ , CO), 145.69 (s,  $\text{C}_{\text{quat}}$  Mes), 141.97 (s,  $\text{C}_{\text{quat}}$  Mes), 141.27 (s,  $\text{C}_{\text{quat}}$  Mes), 139.03 (s,  $\text{C}_{\text{quat}}$  Mes), 138.25 (s,  $\text{C}_{\text{quat}}$  Mes), 136.86 (s,  $\text{C}_{\text{quat}}$  Mes), 136.27 (s,  $\text{C}_{\text{quat}}$  Mes), 130.31 (s, CH, mMes), 130.25 (s, CH, mMes), 127.80 (s, CH, mMes), 127.75 (s, CH, mMes), 107.67 (s,  $\text{C}_{\text{quat}}$  Mes), 65.30 (d,  $J_{\text{CP}}=23.7\text{Hz}$ , CH-am), 62.48 (d,  $J_{\text{CP}}=2.7\text{Hz}$ , CH-am), 24.84 (s,  $\text{CH}_3$ ), 24.80 (s,  $\text{CH}_3$ ), 24.38 (s,  $\text{CH}_3$ ), 21.88 (s,  $\text{CH}_3$ ), 21.19 (s,  $\text{CH}_3$ ), 20.97 (s,  $\text{CH}_3$ ).

### Synthesis of Pd(0) complex containing ligand 1 starting from $[\text{Pd}_2(\text{dba})_3]$

$[\text{Pd}_2(\text{dba})_3]$  was also tested to synthesise Pd(0) complex containing ligand **1**. Rather harsh conditions were required to complete the coordination (1h at 100 °C in toluene). After work-up, an orange solid was isolated. The  $^{31}\text{P}$  NMR spectrum displayed a broad signal at 31.1 ppm, indicating the coordination of the phosphorus atom to the metal center. But the poor solubility of the complex combined with some dynamic phenomenon prevented complete characterization and only crystals of poor quality could be obtained.

### Crystal structure determination of 1-Pd

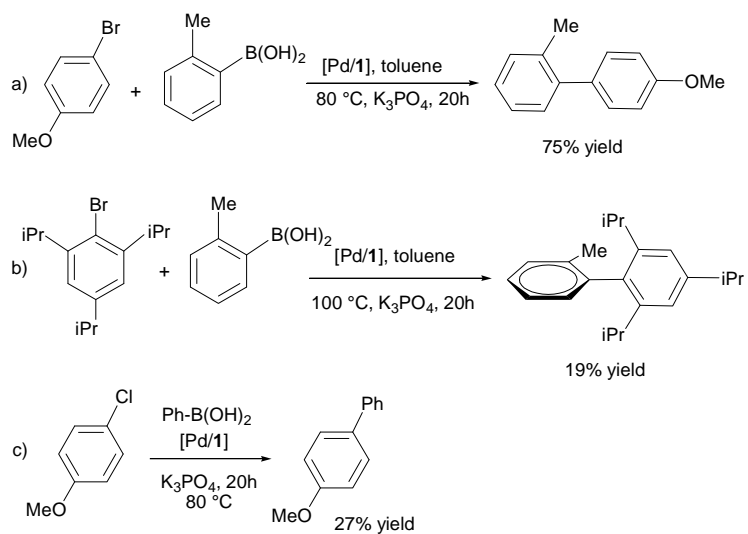
Data were collected on a Bruker-AXS kappa APEX II diffractometer using Mo  $\text{K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 100(2) K with CCD detector. A suitable crystal was mounted on a glass fiber and shock-cooled on the goniometer head. Semi-empirical absorption corrections were employed.<sup>[33]</sup> The structures were solved by direct methods (SHELXS-97),<sup>[34]</sup> and refined using the least-squares method on  $F^2$ .<sup>[35]</sup> Crystal data for **1-Pd**:  $\text{C}_{40}\text{H}_{38}\text{BO}_3\text{PPd}$ ,  $M = 714.88$ , Monoclinic, space group  $P2_1/c$ ,  $a = 8.2541(16)$ ,  $b = 22.531(5)$ ,  $c = 17.726(4) \text{ \AA}$ ,  $\alpha = 90$ ,  $\beta = 90.010(11)$ ,  $\gamma = 90^\circ$ ,  $V = 3296.7(12) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.440 \text{ gcm}^{-3}$ ,  $F(000) = 1472$ ,  $T = 100 (2) \text{ K}$ , crystal size  $0.13 \times 0.13 \times 0.02 \text{ mm}^3$ , 25011 reflections collected (6462 independent,  $R_{\text{int}} = 0.0680$ ),  $\theta \leq 26.02^\circ$ , 421 parameters,  $R1 [I > 2\sigma(I)] = 0.0453$ ,  $wR2$  (all data) = 0.1001, largest diff. peak and hole: 0.525 and  $-0.687 \text{ e. \AA}^{-3}$ . CCDC-802793 (**1-Pd**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### General procedure for catalytic Suzuki C-C coupling

Palladium precursor (0.01 mmol; for  $\text{Pd}(\text{OAc})_2$ : 2.3 mg; for  $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$ : 4.5 mg; for  $[\text{PdCl}_2(\text{cod})]$ : 2.9 mg; for  $[\text{Pd}_2(\text{dba})_3]$ : 9.1 mg; for **1-Pd**, 7.0 mg) and the appropriated ligand (0.02 mmol; for **1**: 10.2 mg; for **2**: 6.5 mg; for **3**: 6.7 mg); for  $\text{PPh}_3$ : 5.2 mg) were transferred in a Schlenk tube in the glove box. Toluene (2mL), phenyl boronic acid (135 mg, 1.1 mmol), base (2.1 mmols; for  $\text{K}_3\text{PO}_4$ : 445 mg; for  $\text{Na}_2\text{CO}_3$ : 223 mg; for  $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ : 483 mg; for  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ : 288 mg), 2-methoxynaphthalene as internal standard (30 mg, 0.19 mmol) and 4-bromo anisole (1 mmol, 125  $\mu\text{L}$ ,) were then successively added under argon. The catalytic mixture was stirred at the desired temperature (80 or 100 °C) for some hours (from 2 to 24h). The mixture was quenched by addition of diethyl ether (2 mL), filtered on celite and consecutively washed with NaOH (2 mL of 1M NaOH aqueous solution) and water. The organic phase was dried on anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and analysed by gas chromatography to determine conversion and yield. 2-methoxy naphthalene was used as internal standard.

### Catalytic Suzuki C-C coupling using 25 mol% catalyst

0.125 mmol (15.6 ml) 4-bromoanisole; 7 ml toluene;  $\text{K}_3\text{PO}_4$ /phenyl boronic acid/4-bromoanisole = 2.1/1.1/1; 0.031 mmol (7.0 mg) of palladium acetate; 0.062 mmol (32.0 mg) of ligand **1**; 0.022 mmol (4.0 mg) of anthracene as internal standard; 80 °C; up to 24h.



**Scheme S1.** Suzuki-Miyaura C-C cross-coupling reactions using hindered reactants (a and b) and 4-chloroanisole (c), catalyzed by Pd/1 system.

**Table S1.** Suzuki cross-coupling reactions between 4-bromoanisole and phenyl boronic acid catalyzed by palladium systems containing ligand **1** (Scheme 1).<sup>a</sup>

Entry	Precursor	Base	<i>T</i> (°C)	<i>t</i> (h)	<b>1</b> /Pd	Boronic acid/ substrate	Yield of <b>1</b> <sup>b</sup> (%)
1	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	80	2	2	1.1	81(90)
2	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub> ·H <sub>2</sub> O	80	2	2	1.1	75(86)
3	Pd(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	80	2	2	1.1	3(4)
4	Pd(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	80	2	2	1.1	75(75)
5	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	80	24	2	1.1	80(90)
6	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	100	3	2	1.1	80(92)
7	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	100	20	2	1.1	86(94)
8	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	80	2	2	2.0	58(77) <sup>c</sup>
9	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	80	2	2	3.0	47.5(81.5) <sup>d</sup>
10	[PdCl(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> ]	K <sub>3</sub> PO <sub>4</sub>	80	2	2	1.1	81(89)
11	[PdCl <sub>2</sub> (cod)]	K <sub>3</sub> PO <sub>4</sub>	80	24	2	1.1	82(88)
12	[Pd <sub>2</sub> (dba) <sub>3</sub> ]	K <sub>3</sub> PO <sub>4</sub>	80	20	2	1.1	47(47)
13	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	80	2	1	1.1	81(89)
14	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	80	6	1	1.1	87(95)
15	<b>1</b> -Pd	K <sub>3</sub> PO <sub>4</sub>	80	6	1	1.1	72(85)
16	<b>1</b> -Pd	K <sub>3</sub> PO <sub>4</sub>	80	20	1	1.1	82(91)

<sup>a</sup> Results from duplicate experiments. Reaction conditions: 1 mmol 4-bromoanisole; 2 ml toluene; base/4-bromoanisole = 2.1/1; 0.01 mmol palladium; the corresponding amount of **1** depending on the **1**/Pd ratio used. <sup>b</sup> Determined by GC analysis. In brackets, substrate conversion. <sup>c</sup> Yield of by-products: 7% homo-coupling products, 10% benzene and 2% anisole. <sup>d</sup> Yield of by-products: 5.4% homo-coupling products, 24% benzene and 4.6% anisole.

**NOTE:** Potassium phosphate induced the highest activities, with slightly better results being obtained with the anhydrous over the hydrated salt (entries 1 and 2). Anhydrous sodium carbonate led to an inactive catalytic system (entry 3), while the hydrated carbonate gave the cross-coupling with a lower activity than that observed using K<sub>3</sub>PO<sub>4</sub> (entry 4 vs 1). These variations in activity are probably related to different transition states along the transmetalation step, depending on the presence of hydroxide groups and the bidentate coordination ability of the anion (B. Wang, H.-X. Sun, Z.-H. Sun, *Eur. J. Org. Chem.* 2009, 3688).

**Table S2.** Suzuki cross-couplings between 4-bromoanisole and phenyl boronic acid catalyzed by Pd/**L** systems (see Scheme of Table 1).<sup>a</sup>

Entry	<b>L</b>	t (h)	Conv (%) <sup>b</sup>	Selectivity(%) <sup>b</sup>			
				<b>I/II/III/Benzene/Ani</b>	<b>sole</b>		
1	<b>1</b>	3	89.0	88.8/5.6/1.1/3.4/1.1			
2 <sup>c</sup>	<b>1</b>	20	94.0	92.1/4.1/1.3/1.0/1.5			
3	<b>2</b>	3	91.0	91.2/6.6/0/0/2.2			
4	<b>2</b>	20	93.8	91.3/5.2/1.8/0/1.7			
5	<b>PPh<sub>3</sub></b>	24	71.8	93.9/4.0/0.8/0.8/0.5			
6	<b>3<sup>f</sup></b>	20	99.8	96.8/2.5/0.3/0.1/0.3			

<sup>[a]</sup> Results from duplicate experiments. Reaction conditions: 1 mmol 4-bromoanisole; 2 ml toluene; K<sub>3</sub>PO<sub>4</sub>/phenyl boronic acid/substrate = 2.1/1.1/1; 0.01 mmol of palladium acetate; 0.02 mmol of the corresponding ligand; 100 °C; 2-methoxy naphthalene used as internal standard. <sup>b</sup> Determined by GC analysis. <sup>c</sup> Results from entry 2 in Table 1. <sup>f</sup> For the synthesis of ligand **3**, see Supplementary Information of reference T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* 2005, **127**, 4685.