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[1,2-Bis(diphenylphosphino)ethane-*P*,*P*′]dichloropalladium(II) tris(deuterochloroform) solvate

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In the title compound, [PdCl$_2$(C$_{26}$H$_{24}$P$_2$)]·3CDCl$_3$, the [PdCl$_2$(dppe)] molecule adopts a distorted square-planar metal coordination and an asymmetrical twist conformation of the five-membered metallocycle. The structure contains infinite channels filled with deuterochloroform of crystallization and displays an (a, b/2, c) subcell.

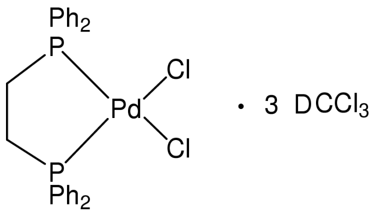
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.013 Å
Disorder in solvent or counterion
R factor = 0.063
wR factor = 0.099
Data-to-parameter ratio = 16.5

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

Comment

[PdCl$_2$(dppe)] [dppe is bis(diphenylphosphino)ethane], (I), was first studied crystallographically by Steffen & Palenik (1976) in the form of its 1:1 solvate with CH$_2$Cl$_2$, (II). Later, Singh *et al.* (1995) determined the crystal structure of pure (I). In the course of our studies of organopalladium phosphine complexes, we found that recrystallization of (I) from deuterochloroform gives a stable 1:3 solvate [PdCl$_2$(dppe)]·3CDCl$_3$, (III), the structure of which is reported herein.



(III)

The asymmetric unit of (III) comprises two [PdCl$_2$(dppe)] molecules (A and B) and six molecules of deuterochloroform (Fig. 1). The [PdCl$_2$(dppe)] molecules are related to each other by an approximate translation of b/2. Atoms related by this pseudo-translation are given the same numbers with letters A or B added. The Pd atoms deviate from the ideal b/2 translation by 0.54 Å, P by 0.50 and 0.56 Å, Cl by 0.62 and 0.70 Å, and C atoms by 0.09–1.10 Å with the average 0.55 Å (Fig. 2). These deviations are relatively small, compared to the length of the translation (b/2 = 9.2 Å). The [PdCl$_2$(dppe)] molecule A has three molecules of deuterochloroform attached to it through C—D···Cl—Pd hydrogen bonds. Two of these molecules, A1 and A3 (see Fig. 1), are hydrogen-bonded to the chloride ligand Cl2A, while molecule A2 forms a bifurcated hydrogen bond with both Cl1A and Cl2A. The positions of deuterochloroform molecules B1, B2 and B3 are roughly related respectively to those of A1, A2 and A3. Molecule B2 also forms a bifurcated hydrogen bond, with Cl1B and Cl2B. Molecule B1 is hydrogen-bonded to Cl2B but, unlike A1, molecule B1 is disordered (see below). In molecule B3, the C5B, Cl9B and Cl0B atoms are related by pseudo-translation to the C5A, Cl9A and Cl0A of molecule A3, but

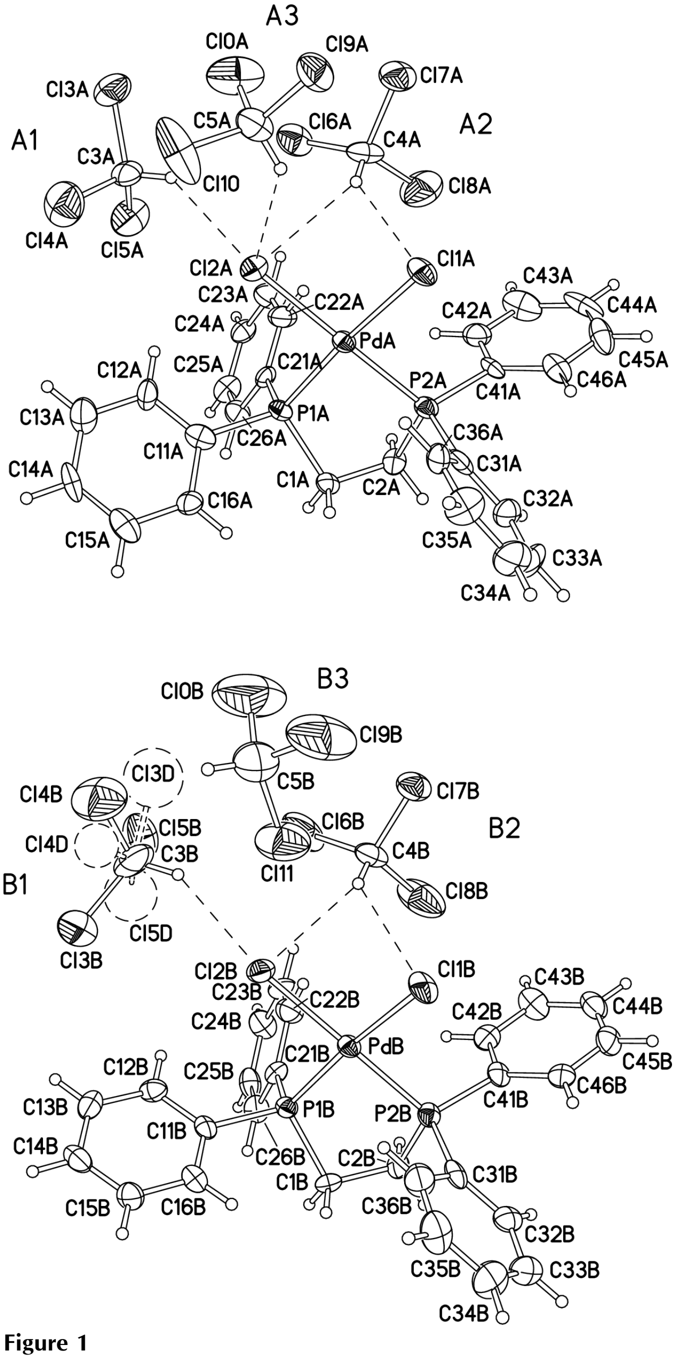


Figure 1

Two independent formula units of $[PdCl_2(dppe)]\cdot 3CDCl_3$ (III), showing hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level. Note different orientations of deuterochloroform molecules *A*3 and *B*3.

Cl11 is not related to Cl10. Thus *B*3 can be described as a pseudo-equivalent of *A*3 with the deuterium and Cl11 atoms exchanged. Consequently, the deuterium atom of *B*3 does not point towards the $[PdCl_2(dppe)]$ molecule *B*, but instead forms a weak hydrogen bond with the Cl7*A* atom of the *A*2 molecule, related to the original one by the crystallographic translation *b*.

Thus structure (III) has an (*a*, *b*/2, *c*) subcell, which is manifested in the diffraction pattern: reflections with even *k* indices have intensities on average twice as high as those with odd *k*. The crystal packing can be described as a clathrate (host–guest complex), in which deuterochloroform molecules occupy infinite channels (parallel to the *b* axis) in the packing of $[PdCl_2(dppe)]$ molecules (Fig. 3).

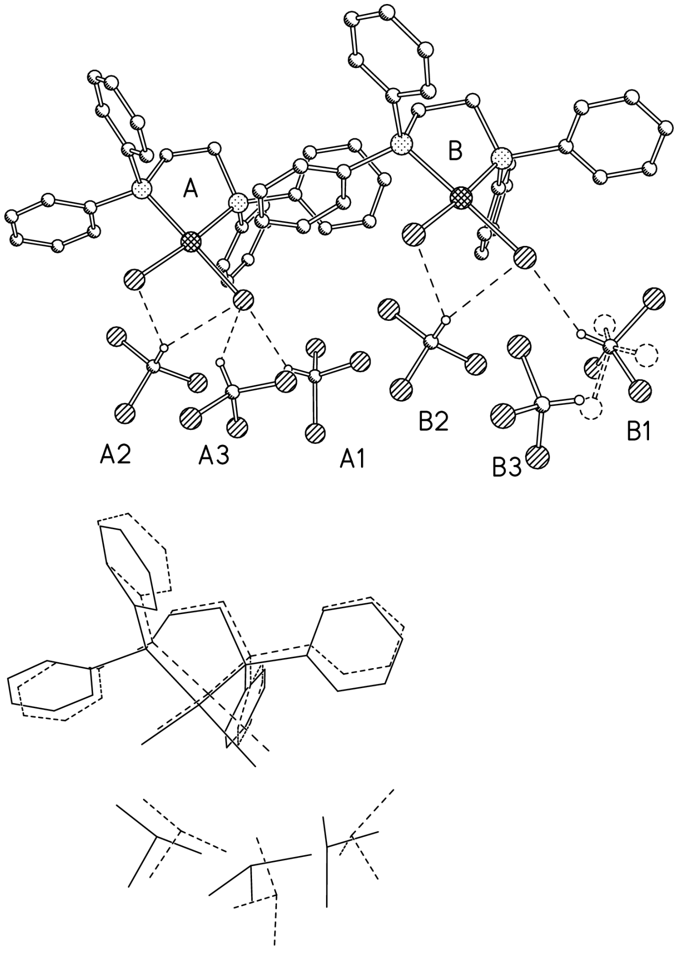


Figure 2

Top: asymmetric unit in the crystal of (III) (H atoms omitted); bottom: its convolution by the *b*/2 pseudo-translation (molecules *A* in solid, *B* in dashed lines; minor components of disordered Cl atoms as well as H and D atoms have been omitted).

The molecular structure of $[PdCl_2(dppe)]$ in (III) is similar to those found in structures (I) and (II). The palladium atom has a slightly distorted square-planar coordination. In molecule *A*, the Pd*A*, P1*A*, P2*A* and Cl1*A* atoms are coplanar, while Cl2*A* deviates from their mean plane by 0.160 (4) Å. Probably because of this asymmetric distortion, the Pd—P bond lengths differ by 0.018 Å, or 9 s.u.'s. In molecule *B*, the distortion is of tetrahedral mode: the the $PdCl_2$ plane is twisted by 6.4 (1)° with respect to the PdP_2 plane, and the Pd—P distances are identical. In any case, the distortion is probably due to steric strain in the chelating ligand (Steffen & Palenik, 1976). In both $[PdCl_2(dppe)]$ molecules of (III) the five-membered metallocycle adopts an asymmetric twist conformation: the C1 and C2 atoms are displaced from the PdP_2 plane in opposite directions, by 0.48 (1) and −0.29 (1) Å in molecule *A*, 0.50 (1) and −0.28 (1) Å in molecule *B*.

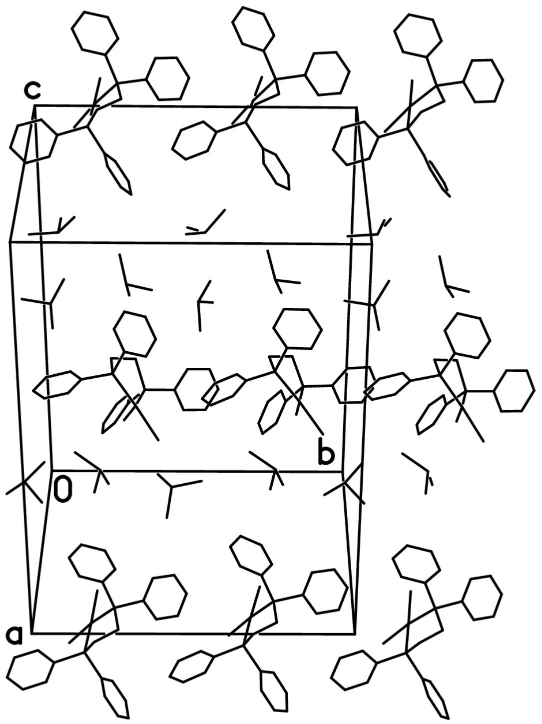


Figure 3
The crystal packing of (III) projected onto the (101) plane.

The average Pd—P and Pd—Cl bond distances of 2.242 (7) and 2.364 (3) Å in (III) are essentially the same as in (II), *viz*. 2.230 (4) and 2.359 (2) Å (Steffen & Palenik, 1976).

Experimental

[$Pd_2(dba)_3$]·$CHCl_3$ (0.10 g, 0.11 mmol), where dba is dibenzylideneacetone, and dppe (0.08 g, 0.20 mmol) were dissolved in toluene (50 mol) under nitrogen and stirred for 2 h. $ClCO_2Me$ (0.02 g, 0.23 mmol) was added and the solution (which turned yellow) was stirred briefly. The solvent was removed *in vacuo*, the residue was identified as (I) and re-crystallized from deuterochloroform by slow evaporation at room temperature.

Crystal data

[$PdCl_2(C_{26}H_{24}P_2)$]·3CCl_3D
M_r = 936.81
Orthorhombic, $P2_12_12_1$
a = 16.292 (1) Å
b = 18.404 (1) Å
c = 25.317 (2) Å
V = 7591 (1) Å^3
Z = 8
D_x = 1.634 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 447 reflections
θ = 12–23°
μ = 1.37 mm^{-1}
T = 150 (2) K
Plate, yellow
0.34 × 0.25 × 0.08 mm

Data collection

SMART 1 K CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*XPREP SHELXTL*; Siemens, 1995)
T_{min} = 0.701, T_{max} = 0.920
41 687 measured reflections

12 994 independent reflections
9802 reflections with $I > 2\sigma(I)$
R_{int} = 0.083
θ_{max} = 25.0°
$h = -18 \rightarrow 19$
$k = -21 \rightarrow 21$
$l = -30 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.099
S = 1.78
12994 reflections
787 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + 5.0304P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 1.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.02 (3)

Table 1
Selected geometric parameters (Å, °).

Pd*A*—P1*A*	2.254 (2)	Pd*B*—P1*B*	2.238 (2)
Pd*A*—P2*A*	2.236 (2)	Pd*B*—P2*B*	2.238 (2)
Pd*A*—Cl1*A*	2.363 (2)	Pd*B*—Cl1*B*	2.365 (2)
Pd*A*—Cl2*A*	2.361 (2)	Pd*B*—Cl2*B*	2.367 (2)
P1*A*—C1*A*	1.840 (7)	P1*B*—C1*B*	1.841 (7)
P1*A*—C11*A*	1.815 (8)	P1*B*—C11*B*	1.820 (8)
P1*A*—C21*A*	1.818 (8)	P1*B*—C21*B*	1.810 (8)
P2*A*—C2*A*	1.816 (7)	P2*B*—C2*B*	1.846 (7)
P2*A*—C31*A*	1.811 (9)	P2*B*—C31*B*	1.818 (9)
P2*A*—C41*A*	1.818 (7)	P2*B*—C41*B*	1.813 (7)
P2*A*—Pd*A*—P1*A*	85.63 (8)	P2*B*—Pd*B*—P1*B*	85.77 (8)
P2*A*—Pd*A*—Cl2*A*	176.27 (8)	P2*B*—Pd*B*—Cl1*B*	90.47 (8)
P1*A*—Pd*A*—Cl2*A*	92.98 (8)	P1*B*—Pd*B*—Cl1*B*	174.30 (8)
P2*A*—Pd*A*—Cl1*A*	89.68 (8)	P2*B*—Pd*B*—Cl2*B*	173.73 (8)
P1*A*—Pd*A*—Cl1*A*	175.26 (8)	P1*B*—Pd*B*—Cl2*B*	90.45 (8)
Cl2*A*—Pd*A*—Cl1*A*	91.74 (8)	Cl1*B*—Pd*B*—Cl2*B*	93.66 (8)
C21*A*—P1*A*—C11*A*	104.4 (4)	C21*B*—P1*B*—C11*B*	106.0 (4)
C21*A*—P1*A*—C1*A*	106.6 (4)	C21*B*—P1*B*—C1*B*	105.7 (4)
C11*A*—P1*A*—C1*A*	106.6 (4)	C11*B*—P1*B*—C1*B*	107.2 (4)
C21*A*—P1*A*—Pd*A*	110.6 (3)	C21*B*—P1*B*—Pd*B*	113.0 (3)
C11*A*—P1*A*—Pd*A*	121.0 (3)	C11*B*—P1*B*—Pd*B*	116.6 (3)
C1*A*—P1*A*—Pd*A*	106.8 (2)	C1*B*—P1*B*—Pd*B*	107.7 (3)
C31*A*—P2*A*—C2*A*	104.6 (4)	C41*B*—P2*B*—C31*B*	109.1 (4)
C31*A*—P2*A*—C41*A*	108.1 (4)	C41*B*—P2*B*—C2*B*	106.6 (3)
C2*A*—P2*A*—C41*A*	104.7 (3)	C31*B*—P2*B*—C2*B*	103.6 (4)
C31*A*—P2*A*—Pd*A*	113.7 (3)	C41*B*—P2*B*—Pd*B*	113.7 (3)
C2*A*—P2*A*—Pd*A*	108.4 (3)	C31B—P2*B*—Pd*B*	114.3 (3)
C41*A*—P2*A*—Pd*A*	116.4 (3)	C2*B*—P2*B*—Pd*B*	108.7 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3*A*—D3*A*···Cl2*A*	1.00	2.62	3.452 (9)	141
C4A—D4*A*···Cl1*A*	1.00	2.81	3.649 (10)	141
C4*A*—D4*A*···Cl2A	1.00	2.88	3.717 (9)	142
C5A—D5A···Cl2*A*	1.00	2.76	3.534 (10)	135
C3*B*—D3*B*···Cl2*B*	1.00	2.61	3.501 (10)	148
C4*B*—D4*B*···Cl1*B*	1.00	2.96	3.759 (9)	137
C4*B*—D4*B*···Cl2*B*	1.00	2.70	3.513 (9)	138
C5*B*—D5*B*···Cl7*A*^{i}	1.00	2.98	3.967 (13)	170

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

All H atoms were treated as riding, with Csp^2—H and Csp^3—H bond distances of 0.95 and 1.00 Å, U_{iso} equal to 1.3U_{eq} of the carrying C atom for the methylene H atoms and 1.2U_{eq} for the deuterium atoms and phenyl H atoms. Molecule *B*1 shows rotational disorder around the threefold molecular axis. The disorder was approximated by two sets of chlorine positions: Cl3*B*, Cl4*B*, Cl5*B* with occupancies 0.85 and Cl3*D*, Cl4*D*, Cl5*D* with occupancies 0.15, but the high residual electron density (up to 1.36 e Å^{-3}) may indicate a continuous rotational disorder. All C—Cl bonds in both orientations of molecule *B*1 were restrained to similar lengths. Anomalous distribution of reflection intensities, due to the sublattice and the disorder

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of relatively heavy (Cl) atoms, results in high *S* and/or weighting scheme parameters. The actual weighting scheme was optimized for the data set, excluding non-positive F^2.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART* (Siemens, 1995); data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL* (Siemens, 1995); software used to prepare material for publication: *SHELXTL*.

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