

**Synthesis of *N*-Heterocyclic Carbene Palladium(II) Bis-  
Phosphine Complexes and Decomposition in the Presence of  
Aryl Halides**

**Supporting Information**

*Alison M. Magill, Brian F. Yates, Kingsley J. Cavell, \*Brian W. Skelton and Allan H. White*

**[Pd(tmiy)Cl( $\mu$ -Cl)]<sub>2</sub> (5).** To a solution of Pd(NCPh)<sub>2</sub>Cl<sub>2</sub> (0.25 g, 0.65 mmol) in THF (10 mL) and toluene (10 mL) was added, via syringe, a solution of tmiy (0.079 g, 0.64 mmol) in THF (15 mL). Immediately a brown precipitate formed. The mixture was stirred for 30 minutes at room temperature, before the volatiles were removed *in vacuo*. To the residue was added DCM (10 mL) and the dark mixture filtered through Celite®. Concentration of the filtrate to ~4 mL followed by addition of light petroleum lead to the precipitation of a brown solid, together with some dark, sticky material. The volatiles were again removed *in vacuo*, and the residue taken up in DCM (5 mL). Treatment of this solution with activated charcoal overnight, followed by filtration, reduction of the filtrate to ~0.5 mL and addition of light petroleum lead to the precipitation of a yellow solid. The mother liquor was decanted and the solid dried *in vacuo*. Yield: 0.08 g (41%). The complex could also be prepared in higher yield by the reaction of 1,3,4,5-tetramethylimidazolium iodide (0.25 g, 0.99 mmol), Ag<sub>2</sub>O (0.12 g, 0.52 mmol) and Pd(NCPh)<sub>2</sub>Cl<sub>2</sub> (0.38 g, 0.99 mmol) in a manner similar to that described for **1a** (Yield: 0.21 g (72%)). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  4.06 (s, 12H, N-CH<sub>3</sub>), 2.09 (s, 12H, C-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  136.7 (NCN), 127.2 (C=C), 35.32 (N-CH<sub>3</sub>), 9.30 (C-CH<sub>3</sub>).

**[Pd(tmiy)Cl(dppp)]BF<sub>4</sub> (6a).** Prepared from [Pd(tmiy)Cl( $\mu$ -Cl)]<sub>2</sub> (0.0316 g, 0.0524 mmol), dppp (0.0437 g, 0.106 mmol) and AgBF<sub>4</sub> (0.021 g, 0.108 mmol) in a manner similar to that described for **1a**. Yield: 0.06 g (75%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  7.81-7.23 (m, 20H, ArH), 3.40 (s, N-CH<sub>3</sub>), 2.83 (m, 2H, P-CH<sub>2</sub>), 2.59 (m, 2H, P-CH<sub>2</sub>), 1.97 (br m, 2H, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 1.83 (s, 3H, C-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.4 MHz):  $\delta$  12.91 (d, J=40.3 Hz), -3.13 (d, J=40.3 Hz).

**[Pd(tmiy)Cl(dppe)]BF<sub>4</sub> (6b).** Prepared from [Pd(tmiy)Cl( $\mu$ -Cl)]<sub>2</sub> (0.0849 g, 0.141 mmol), dppe (0.1155 g, 0.290 mmol) and AgBF<sub>4</sub> (0.056 g, 0.289 mmol) as described

for **1a**. Yield: 0.14 g (66%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz):  $\delta$  7.93-7.89 (m, 4H, ArH), 7.66-7.40 (m, 16H, ArH), 3.25 (s, 6H, N- $\text{CH}_3$ ), 2.92-2.40 (m, 4H,  $\text{PCH}_2\text{CH}_2\text{P}$ ), 1.99 (s, 6H, C- $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 121.4 MHz):  $\delta$  59.51 (d,  $J=14.1$  Hz), 50.34 (d,  $J=14.1$  Hz).

**[Pd(tmiy)Cl(dcype)]BF<sub>4</sub> (6c)**. Prepared from  $[\text{Pd}(\text{tmiy})\text{Cl}(\mu\text{-Cl})]_2$  (0.0864 g, 0.143 mmol), dcype (0.125 g, 0.296 mmol) and  $\text{AgBF}_4$  (0.057 g, 0.293 mmol) as described for **1a**. Yield: 0.16 g (72%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.72 (s, 6H, N- $\text{CH}_3$ ), 2.5-0.8 (br m, 48H, CyH +  $\text{PCH}_2\text{CH}_2\text{P}$ ), 2.18 (s, 6H, C- $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  84.77 (d,  $J=3.1$  Hz), 81.61 (d,  $J=3.1$  Hz).

**[Pd(tmiy)I(dppp)]BF<sub>4</sub> (7a)**. A solution of **6a** (0.0312 g, 0.0408 mmol) and NaI (0.0063 g, 0.0420 mmol) in acetone (5 mL) was stirred overnight at room temperature. The volatiles were removed *in vacuo* and the residue taken up in DCM, filtered through Celite® and concentrated to dryness to yield a pale yellow-orange solid. Yield: 0.029 g, (83%). HRMS calc. for  $\text{C}_{34}\text{H}_{38}\text{N}_2\text{P}_2^{104}\text{PdI}$ , 767.05952; found, 767.05901. MS (LSIMS)  $m/z$  (intensity): 769.2 (100%) [ $\text{M}^+$ ], 644.1 (10%) [ $\text{M-I+H}^+$ ].  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82-7.75 (m, 5H, ArH), 7.59-7.19 (m, 15H, ArH), 3.33 (s, 6H, N- $\text{CH}_3$ ), 2.89 (m, 2H,  $\text{PCH}_2$ ), 2.68 (m, 2H,  $\text{PCH}_2$ ), 2.04 (m, 2H,  $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 1.82 (s, 6H, C- $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  3.19 (d,  $J=43.6$  Hz), -7.28 (d,  $J=43.6$  Hz).

**[Pd(tmiy)I(dppe)]BF<sub>4</sub> (7b)**. Prepared as described for **7a**, from **6b** (0.0671 g, 0.0893 mmol) and NaI (0.0135 g, 0.0900 mmol) to yield a yellow-orange powder. Yield: 0.05 g, 66%. HRMS calc. for  $\text{C}_{33}\text{H}_{36}\text{N}_2\text{P}_2^{104}\text{PdI}$ , 753.04387; found, 753.04319. MS (ESI)  $m/z$  (intensity): 755.0 (100%) [ $\text{M}^+$ ]. MS (negative ion ESI)  $m/z$  (intensity): 87.0 (100%) [ $\text{BF}_4^-$ ].  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.91-7.82 (m, 4H, ArH), 7.75-7.35 (m, 16H, ArH), 3.16 (s, 6H, N- $\text{CH}_3$ ), 2.72-2.46 (m, 4H,  $\text{PCH}_2\text{CH}_2\text{P}$ ), 2.01 (s, 6H,

C-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 54.34 (d, J=14.0 Hz), 50.28 (d, J=14.0 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CDCl<sub>3</sub>): δ 56.08, (d, J=13.2 Hz), 51.12 (d, J=13.2 Hz).

**[Pd(tmiy)I(dcyep)]BF<sub>4</sub> (7c)**. Prepared as described for **7a**, from **6a** (0.0460 g, 0.0594 mmol) and NaI (0.0091 g, 0.0607 mmol) to yield a yellow powder. Yield: 0.04 g (78%). HRMS calc. for C<sub>33</sub>H<sub>60</sub>N<sub>2</sub>P<sub>2</sub><sup>104</sup>PdI, 777.23167; found, 777.23017. MS (LSIMS) *m/z* (intensity): 779.4 (65%) [M<sup>+</sup>], 125.1 (100%) [ylidene+H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.61 (s, 6H, N-CH<sub>3</sub>), 2.5-0.7 (br m, 48H, CyH + PCH<sub>2</sub>CH<sub>2</sub>P), 2.20 (s, 6H, C-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CDCl<sub>3</sub>): δ 80.18 (s), 79.52 (s).<sup>1</sup>

**[Pd(tmiy)Br(dppp)]BF<sub>4</sub> (8a)**. An equimolar mixture of [Pd(tmiy)Cl(dppp)]BF<sub>4</sub> (**6a**) and NaBr was refluxed in acetone overnight. The mixture was then cooled, the acetone removed on a rotary evaporator and DCM added. The resulting suspension was filtered through Celite®, and concentrated *in vacuo* to yield a white powder. Yield: 0.08 g (69%). HRMS calc. for C<sub>34</sub>H<sub>38</sub>N<sub>2</sub>P<sub>2</sub><sup>105</sup>PdBr, 720.074437; found, 720.07293. MS (LSIMS) *m/z* (intensity): 723.3 (0.0002%) [M]<sup>+</sup>, 335.1 (70%), 201.1 (100%) [ylidene+Ph]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.83-7.14 (m, 20H, ArH), 3.43 (s, N-CH<sub>3</sub>), 3.02 (m, 2H, PCH<sub>2</sub>), 2.71 (m, 2H, PCH<sub>2</sub>), 1.98 (br m, 2H PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 1.76 (s, 6H, C-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 9.86 (d, J=40.9 Hz), -5.30 (d, J=40.9 Hz).

**[Pd(tmiy)Br(dppe)]BF<sub>4</sub> (8b)**. Prepared as described for **8a**, from **6b** (0.0782 g, 0.104 mmol) and NaBr (0.0156 g, 0.152 mmol). Yield: 0.06 g (73%). HRMS calc. for C<sub>33</sub>H<sub>36</sub>N<sub>2</sub>P<sub>2</sub><sup>105</sup>PdBr, 706.05879; found, 706.05691. MS (LSIMS) *m/z* (intensity): 709.2

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<sup>1</sup> Negligible phosphorus-phosphorus coupling constants (J<sub>P,P</sub> < 3 Hz) have previously been reported in the case of platinum dcyep complexes. (9) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436-1448.

(100%) [M<sup>+</sup>], 628.2 (8%) [M-Br]<sup>+</sup>, 201.2 (20%) [ylidene+Ph]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.95-7.86 (m, 4H, ArH), 7.65-7.37 (m, 16H, ArH), 3.21 (s, 6H, N-CH<sub>3</sub>), 2.81-2.38 (m, 4H, PCH<sub>2</sub>CH<sub>2</sub>P), 2.00 (s, 6H, C-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 58.71 (d, J=14.1 Hz), 50.57 (d, J=14.1 Hz).

**[Pd(tmiy)Br(dcype)]BF<sub>4</sub> (8c)**. Prepared as described for **8a**, from **6c** (0.0402 g, 0.0518 mmol) and NaBr (0.0105 g, 0.102 mmol). Yield: 0.0384 g (90 %). HRMS calc. for C<sub>33</sub>H<sub>60</sub>N<sub>2</sub>P<sub>2</sub><sup>105</sup>PdBr, 730.246587; found, 730.24931. MS (LSIMS) *m/z* (intensity): 733.4 (100%) [M<sup>+</sup>], 650.3 (10%), 609.2 (20%), 567.1 (8%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 3.75 (s, 6H, N-CH<sub>3</sub>), 2.5-0.8 (br featureless resonance, 44H, CyH), 2.20 (s, 6H, C-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CDCl<sub>3</sub>): δ 84.60 (d, J=1.9 Hz), 80.68 (d, J=1.9 Hz).

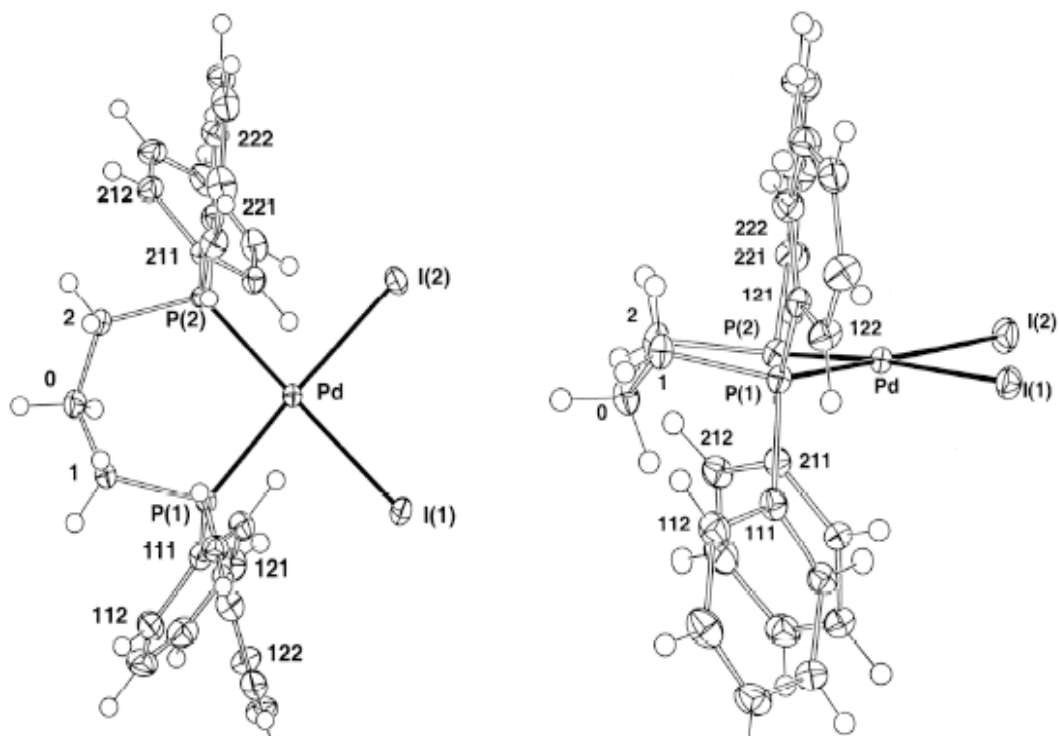
**Pd(Me)I(dppp) (9a)**. A mixture of Pd(Me)Cl(dppp) (0.10 g, 0.176 mmol) and NaI (0.0287 g, 0.191 mmol) was stirred in 10 mL of acetone overnight. Following this, the cloudy red solution was concentrated to dryness, and the residue taken up DCM (10 mL). The resultant suspension was filtered through Celite®, concentrated to ~3 mL and diluted with Et<sub>2</sub>O (15 mL). A yellow precipitate slowly formed. After 1 hour at room temperature, the purple supernatant was decanted from the yellow precipitate, which was washed with Et<sub>2</sub>O (2 x 5 mL) and dried *in vacuo* to yield a yellow powder. Yield: 0.05 g (42%). <sup>1</sup>H NMR (300 MHz, Acetone-*d*<sub>6</sub>): δ 7.79-7.70 (m, 8H, ArH), 7.51-7.34 (m, 12H, ArH), 2.76 (m, 2H, PCH<sub>2</sub>), 2.58 (m, 2H, PCH<sub>2</sub>), 1.86 (m, 2H, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 0.648 (dd, J=5.3, 7.5 Hz, 3H, Pd-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, Acetone-*d*<sub>6</sub>): δ 20.69 (d, J=52.2 Hz), -6.96 (d, J=52.2 Hz).

**Pd(Me)Br(dppp) (9b)**. Prepared as described for **9a**, from Pd(Me)Cl(dppp) (0.0735 g, 0.129 mmol) and LiBr (0.0200 g, 0.230 mmol). Yield: 0.0527 g (67%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.71-7.35 (m, 20H, ArH), 2.48 (m, 2H, PCH<sub>2</sub>), 2.35 (m, 2H,

PCH<sub>2</sub>), 1.87 (m, 2H, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P), 0.70 (dd, J=3.9, 7.8 Hz, 3H, Pd-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CDCl<sub>3</sub>): δ 26.24 (d, J=51.9 Hz), -6.33 (d, J=51.9 Hz).

**PdI<sub>2</sub>(dppp) (10).** PdCl<sub>2</sub>(MeCN)<sub>2</sub> (0.11 g, 0.424 mmol), LiI (0.12 g, 0.897 mmol) and dppp (0.18 g, 0.436 mmol) were stirred in MeCN (30 mL) overnight with exclusion of light. After this time the volatiles were removed *in vacuo* and the residue extracted with DCM (40 mL) and filtered through Celite. Concentration of the solvent, followed by addition of Et<sub>2</sub>O resulted in the precipitation of a bright orange powder that was collected and dried in vacuo. Yield: 0.134 g (41%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.78-7.28 (br m, 20H, ArH), 2.39 (br s, 4H, PCH<sub>2</sub>), 2.00 (br s, 2H, CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 0.495. This complex was sparingly soluble in DCM and DMSO, and virtually insoluble in acetone. The complex was insufficiently soluble in acetone-d<sub>6</sub> to allow a NMR spectrum to be recorded in this solvent. The insoluble nature of this complex is consistent with that observed for the major decomposition product in the reaction of [Pd(tmiy)Me(dppp)]BF<sub>4</sub> with PhI, which rapidly precipitated from the NMR solution upon transferral to a sample vial. X-Ray quality crystals were grown by solvent diffusion of ether into a CD<sub>2</sub>Cl<sub>2</sub>/DMSO-d<sub>6</sub> mixture of the product.

**Crystal/refinement data.** C<sub>27</sub>H<sub>26</sub>I<sub>2</sub>P<sub>2</sub>Pd<sub>1</sub>, M = 772.68. Monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 11.7468(7), *b* = 12.3711(8), *c* = 28.598(2) Å, β=94.917(1)° *V* = 4140.6(5) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.330 g cm<sup>-3</sup>, μ<sub>Mo</sub> = 0.574 mm<sup>-1</sup>; specimen: 0.18 x 0.13 x 0.04 mm; *T*<sub>min/max</sub> = 0.89. *N*<sub>t</sub> = 51975, *N* = 21630 (*R*<sub>int</sub> = 0.045), *N*<sub>o</sub> = 13536; *R* = 0.034, *R*<sub>w</sub> = 0.046 (*n*<sub>w</sub> = 2); *S* = 1.06, |Δρ<sub>max</sub>| = 1.1 e Å<sup>-3</sup>. CCDC 645600 contains the supplementary crystallographic data for this compound. 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).



**Figure 1.** ORTEP illustration of the structure of PdI<sub>2</sub>(dppp). Thermal ellipsoids are at the 50% probability level, while hydrogen atoms have an arbitrary radius of 0.1 Å.

**Table S1.** Selected geometric parameters for PdI<sub>2</sub>(dppp). Bond lengths are in Ångstroms, bond angles in degrees.

<i>Bond Lengths</i>			
Pd-I(1)	2.6632(3)	Pd-I(2)	2.6598(3)
Pd-P(1)	2.2680(7)	Pd-P(2)	2.2813(7)
<i>Bond Angles</i>			
I(1)-Pd-I(2)	91.42(1)	P(1)-Pd-P(2)	95.30(3)
I(1)-Pd-P(1)	86.50(2)	I(2)-Pd-P(2)	86.85(2)
I(1)-Pd-P(2)	175.00(2)	I(2)-Pd-P(1)	177.72(3)