

**Profound Steric Control of Reactivity in Aryl Halide  
Addition to Bis-Phosphine Palladium[0] Complexes [\*\*]**

**E. Galardon, S. Ramdeehul, J. M. Brown\*, A. Cowley, K. Kuok,  
and A. Jutand**

[\*] Dr. Erwan Galardon, Dr. Shailesh Ramdeehul, Dr. John M. Brown\*;  
Dyson Perrins Laboratory, South Parks Rd. OXFORD OX1 3QY, U.K.; FAX  
44 1865 275642, e-Mail: bjm@herald.ox.ac.uk.

[\*] Dr. Andrew Cowley, Chemical Crystallography Laboratory, Parks  
Rd., OXFORD OX1 3QZ

[\*] Dr King Kuok (Mimi) Hii, Department of Chemistry, King's  
College, Strand, LONDON WC2R 2LS, UK

[\*] Dr. Anny Jutand, Ecole Normale Supérieure, Département de  
Chimie, CNRS UMR 8640, 24 Rue Lhomond 75231 PARIS Cedex 5, France.

### **P(*t*Bu)(C<sub>x</sub>)<sub>2</sub> (1)**

To a solution of 5.0 ml of *tert*butyllithium (1.7M in pentane, 8.6 mmol, Aldrich) in 25 ml of diethyl ether cooled at -78°C was slowly added 1.0 g (4.3 mmol) of dicyclohexylchlorophosphine (Strem). The solution was then slowly allowed to reach room temperature and stirred overnight. After filtration, 10 ml of degassed water were added, and the organic layer transferred to a Schlenk tube containing magnesium sulfate. After filtration and removal of the ether, the phosphine was obtained as a colorless liquid (0.71g, 65%).

<sup>1</sup>H (δ, C<sub>6</sub>D<sub>6</sub>): 2.05 - 1.19 (m, 22H, C<sub>x</sub>); 1.26 (d, 9H, 10.3 Hz, *t*Bu).

<sup>13</sup>C (δ, C<sub>6</sub>D<sub>6</sub>): 34.0 (d, 23 Hz, CH C<sub>x</sub>); 33.3 (d, 16 Hz, CH<sub>2</sub> C<sub>x</sub>); 31.7 (d, 10 Hz, CH<sub>2</sub> C<sub>x</sub>); 30.9 (d, 13 Hz, CH<sub>3</sub> *t*Bu); 30.2 (d, 21 Hz, C *t*Bu); 28.4 (d, 16 Hz, CH<sub>2</sub> C<sub>x</sub>); 28.3 (d, 13 Hz, CH<sub>2</sub> C<sub>x</sub>); 27.1 (s, CH<sub>2</sub> C<sub>x</sub>).

<sup>31</sup>P (δ, C<sub>6</sub>D<sub>6</sub>): 28.2 (s)

HRMS (m / z) (as the oxide) : 271.219079 (calc : 271.219852).

### **Pd[P(*t*BuC<sub>x</sub>)<sub>2</sub>]<sub>2</sub> (3)**

In the glove box were introduced in a Schlenk tube 0.212g (1.00 mmol) of complex CpPd(allyl) and 0.584g (2.3 mmol) of *tert*butyldicyclohexylphosphine. 10 ml of toluene were then added and the red solution was heated for 2.5 hours at 75°C. After being allowed to cool down, the solvent was removed and the brown solid washed twice with methanol ( 2 \* 7ml) to give a white solid. After recrystallisation from toluene / methanol, 350 mg of microcrystals were obtained (57%).

<sup>1</sup>H (δ, C<sub>6</sub>D<sub>6</sub>): 2.44 - 1.38 (m, 44H, C<sub>x</sub>); 1.51 (t, 9H, <sup>3</sup>J<sub>PH</sub> + <sup>5</sup>J<sub>PH</sub> = 11.7 Hz)

$^{13}\text{C}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 36.0 (t,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 8$  Hz, CH Cx); 33.9 (t,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 10$  Hz,  $\text{CH}_2$  Cx); 33.1 (t,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 9$  Hz, C, tBu); 32.2 (t,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 6$  Hz,  $\text{CH}_2$  Cx); 31.7 (t,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 10$  Hz,  $\text{CH}_2$  Cx); 28.3 (t,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 11$  Hz,  $\text{CH}_2$  Cx); 28.2 (t,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 10$  Hz,  $\text{CH}_2$  Cx); 27.2 (s,  $\text{CH}_2$  tBu).

$^{31}\text{P}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 55.4 (s)

HRMS (m / z): (Calc for  $\text{C}_{32}\text{H}_{62}\text{P}_2\text{Pd}$ (106)614.3362); Found 614.3365

#### **P(tBu)<sub>2</sub>Cx (2)**

To a solution of 25.0 ml of *tert*-butyllithium (1.7M in pentane, 40 mmol, Aldrich) in 50 ml of diethylether cooled at  $-78^\circ\text{C}$  were slowly added 1.60 ml (10 mmol) of cyclohexyldichlorophosphine.[5] The solution was then kept at this temperature for 7 hours then slowly allowed to reach room temperature and stirred overnight. After filtration, 10 ml of degassed water were added, and the organic layer transferred to a schlenk tube containing magnesium sulfate. After filtration and removal of the ether, the crude phosphine was obtained as a slightly yellow liquid which was then distilled under reduced pressure to give the pure phosphine as a colorless liquid (1.22 g, 53%).

$^1\text{H}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 2.23 - 1.19 (m, 11H, Cx); 1.32 (d, 18H, 10.5 Hz, tBu).

$^{13}\text{C}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 37.1 (d, 28.8 Hz, CH Cx); 34.1 (d, 14 Hz,  $\text{CH}_2$  Cx); 33.0 (d, 27 Hz, C tBu); 31.4 (d, 14 Hz,  $\text{CH}_3$  tBu); 29.3 (d, 9 Hz,  $\text{CH}_2$  Cx); 27.1 (s,  $\text{CH}_2$  Cx).

$^{31}\text{P}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 49.2 (s)

HRMS (m / z) (as the oxide) : 245.203676 (calc : 245.203429).

#### **Pd[P(tBu)<sub>2</sub>Cx]<sub>2</sub> (4)**

In the glove box were introduced in a Schlenk tube 0.212g (1.00 mmol) of complex  $\text{CpPd}(\text{allyl})$  and 0.563g (2.3 mmol) of *tert*-butylcyclohexylphosphine. 10 ml of toluene were then added and the red solution was heated for 2.5 hours at  $75^\circ\text{C}$ . After being

allowed to cool down, the solvent was removed and the brown solid washed twice with methanol ( 2 \* 5 ml) to give a white solid. After recrystallisation from toluene / methanol, 330 mg of microcrystals were obtained (55%).

$^1\text{H}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 2.70 (m, 4H, Cx); 1.75 (m, 6H, Cx); 1.62 (m, 6H, Cx); 1.48 (t, 36H,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 11.5$  Hz); 1.17 (m, 6H, Cx).

$^{13}\text{C}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 39.7 (s, CH Cx); 35.9 (s, C, tBu); 35.2 (s,  $\text{CH}_2$ , Cx); 32.1 (t,  $^3\text{J}_{\text{PH}} + ^5\text{J}_{\text{PH}} = 10$  Hz,  $\text{CH}_3$  tBu); 29.2 (s,  $\text{CH}_2$ , Cx); 27.16 (s,  $\text{CH}_2$ , Cx).

$^{31}\text{P}$  ( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 73.3 (s)

HRMS (m / z): (calc. for  $\text{C}_{28}\text{H}_{58}\text{P}_2\text{Pd}(106)$  562.3049; Found 562.3049

#### Products from oxidative addition reactions :

**9a**  $^1\text{H}$  NMR (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 1.25 - 2.09 (m, 44H, Cx); 1.69 (t, 18H,  $^3\text{J} + ^5\text{J} = 12.4$  Hz, tBu); 6.93 - 7.05 (m, 3H, Ar); 7.69 (m, 2H, Ar).  
 $^{31}\text{P}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 32.6 (br).

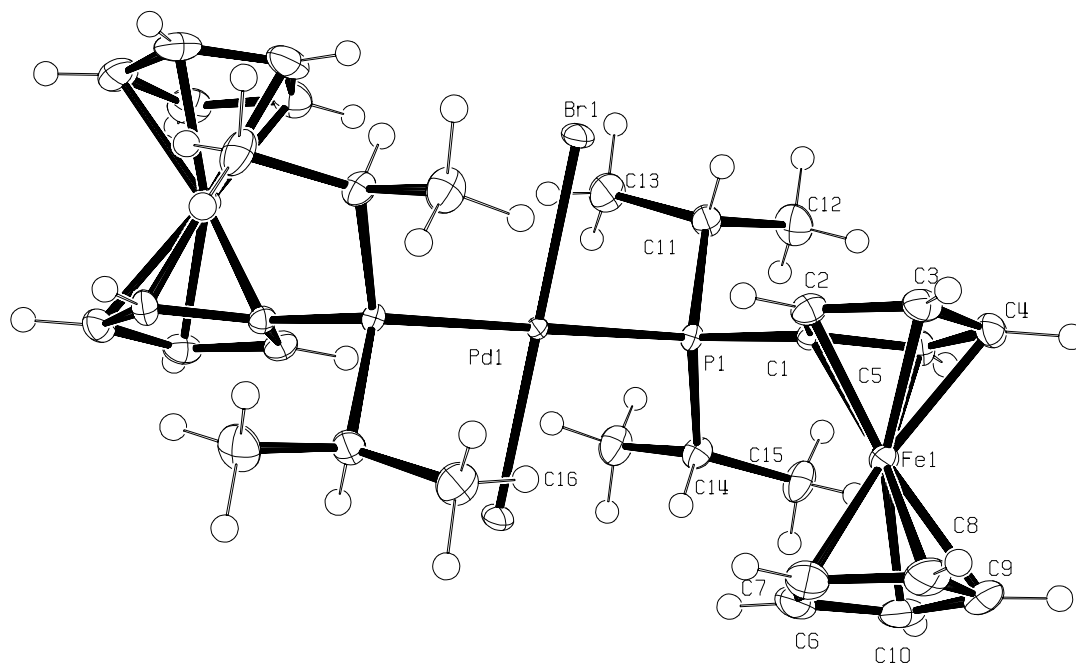
**10**  $^1\text{H}$  NMR (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 0.97 - 1.92 (m, 11H, Cx); 1.45 (d, 18H, 12.6 Hz, tBu); 6.90 (t, 1H, 7.2 Hz, Ar); 7.07 (t, 2H, 7.8 Hz, Ar); 7.86 (d, 2H, 7.8 Hz, Ar).  $^{31}\text{P}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 64.4 (s).

**12**  $^1\text{H}$  NMR (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 1.09 (d, 27H, 12.5 Hz, tBu); 6.87 (m, 3H, Ph); 7.47 (m, 2H, Ph).  $^{31}\text{P}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 57.9 (s).

X-ray crystal structure for compound 15

$C_{32}H_{46}Br_2Fe_2P_2Pd$ ,  $M_r = 870.56$ , monoclinic, space group  $P 2_1/a$ ,  $a$  (Å) = 9.4027(1),  $b$  (Å) = 19.1503(3),  $c$  (Å) = 9.6947(1),  $\alpha$  (°) = 90,  $\beta$  (°) = 113.2419(7),  $\gamma$  (°) = 90, cell volume (Å<sup>3</sup>) = 1604.0,  $Z = 2$ ,  $R = 0.0167$ .

Molecular structure of **15**. The hydrogen atoms on the peripheral ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)-P(1) 2.3648(4), Pd(1)-Br(1) 2.43408(15); Br(1)-Pd(1)-P(1) 88.07(1).



Labels shown for one asymmetric unit only

A single crystal having dimensions approximately 0.24 x 0.24 x 0.42 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N<sub>2</sub> using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK<sub>α</sub> radiation,  $\lambda = 0.71073$  Å). Intensity data were processed using the DENZO-SMN package<sup>1</sup>.

Examination of the systematic absences of the intensity data showed the space group to be  $P 2_1/a$ . The structure was solved using the direct-methods program SIR92<sup>2</sup>, which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite<sup>3</sup>. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give  $R = 0.0193$ ,  $wR = 0.0167$ .

Attached is a thermal ellipsoid plot (ORTEP-3<sup>4</sup>) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

#### References:

- 1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.
- 2 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.* 1994, **27**, 435.
- 3 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, CRYSTALS issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.
- 4 ORTEP-3 v. 1.0.2, C. K. Johnson and M. K. Burnett, 1998.