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Dichloro({*N*-[2-(diphenylphosphino-κP)benzyl]-benzylamino}diphenylphosphine-κP)palladium(II) toluene solvate

Marié Pretorius, D. Bradley G. Williams,* Andreas Roodt* and Alfred Muller

Department of Chemistry and Biochemistry, Rand Afrikaans University (Name changes to 'University of Johannesburg' on 1 January 2005), PO Box 524, Auckland Park, Johannesburg, 2006, South Africa

Correspondence e-mail: dbgw@rau.ac.za , aroo@rau.ac.za

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.041
wR factor = 0.088
Data-to-parameter ratio = 21.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[PdCl_2(C_{38}H_{33}NP_2)]\cdot C_7H_8$, crystallizes with an accompanying toluene solvent molecule. Important geometrical parameters are Pd—P = 2.2556 (8) and 2.2749 (8) Å, Pd—Cl = 2.3521 (9) and 2.3338 (8) Å, P—Pd—P = 96.31 (3)°, and Cl—Pd—Cl = 89.59 (3)°.

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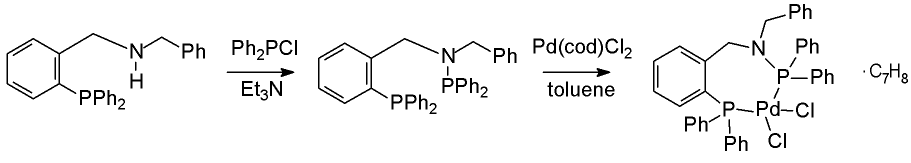
Comment

We have previously published crystal structure data regarding two homologous P—N type ligands as part of our continuing interest in the manipulation of multifunctional phosphorus–nitrogen-based ligands (Pretorius *et al.*, 2004). We are especially interested in these ligands and their transition metal complexes for their ability to catalyze certain chemical transformations.

As part of this ongoing study, we have prepared a bisphosphine ligand derivative of the P–N ligand (I), namely the P–P product (II), which has formed the crystalline title compound, (III), with Pd^{II} from toluene solution. This ligand is of special interest since the two P atoms have different σ-donor/π-acceptor characteristics, which can be important in manipulating the catalytic ability of its transition metal complexes.



(I) (II) (III)

The title compound, (III) (Fig. 1), cocrystallizes with a toluene solvent molecule. The crystal packing is stabilized by C—H···acceptor interactions (Table 2). The coordination at the metal center is square planar with slight distortion (Table 1), and the Pd atom is displaced 0.0690 (4) Å from the plane formed by atoms P1, P2, Cl1 and Cl2. As a result of the hybridization of the chelating C and N atoms, the ligand is significantly distorted from the coordination plane (Fig. 2). Although the bulky bisphosphine ligand in (I) has a larger bite angle [96.31 (3)°] than that in a similar *cis*-$[PtCl_2(PNP)]$ complex [PNP = $Ph_2PNHC_6H_4PPh_2$ and Ph = phenyl; 91.03 (5)°; Aucott *et al.*, 2001], the Cl—*M*—Cl angle remains unchanged at *ca* 90°, showing negligible steric influence of the bisphosphine on the Cl—*M*—Cl angle. It is only in examples with diphenyl bisphosphines having bite angles of less than 90° where larger Cl—*M*—Cl angles are observed, as in the case of the *cis*-$[PdCl_2(dppe)]$ complex [dppe = 1,2-bis(diphenylphosphino)ethene; Juanatey *et al.*, 1999].

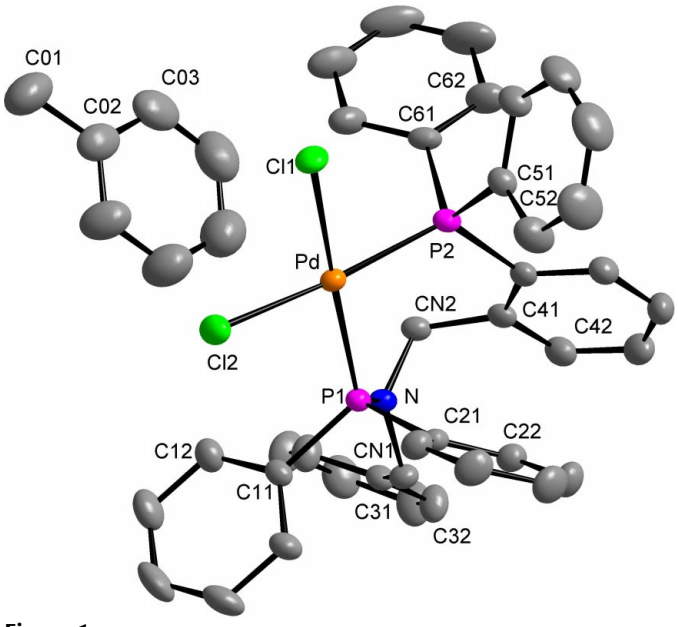


Figure 1
View of (III), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity. For the phenyl C atoms, the first digit indicates ring number, and the second digit indicates the number of the atom in the ring.

Experimental

The bisphosphine ligand (II) employed in this study was prepared from the amine precursor (I), the crystal structure of which has already been reported (Pretorius *et al.*, 2004). The synthesis involved treatment of (I) (355 mg, 0.931 mmol) with five equivalents of triethylamine and 1.2 equivalents of chlorodiphenylphosphine (247 mg, 1.11 mmol), with toluene as solvent (15 ml). The reaction mixture was stirred at room temperature for 14 h, after which it was filtered under argon, and the solvent was removed *in vacuo*. Compound (II) was isolated by flash silica chromatography (hexane/EtOAc 6:1) in a yield of 61% (320 mg). Complexation of compound (II) to Pd^{II} was achieved by mixing one equivalent of $Pd(cod)Cl_2$ (cod = cyclooctadiene) (15 mg, 0.052 mmol) with one equivalent of bisphosphine (II) (28 mg, 0.052 mmol) in toluene (5 ml), followed by slow evaporation of the solvent. Yield 38 mg, 98%. $^{31}P\{H\}$ NMR ($CDCl_3$, 121.42 MHz, p.p.m.): 78.3 [*d*, $^1J_{(P-P)}$ = 7.3 Hz], 21.9 [*d*, $^1J_{(P-P)}$ = 7.4 Hz].

Crystal data

$[PdCl_2(C_{38}H_{33}NP_2)]\cdot C_7H_8$
M_r = 835.03
Monoclinic, $P2_1/n$
a = 13.261 (3) Å
b = 21.510 (4) Å
c = 13.978 (3) Å
β = 95.30 (3)°
V = 3970.0 (14) Å^3
Z = 4
D_x = 1.397 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1002 reflections
θ = 2.9–25.8°
μ = 0.72 mm^{-1}
T = 293 (2) K
Rectangular block, yellow
0.54 × 0.18 × 0.16 mm

Data collection

Bruker SMART 1K CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.699, T_{max} = 0.894
27 177 measured reflections
9803 independent reflections
6070 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 28.3°
$h = -17 \rightarrow 17$
$k = -28 \rightarrow 18$
$l = -18 \rightarrow 15$

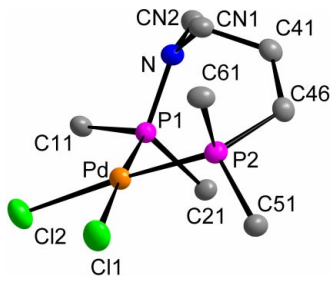


Figure 2
Detail of (III), showing the distorted chelating coordination of the bisphosphine to Pd.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.088
S = 0.98
9803 reflections
461 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—P1	2.2556 (8)	P1—N	1.671 (2)
Pd—P2	2.2749 (8)	N—CN1	1.481 (3)
Pd—Cl2	2.3338 (8)	N—CN2	1.481 (3)
Pd—Cl1	2.3521 (9)		
P1—Pd—P2	96.31 (3)	P2—Pd—Cl1	84.21 (3)
P1—Pd—Cl2	89.73 (3)	Cl2—Pd—Cl1	89.59 (3)
P2—Pd—Cl2	173.65 (3)	CN1—N—P1	119.84 (16)
P1—Pd—Cl1	174.78 (3)	CN2—N—P1	120.59 (17)
Cl2—Pd—P1—C11	11.15 (10)	Cl1—Pd—P2—C46	172.76 (11)
Cl2—Pd—P1—C21	−104.32 (9)	P2—C46—C41—CN2	−10.3 (3)
Cl2—Pd—P1—N	130.91 (9)	P1—N—CN2—C41	76.8 (3)
Cl1—Pd—P2—C51	51.98 (11)	C46—C41—CN2—N	−86.6 (3)
Cl1—Pd—P2—C61	−68.08 (10)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
CN1—HN1B···Cl1^{i}	0.97	2.81	3.709 (3)	155
C64—H64···Cl2^{ii}	0.93	2.78	3.664 (4)	159

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$.

H atoms were placed in idealized positions (C—H = 0.93–0.98 Å) and refined as riding on their parent atoms, with the constraint U_{iso}(H) = 1.2U_{eq}(C) or U_{iso}(H) = 1.2U_{eq}(methyl C) applied as appropriate.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1998); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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