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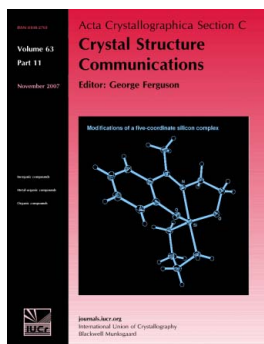
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(6-Chloropyridin-2-yl)iodobis(triphenylphosphine)palladium(II)

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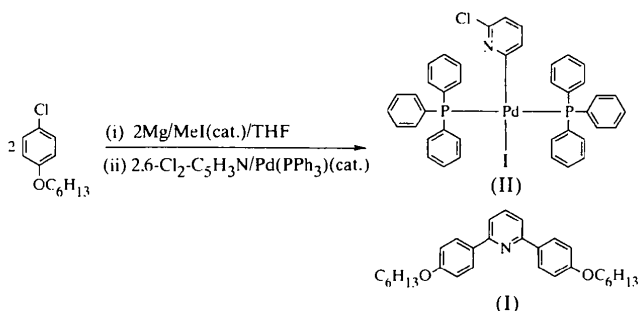
(Received 5 May 1999; accepted 8 June 1999)

Abstract

The title compound, $[\text{PdI}(\text{C}_5\text{H}_3\text{ClN})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$, a key intermediate in the palladium-catalysed coupling of two aryl rings, has been isolated and shown to have a square-planar structure with the iodo and 6-chloropyridin-2-yl ligands in *trans* positions.

Comment

In the course of our studies into the effects of metal and co-ligands on the mesogenic behaviour of cyclo-metallated palladium and platinum compounds, we have synthesized several novel ligands based upon 2,6-diphenylpyridine (Cave *et al.*, 1998). The route to these compounds involves the coupling of a Grignard reagent with a 2,6-dihalogenated pyridine using tetrakis(triphenylphosphine)palladium as a catalyst (Minato *et al.*, 1980). Thus, in the synthesis of ligand (I), the Grignard reagent derived from 4-hexyloxychlorobenzene was used together with 2,6-dichloropyridine and 2 mol% of $[\text{Pd}(\text{PPh}_3)_4]$ in tetrahydrofuran (Cave, Wong *et al.*, 1999). After a reaction time of 24 h, the intermediate palladium title complex, (II), was isolated together with the desired ligand (I). The structure of (II) was investigated in order to gain a greater understanding of the role of the palladium catalyst in the cross-coupling reactions of a Grignard reagent with a dihalopyridine compound.



The Pd^{II} atom is in a square-planar environment, with the iodo and η^1 -6-chloropyridin-2-yl ligands in *trans* positions (Fig. 1 and Table 1). The mean plane

through the four donor atoms and the Pd^{II} atom has an r.m.s. deviation of 0.074 Å; the plane of the 6-chloropyridin-2-yl ligand is inclined at an angle of 83.1 (1)° to this plane. The bond lengths and angles are largely unexceptional. The Pd—P and Pd—I distances are very close to those reported previously for the iodo[2-(methylthiomethyl)phenyl]bis(triphenylphosphine)palladium(II) complex, in which the iodine is also *trans* to a Csp³ atom (van der Voort *et al.*, 1987). In the latter compound, the Pd—P distances are 2.327 (2) and 2.339 (2) Å [*cf.* 2.3311 (19) and 2.3271 (19) Å in (II)], whilst the Pd—I distance is 2.6804 (8) Å [*cf.* 2.6806 (8) Å in (II)]. Both of these Pd—I distances are slightly longer than the value of 2.5975 (3) Å observed in $[\text{Pd}(\text{PPh}_3)_2\text{I}_2]$, where the two iodo ligands are mutually *trans* (Cave, Errington & Rourke, 1999).

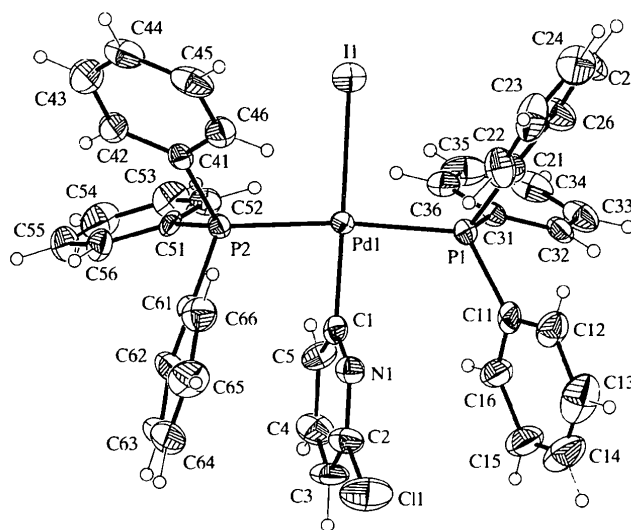


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms and H atoms are shown as spheres of arbitrary radii.

The isolation of the title complex suggests that 2,6-dichloropyridine oxidatively adds to tetrakis(triphenylphosphine)palladium(0) to form chloro(6-chloropyridin-2-yl)bis(triphenylphosphine)palladium(II), with the two triphenylphosphine ligands *cis* to each other. It follows that this reaction is reversible *via* a reductive elimination, made facile by the *cis* geometry of the molecule. However, the presence of iodide in the reaction mixture allows the displacement of the chloride ion *trans* to chloropyridine by an iodide ion. Thus, a sterically less crowded and more stable square-planar palladium(II) complex is formed. This active intermediate can then react with the Grignard reagent derived from 4-hexyloxychlorobenzene by a series of additions/eliminations to produce ligand (I) and a trace amount of *trans*-diiodobis(triphenylphosphine)palladium(II).

Experimental

4-Hexyloxychlorobenzene (10.2 g, 48.0 mmol) was added dropwise to a stirred solution of magnesium (1.22 g, 50.0 mmol) and methyl iodide (0.30 g, 2.11 mmol) in tetrahydrofuran (25 ml) under an inert atmosphere. The resulting Grignard reagent was transferred via a cannula to a stirred solution of 2,6-dichloropyridine (2.96 g, 20.0 mmol) and tetrakis(triphenylphosphine)palladium (0.45 g, 0.50 mmol) in tetrahydrofuran (25 ml). The reaction was then refluxed for 24 h under an inert atmosphere. Excess Grignard reagent was destroyed with dilute acid. The neutralized reaction mixture was extracted with diethyl ether (2 × 200 ml) and dried (saturated NaCl and magnesium sulfate). The solvent was removed under vacuum and the products were recrystallized from ethyl acetate. The expected product, 2,6-bis(4-hexyloxyphenyl)pyridine, crystallized out as white needle crystals (yield: 95%, 10.2 g, 19.0 mmol) and the (6-chloropyridin-2-yl)iodobis(triphenylphosphine)palladium(II) complex, (II), formed as yellow needles (yield: 22%, 0.096 g, 0.11 mmol). The two products were separated by crystal picking. Crystals of (II) of X-ray quality were obtained by recrystallization from hot ethyl acetate. FAB MS [in 3-nitrobenzyl alcohol (NBA)]: m/z 872 {calculated for [PdI(C₅H₃ClN)(PPh₃)₂] 872}; ¹H NMR (CDCl₃, 300.13 MHz): δ (p.p.m.) 7.20–7.38 (H1–6); ³¹P NMR (CDCl₃, 121.4 MHz): δ (p.p.m.) –6.23.

Crystal data

[PdI(C ₅ H ₃ ClN)(C ₁₈ H ₁₅ P) ₂]	Mo $K\alpha$ radiation
$M_r = 870.37$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 6496 reflections
$P2_1/n$	$\theta = 1.71\text{--}25.00^\circ$
$a = 12.1621(9) \text{ \AA}$	$\mu = 1.554 \text{ mm}^{-1}$
$b = 14.7472(9) \text{ \AA}$	$T = 180(2) \text{ K}$
$c = 20.8082(9) \text{ \AA}$	Plate
$\beta = 103.451(2)^\circ$	$0.38 \times 0.16 \times 0.04 \text{ mm}$
$V = 3629.7(4) \text{ \AA}^3$	Yellow
$Z = 4$	
$D_x = 1.593 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens SMART CCD area-detector diffractometer	4213 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.064$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 25^\circ$
$T_{\text{min}} = 0.590$, $T_{\text{max}} = 0.941$	$h = -9 \rightarrow 14$
17 496 measured reflections	$k = -17 \rightarrow 17$
6363 independent reflections	$l = -24 \rightarrow 24$
	Intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 10.4404P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.139$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.001$	$\Delta\rho_{\text{max}} = 1.257 \text{ e \AA}^{-3}$
6363 reflections	$\Delta\rho_{\text{min}} = -1.495 \text{ e \AA}^{-3}$
424 parameters	

H-atom parameters constrained

Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Pd1—C1	2.041 (7)	P1—C11	1.838 (8)
Pd1—P2	2.3271 (19)	P2—C41	1.816 (7)
Pd1—P1	2.3311 (19)	P2—C51	1.827 (7)
Pd1—I1	2.6806 (8)	P2—C61	1.839 (7)
C11—C2	1.744 (8)	C1—N1	1.332 (9)
P1—C21	1.817 (7)	N1—C2	1.332 (9)
P1—C31	1.827 (7)		
C1—Pd1—P2	85.79 (19)	C1—Pd1—I1	172.6 (2)
C1—Pd1—P1	88.4 (2)	P2—Pd1—I1	94.36 (5)
P2—Pd1—P1	174.14 (7)	P1—Pd1—I1	91.50 (5)

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). The highest residual electron-density peak was located at a distance of 0.8 \AA from the Pd atom and the deepest hole was close to the I atom.

Data collection: SMART (Siemens, 1994). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b). Molecular graphics: SHELXTL/PC (Sheldrick, 1994). Software used to prepare material for publication: SHELXTL/PC.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). We also wish to thank the EPSRC for financial support (GWVC) and Johnson–Matthey for the loan of chemicals.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1319). Services for accessing these data are described at the back of the journal.

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Commensurately modulated 1/4 and 1/5 phases of deuterated betaine calcium chloride dihydrate: a neutron structural study

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Abstract

The structures of the commensurate 1/4 and 1/5 phases of the displacively modulated compound D-BCCD [deuterated betaine (trimethylammonioacetate) calcium chloride dihydrate, *i.e.* (CD₃)₃NCD₂COOCaCl₂(D₂O)₂ or CaCl₂·C₅D₁₁NO₂·2D₂O] have been determined by single-crystal neutron diffraction at 100 and 68 K, respectively. The structural model of the 1/4 phase is found to be quite different from that obtained previously from X-ray diffraction data of the hydrogenated compound. This discrepancy comes from the fact that X-ray irradiation induces in this compound an unusual time-dependent decrease of the intensity of high-order

satellite diffraction peaks. As a consequence and due to the commensurate nature of the phases investigated, X-ray diffraction failed to detect the large anharmonicity of the structural modulation which is clearly present in the two structures determined by neutron diffraction.

Comment

The structure determination of the low-temperature commensurately modulated 1/5 phase of the title compound [with a temperature range of stability of 53.3–75.2 K at atmospheric pressure (Unruh *et al.*, 1989)] was undertaken to check if, disregarding the change of the modulation periodicity, the modulated structure of BCCD remains at lower temperature globally close to those determined by X-ray diffraction at 90 (1/4 phase; Ezpeleta *et al.*, 1992) and 130 K (first incommensurate phase; Zúñiga *et al.*, 1991). Indeed, these two latter modulated structures were found to be very similar, being particularly well described by a single-harmonic modulation, whereas the qualitative conclusions of a recent neutron diffraction study (Hernandez *et al.*, 1996) indicate that the modulation on cooling becomes clearly anharmonic below 115 K. A second motivation for this work was to verify the group theory predictions of Pérez-Mato (1988), which give, assuming an unique order parameter of Λ_3 symmetry for the whole sequence of phase transitions, all the possible space groups of the different commensurate phases of the Devil's staircase-type phase diagram of BCCD. Finally, in order to obtain a complete set of data which can be compared to X-ray results, data collection by single-crystal neutron diffraction was undertaken not only in the 1/5 phase at 68 K, but also in the 1/4 phase at 100 K.

The structural model of the 1/4 phase obtained by means of neutron diffraction is different from that refined with the X-ray data (Ezpeleta *et al.*, 1992). A systematic comparison of equivalent interatomic distances and angles determined from these two models (see Table 1 for some typical examples) indicates that the organic betaine molecule appears more distorted along the *c* modulation axis in the 'neutron' model than in the 'X-ray' one, whereas for the distorted octahedron centred on the Ca atom, this effect is weaker. For instance, one observes that in these two models, the bond lengths N2—C32 and N4—C34 differ by 0.22 (2) and 0.16 (2) Å, respectively, while the angles O14—C44—C34 and C25—N3—C13 differ by 13 (2) and 13.5 (9)°, respectively. A similar comparison made for the atoms surrounding the Ca atoms, leads to differences of 0.11 (3) and 0.10 (3) Å for the bond lengths Ca1—O31 and Ca4—O12, respectively, and to a maximum angle difference of only 4.3 (6)° for the angle O23—Ca3—Cl8. The molecular diagram (Fig. 1) shows the formula unit of the 1/5 phase constituted by five inequivalent BCCD molecules. Two different geo-

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