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Di-μ_2-chloro-bis[(benzyldiphenylphosphine)-chloropalladium(II)]

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.025
wR factor = 0.064
Data-to-parameter ratio = 21.8

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

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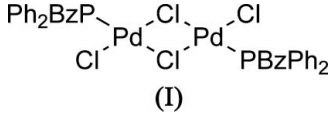
The molecule of the title compound, $[Pd_2Cl_4(C_{19}H_{17}P)_2]$ or $[Pd(\mu_2\text{-}Cl)Cl(PPh_2Bz)]_2$, where Bz = CH_2Ph, lies on an inversion centre. The Pd atom has a distorted square-planar coordination environment formed by a benzyldiphenylphosphine [Pd—P = 2.2218 (6) Å], a terminal chloride [Pd—Cl = 2.2729 (5) Å] and two bridging chloride ligands. The Pd—Cl bond in the position *trans* to the phosphine ligand [Pd—Cl = 2.4123 (5) Å] is considerably longer than the Pd—Cl bond in the position *trans* to the terminal chloride [Pd—Cl = 2.3155 (5) Å].

Comment

Palladium complexes have become the most popular organometallics used in organic synthesis as a result of their remarkable catalytic potential and their versatility. In particular, most of the carbon–carbon bond-forming reactions, such as the Heck reaction, the Stille reaction and the Suzuki reaction, are palladium-catalysed (Bedford *et al.*, 2004). The general class of $[Pd(\mu_2\text{-}Cl)ClP]_2$ (P = phosphine ligand) complexes has been known since the early studies of Mann and co-workers (Mann & Purdie, 1935; Mann & Wells, 1938). The title complex, (I), was isolated as a side-product in the synthesis of the bisphosphine–palladium complex $[PdCl_2(PBzPh_2)_2]$ (Bz = CH_2Ph).



(I)

In contrast to the numerous crystallographic characterizations of $[PdCl_2P_2]$ complexes, those of $[Pd(\mu_2\text{-}Cl)ClP]_2$ compounds are sparse. In the crystal structure of (I) (Fig. 1), the dimeric molecule of the complex, $[Pd(\mu_2\text{-}Cl)Cl(PPh_2Bz)]_2$, is located around an inversion centre. The structures of a range of related palladium complexes have been determined (Chaloner *et al.*, 1995; Coles *et al.*, 1999; Grigsby & Nicholson, 1992; Sui-Seng *et al.*, 2003*a*,*b*; Vicente *et al.*, 1997; Zoufalá *et al.*, 2004), all presenting virtually the same structural parameters (Table 3) as those of the complex reported here.

The structure of (I) consists of a centrosymmetric dinuclear complex in which each Pd atom exists in a square-planar geometry formed from a terminal chloride, a phosphine and two bridging chloride ligands. These bridging anions form almost orthogonal bonds [Cl1—Pd—Cl1′ = 85.544 (18)°] to the palladium centres. The bridging Pd—Cl bond distances are asymmetric, with the longer bonds lying opposite the more strongly *trans*-influencing phosphine ligand (Table 3). Some

weak interactions were observed, as reported in Table 2.

The most widely used method for determining ligand steric behaviour at a metal centre is the calculation of the Tolman cone angle (θ_T), as described previously by Tolman (1977) and Otto *et al.* (2000). For the current study, actual Pd—P bond distances were used, with a van der Waals radius of 1.20 Å for H, yielding effective cone angles (θ_E). The substituents of the phosphine may have different orientations, resulting in variations in cone angle sizes, as observed by Ferguson *et al.* (1978), and may not necessarily be a true indication of the steric properties of the phosphine in solution. The value of 172° obtained for benzyldiphenylphosphine is larger than the 148° cone angle obtained for triphenylphosphine (data extracted and calculated from the Cambridge Structural Database; Version 5.27, update of January 2006; Allen, 2002).

Experimental

The title compound was isolated as a side-product of the reaction of $[PdCl_2(COD)]$ with benzyldiphenylphosphine. Dichloro(1,5-cyclooctadiene)palladium(II), $[PdCl_2(COD)]$, was prepared according to the literature procedure of Drew & Doyle (1990). A solution of benzyldiphenylphosphine (55 mg, 0.2 mmol) in dichloromethane (2.0 ml) was added to a solution of $[PdCl_2(COD)]$ (29 mg, 0.1 mmol) in dichloromethane (3.0 ml). The solvent was evaporated and the remaining yellow residue was washed with pentane (2.0 ml). Crystallization from toluene gave a small amount of red crystalline compound (I), as well as nearly quantitative amounts of yellow crystalline *trans*-$[PdCl_2(PPh_2Bz)]$.

Crystal data

$[Pd_2Cl_4(C_{19}H_{17}P)_2]$
M_r = 907.19
Triclinic, $P\overline{1}$
a = 9.2060 (2) Å
b = 10.2804 (2) Å
c = 10.8020 (4) Å
α = 99.347 (2)°
β = 96.505 (2)°
γ = 113.143 (1)°
V = 909.72 (4) Å^3
Z = 1
D_x = 1.656 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6089 reflections
θ = 2.5–28.3°
μ = 1.40 mm^{-1}
T = 100 (2) K
Block, red
0.15 × 0.08 × 0.05 mm

Data collection

Bruker X8 APEXII diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.818, T_{max} = 0.933
15329 measured reflections
4530 independent reflections
3853 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 28.3°
$h = -11 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.064
S = 1.06
4530 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.2322P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

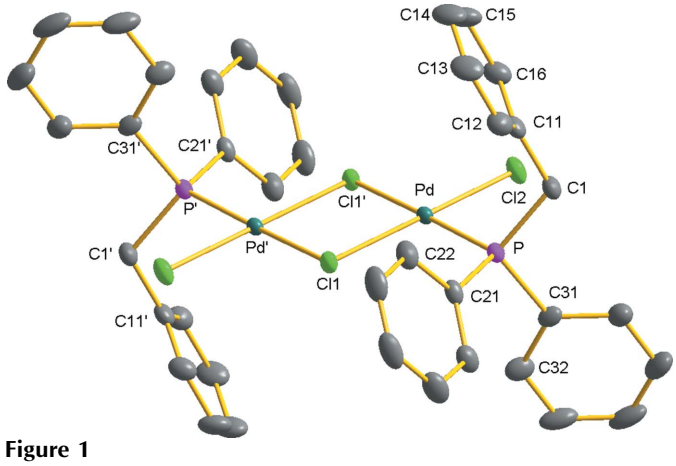


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. For the C atoms, the first digit indicates ring number and the second digit indicates the position of the atom in the ring. Primed atoms correspond to symmetry code (i) in Table 1.

Table 1
Selected geometric parameters (Å, °).

Pd—P	2.2218 (6)	Pd—Cl1	2.3155 (5)
Pd—Cl2	2.2729 (5)	Pd—Cl1^{i}	2.4123 (5)
P—Pd—Cl2	87.18 (2)	Cl2—Pd—Cl1^{i}	91.437 (19)
P—Pd—Cl1	95.735 (19)	Cl1—Pd—Cl1^{i}	85.544 (18)
Cl2—Pd—Cl1	176.50 (2)	Pd—Cl1—Pd^{i}	94.457 (18)
P—Pd—Cl1^{i}	176.47 (2)		
Cl2—Pd—P—C21	174.66 (9)	Cl1—Pd—P—C1	−129.45 (8)
Cl1—Pd—P—C21	−7.30 (9)	P—Pd—Cl1—Pd^{i}	−176.69 (2)
Cl2—Pd—P—C1	52.50 (8)		

Symmetry code: (i) $-x+2, -y+1, -z+2$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···Cl2^{ii}	0.99	2.68	3.636 (2)	163

Symmetry code: (ii) $-x+1, -y, -z+2$.

Table 3
Comparative geometrical parameters for selected $[PdCl(\mu_2\text{-}Cl)PL]_2$ (L = tertiary phosphine ligand) complexes.

L	Pd—P (Å)	Pd—Cl1 (Å)	Pd—Cl1′ (Å)	Pd—Cl2 (Å)	Notes
PBu_3	2.216 (1)	2.439 (1)	2.314 (1)	2.270 (1)	i
PCy_3	2.2495 (7)	2.4370 (7)	2.3217 (8)	2.2862 (8)	ii
PPh_3	2.2278 (6)	2.4128 (6)	2.3228 (6)	2.2722 (7)	iii
$PPh_2(CH_2\text{-}CH{=}CH_2)$	2.2222 (2)	2.429 (2)	2.321 (5)	2.275 (2)	iv
PPh_2Pr	2.2275 (6)	2.4444 (5)	2.3208 (6)	2.2684 (7)	iv
PPh_2Bz	2.2218 (6)	2.4123 (5)	2.3155 (5)	2.2729 (5)	TW
$P(2\text{-fur})_3$	2.2141 (6)	2.4230 (6)	2.3268 (5)	2.2793 (5)	v
$P(OPh)_3$	2.187 (3)	2.413 (2)	2.309 (2)	2.269 (3)	vi

Notes: Cy is cyclohexyl; 2-fur is 2-furyl; TW is this work; (i) Chaloner *et al.* (1995); (ii) Sui-Seng et al. (2003*b*); (iii) Sui-Seng et al. (2003*a*); (iv) Coles *et al.* (1999); (v) Zoufalá *et al.* (2004); (vi) Grigsby & Nicholson (1992).

The aromatic and methylene H atoms were placed in geometrically idealized positions (C—H = 0.95–0.99 Å) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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