

trans-Dibromidobis[tris(4-chlorophenyl)-phosphine]palladium(II)

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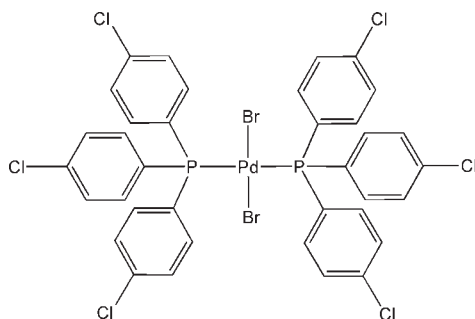
Received 21 October 2009; accepted 29 October 2009

 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.060; data-to-parameter ratio = 21.0.

In the title compound, $[\text{PdBr}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_2]$, the Pd^{II} ion is situated on a centre of symmetry and is coordinated by two Br anions [$\text{Pd}-\text{Br} = 2.4252$ (2) Å] and two P-donor ligands [$\text{Pd}-\text{P} = 2.3317$ (6) Å] in a slightly distorted square-planar geometry [$\text{P}-\text{Pd}-\text{Br} = 86.589$ (15)°].

Related literature

The title compound is isostructural with the corresponding dichlorido complex, *trans*- $[\text{PdCl}_2\{\text{P}(p\text{-ClPh})_3\}_2]$, see: Kolosova *et al.* (1986).



Experimental

Crystal data

 $[\text{PdBr}_2(\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P})_2]$
 $M_r = 997.41$

 Monoclinic, $P2_1/n$
 $a = 10.3453$ (3) Å

 $b = 17.4489$ (6) Å

 $c = 10.6180$ (4) Å

 $\beta = 103.385$ (2)°

 $V = 1864.63$ (11) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 3.18$ mm⁻¹
 $T = 100$ K

 $0.33 \times 0.30 \times 0.25$ mm

Data collection

Bruker X8 APEXII 4K Kappa CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 1998)

 $T_{\text{min}} = 0.378$, $T_{\text{max}} = 0.453$

20106 measured reflections

4487 independent reflections

 3916 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.060$
 $S = 1.04$

4487 reflections

214 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.67$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.74$ e Å⁻³

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: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg & Putz, 2006); software used to prepare material for publication: SHELXL97.

Financial assistance from the University of the Free State and Professor A. Roodt is gratefully acknowledged. Part of this material is based on work supported by the South African National Research Foundation (NRF) under grant No. GUN 2068915.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2637).

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supplementary materials

Acta Cryst. (2009). E65, m1565 [doi:10.1107/S1600536809045413]

***trans*-Dibromidobis[tris(4-chlorophenyl)phosphine]palladium(II)**

L. Kirsten and G. Steyl

Comment

The title compound, (I), is one of a few literature structures containing a Pd centre coordinated by two Br atoms and two P donor ligands in a *trans* configuration. Our research is aimed at expanding the number of known structures of the aforementioned type and to finally generalize on the crystallization mode, if any, of these complexes.

The molecule of (I) (Fig. 1), is centrosymmetric with pairs of equivalent P donor ligands *trans* to one another in a slightly distorted square-planar geometry [P—Pd—Br 86.589 (15)°].

The corresponding chloro complex (Kolossova *et al.*, 1986) is iso-structural to (I) when comparing the geometrical parameters. The RMS error of 0.097 Å also indicates the iso-structurality of the two complexes (the title complex superimposed with the corresponding dichloro-palladium complex (Kolossova *et al.*, 1986) including all the atoms except the hydrogen atoms).

Experimental

The title complex was synthesized by the addition of 2.2 equivalents of tris(4-Cl-phenyl)-phosphine (21 mg, 0.059 mmol) to [Pd(COD)Br₂] (10 mg, 0.026 mmol) in 10 ml of dichloromethane while stirring for 5 minutes. Slow evaporation of the solvent resulted in orange crystals suitable for X-Ray diffraction (yield 74%, 19 mg).

Refinement

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

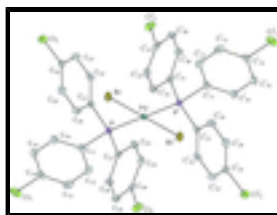


Fig. 1. Representation of the title compound, showing the numbering scheme and displacement ellipsoids (50% probability). For the carbon rings, the first digit refers to ring number, second digit to atom in the ring. Hydrogen atoms omitted for clarity [symmetry code: (i) 1 - x, 1 - y, 1 - z].

***trans*-Dibromidobis[tris(4-chlorophenyl)phosphine]palladium(II)**

Crystal data

[PdBr₂(C₁₈H₁₂Cl₃P₁)₂]

$F_{000} = 976$

supplementary materials

$M_r = 997.41$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 10.3453$ (3) Å

$b = 17.4489$ (6) Å

$c = 10.6180$ (4) Å

$\beta = 103.385$ (2)°

$V = 1864.63$ (11) Å³

$Z = 2$

$D_x = 1.776$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7624 reflections

$\theta = 2.3$ – 28.4 °

$\mu = 3.18$ mm⁻¹

$T = 100$ K

Cuboid, orange

$0.33 \times 0.30 \times 0.25$ mm

Data collection

Bruker X8 APEXII 4K Kappa CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 512 pixels mm⁻¹

$T = 100$ K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 1998)

$T_{\min} = 0.378$, $T_{\max} = 0.453$

20106 measured reflections

4487 independent reflections

3916 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\text{max}} = 28.0$ °

$\theta_{\text{min}} = 2.3$ °

$h = -13 \rightarrow 13$

$k = -20 \rightarrow 23$

$l = -10 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.060$

$S = 1.04$

4487 reflections

214 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: riding model

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 1.3608P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.67$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.74$ e Å⁻³

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -

factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd	0.5000	0.5000	0.5000	0.01113 (6)
Br	0.66195 (2)	0.551557 (14)	0.68290 (2)	0.01764 (7)
P	0.54624 (5)	0.60598 (3)	0.38405 (5)	0.01106 (12)
C11	0.7244 (2)	0.61782 (12)	0.4023 (2)	0.0121 (4)
C12	0.7977 (2)	0.55569 (14)	0.3742 (2)	0.0181 (5)
H12	0.7539	0.5087	0.3466	0.022*
C13	0.9335 (2)	0.56171 (14)	0.3862 (2)	0.0202 (5)
H13	0.9827	0.5200	0.3637	0.024*
C14	0.9961 (2)	0.62964 (14)	0.4314 (2)	0.0167 (5)
C15	0.9267 (2)	0.69103 (14)	0.4626 (2)	0.0180 (5)
H15	0.9716	0.7371	0.4943	0.022*
C16	0.7899 (2)	0.68506 (13)	0.4474 (2)	0.0166 (5)
H16	0.7410	0.7274	0.4682	0.020*
Cl1	1.16679 (6)	0.63849 (4)	0.44886 (6)	0.02709 (15)
C21	0.4895 (2)	0.69919 (13)	0.4282 (2)	0.0127 (4)
C22	0.4671 (2)	0.71256 (14)	0.5508 (2)	0.0165 (5)
H22	0.4778	0.6720	0.6121	0.020*
C23	0.4291 (2)	0.78460 (14)	0.5841 (2)	0.0193 (5)
H23	0.4141	0.7936	0.6678	0.023*
C24	0.4134 (2)	0.84297 (13)	0.4944 (2)	0.0158 (5)
C25	0.4340 (2)	0.83135 (14)	0.3719 (2)	0.0169 (5)
H25	0.4222	0.8721	0.3109	0.020*
C26	0.4722 (2)	0.75940 (13)	0.3396 (2)	0.0160 (5)
H26	0.4869	0.7509	0.2557	0.019*
Cl2	0.36890 (6)	0.93429 (3)	0.53545 (6)	0.02335 (14)
C31	0.4774 (2)	0.60521 (12)	0.2097 (2)	0.0123 (4)
C32	0.3402 (2)	0.61279 (13)	0.1658 (2)	0.0151 (5)
H32	0.2860	0.6153	0.2267	0.018*
C33	0.2820 (2)	0.61675 (13)	0.0353 (2)	0.0154 (5)
H33	0.1885	0.6221	0.0059	0.018*
C34	0.3626 (2)	0.61276 (12)	-0.0525 (2)	0.0150 (5)
C35	0.4977 (2)	0.60225 (13)	-0.0127 (2)	0.0170 (5)
H35	0.5508	0.5975	-0.0743	0.020*
C36	0.5555 (2)	0.59876 (13)	0.1195 (2)	0.0151 (5)
H36	0.6488	0.5919	0.1483	0.018*
Cl3	0.28975 (6)	0.62480 (3)	-0.21644 (5)	0.02222 (13)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd	0.01157 (11)	0.01282 (13)	0.00824 (12)	-0.00270 (9)	0.00075 (8)	0.00108 (9)
Br	0.01929 (12)	0.01956 (13)	0.01117 (12)	-0.00653 (9)	-0.00241 (9)	0.00144 (9)

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P	0.0110 (3)	0.0124 (3)	0.0096 (3)	-0.0017 (2)	0.0020 (2)	0.0013 (2)
C11	0.0124 (10)	0.0127 (11)	0.0109 (10)	-0.0004 (8)	0.0019 (8)	0.0035 (8)
C12	0.0186 (11)	0.0145 (12)	0.0192 (12)	0.0000 (9)	0.0002 (9)	-0.0033 (9)
C13	0.0218 (12)	0.0213 (13)	0.0168 (12)	0.0098 (10)	0.0033 (10)	-0.0025 (10)
C14	0.0118 (10)	0.0272 (13)	0.0112 (11)	0.0012 (10)	0.0027 (8)	0.0019 (9)
C15	0.0157 (11)	0.0157 (12)	0.0229 (13)	-0.0039 (9)	0.0051 (9)	-0.0008 (9)
C16	0.0153 (11)	0.0121 (11)	0.0237 (13)	0.0013 (9)	0.0069 (9)	0.0000 (9)
C11	0.0114 (3)	0.0469 (4)	0.0236 (3)	0.0021 (3)	0.0054 (2)	0.0013 (3)
C21	0.0094 (10)	0.0157 (12)	0.0126 (11)	-0.0022 (8)	0.0020 (8)	-0.0005 (9)
C22	0.0165 (11)	0.0195 (12)	0.0149 (11)	-0.0026 (9)	0.0062 (9)	0.0029 (9)
C23	0.0200 (12)	0.0221 (13)	0.0184 (12)	-0.0005 (10)	0.0099 (10)	-0.0033 (10)
C24	0.0105 (10)	0.0146 (12)	0.0235 (12)	-0.0017 (9)	0.0065 (9)	-0.0043 (9)
C25	0.0155 (11)	0.0181 (12)	0.0168 (11)	0.0004 (9)	0.0030 (9)	0.0033 (9)
C26	0.0176 (11)	0.0189 (12)	0.0124 (11)	0.0009 (9)	0.0054 (9)	0.0009 (9)
C12	0.0251 (3)	0.0184 (3)	0.0303 (3)	0.0016 (2)	0.0141 (3)	-0.0046 (2)
C31	0.0165 (11)	0.0090 (11)	0.0110 (10)	-0.0012 (8)	0.0022 (8)	0.0011 (8)
C32	0.0166 (11)	0.0169 (12)	0.0125 (11)	-0.0008 (9)	0.0050 (9)	0.0017 (9)
C33	0.0152 (11)	0.0128 (12)	0.0164 (11)	-0.0010 (9)	0.0002 (9)	0.0021 (9)
C34	0.0247 (12)	0.0098 (11)	0.0082 (10)	-0.0006 (9)	-0.0006 (9)	-0.0015 (8)
C35	0.0237 (12)	0.0161 (12)	0.0131 (11)	0.0016 (9)	0.0079 (9)	-0.0009 (9)
C36	0.0156 (11)	0.0151 (12)	0.0158 (11)	0.0016 (9)	0.0058 (9)	0.0005 (9)
C13	0.0325 (3)	0.0227 (3)	0.0093 (3)	0.0015 (3)	0.0003 (2)	-0.0014 (2)

Geometric parameters (Å, °)

Pd—P ⁱ	2.3317 (6)	C22—C23	1.387 (3)
Pd—P	2.3317 (6)	C22—H22	0.9500
Pd—Br	2.4252 (2)	C23—C24	1.378 (3)
Pd—Br ⁱ	2.4252 (2)	C23—H23	0.9500
P—C11	1.820 (2)	C24—C25	1.381 (3)
P—C31	1.823 (2)	C24—C12	1.742 (2)
P—C21	1.827 (2)	C25—C26	1.383 (3)
C11—C16	1.384 (3)	C25—H25	0.9500
C11—C12	1.394 (3)	C26—H26	0.9500
C12—C13	1.386 (3)	C31—C36	1.393 (3)
C12—H12	0.9500	C31—C32	1.394 (3)
C13—C14	1.382 (3)	C32—C33	1.379 (3)
C13—H13	0.9500	C32—H32	0.9500
C14—C15	1.372 (3)	C33—C34	1.389 (3)
C14—C11	1.739 (2)	C33—H33	0.9500
C15—C16	1.391 (3)	C34—C35	1.376 (3)
C15—H15	0.9500	C34—C13	1.742 (2)
C16—H16	0.9500	C35—C36	1.394 (3)
C21—C26	1.394 (3)	C35—H35	0.9500
C21—C22	1.395 (3)	C36—H36	0.9500
P ⁱ —Pd—P	180.000 (17)	C23—C22—C21	120.5 (2)
P ⁱ —Pd—Br	93.411 (15)	C23—C22—H22	119.7
P—Pd—Br	86.589 (15)	C21—C22—H22	119.7

P ⁱ —Pd—Br ⁱ	86.589 (15)	C24—C23—C22	119.3 (2)
P—Pd—Br ⁱ	93.411 (15)	C24—C23—H23	120.4
Br—Pd—Br ⁱ	180.000 (10)	C22—C23—H23	120.4
C11—P—C31	104.88 (10)	C23—C24—C25	121.6 (2)
C11—P—C21	104.43 (10)	C23—C24—Cl2	119.94 (17)
C31—P—C21	101.18 (10)	C25—C24—Cl2	118.50 (18)
C11—P—Pd	111.12 (7)	C24—C25—C26	118.8 (2)
C31—P—Pd	116.79 (7)	C24—C25—H25	120.6
C21—P—Pd	116.95 (7)	C26—C25—H25	120.6
C16—C11—C12	119.1 (2)	C25—C26—C21	121.1 (2)
C16—C11—P	122.37 (17)	C25—C26—H26	119.5
C12—C11—P	118.44 (17)	C21—C26—H26	119.5
C13—C12—C11	120.8 (2)	C36—C31—C32	119.1 (2)
C13—C12—H12	119.6	C36—C31—P	123.10 (17)
C11—C12—H12	119.6	C32—C31—P	117.81 (16)
C14—C13—C12	118.7 (2)	C33—C32—C31	121.0 (2)
C14—C13—H13	120.6	C33—C32—H32	119.5
C12—C13—H13	120.6	C31—C32—H32	119.5
C15—C14—C13	121.6 (2)	C32—C33—C34	118.8 (2)
C15—C14—Cl1	118.69 (18)	C32—C33—H33	120.6
C13—C14—Cl1	119.69 (18)	C34—C33—H33	120.6
C14—C15—C16	119.3 (2)	C35—C34—C33	121.7 (2)
C14—C15—H15	120.4	C35—C34—Cl3	119.80 (17)
C16—C15—H15	120.4	C33—C34—Cl3	118.46 (18)
C11—C16—C15	120.5 (2)	C34—C35—C36	118.9 (2)
C11—C16—H16	119.8	C34—C35—H35	120.5
C15—C16—H16	119.8	C36—C35—H35	120.5
C26—C21—C22	118.8 (2)	C31—C36—C35	120.4 (2)
C26—C21—P	119.79 (16)	C31—C36—H36	119.8
C22—C21—P	121.43 (17)	C35—C36—H36	119.8
Br—Pd—P—C11	49.81 (8)	Pd—P—C21—C22	23.8 (2)
Br ⁱ —Pd—P—C11	-130.19 (8)	C26—C21—C22—C23	-0.4 (3)
Br—Pd—P—C31	170.03 (8)	P—C21—C22—C23	177.41 (17)
Br ⁱ —Pd—P—C31	-9.97 (8)	C21—C22—C23—C24	0.2 (3)
Br—Pd—P—C21	-69.94 (8)	C22—C23—C24—C25	0.3 (3)
Br ⁱ —Pd—P—C21	110.06 (8)	C22—C23—C24—Cl2	-178.76 (17)
C31—P—C11—C16	109.0 (2)	C23—C24—C25—C26	-0.4 (3)
C21—P—C11—C16	3.0 (2)	Cl2—C24—C25—C26	178.59 (17)
Pd—P—C11—C16	-123.98 (18)	C24—C25—C26—C21	0.2 (3)
C31—P—C11—C12	-73.49 (19)	C22—C21—C26—C25	0.2 (3)
C21—P—C11—C12	-179.49 (17)	P—C21—C26—C25	-177.63 (17)
Pd—P—C11—C12	53.56 (19)	C11—P—C31—C36	11.9 (2)
C16—C11—C12—C13	-2.6 (3)	C21—P—C31—C36	120.28 (19)
P—C11—C12—C13	179.82 (18)	Pd—P—C31—C36	-111.59 (18)
C11—C12—C13—C14	2.5 (4)	C11—P—C31—C32	-166.98 (17)
C12—C13—C14—C15	-0.9 (4)	C21—P—C31—C32	-58.60 (19)
C12—C13—C14—Cl1	179.37 (18)	Pd—P—C31—C32	69.53 (18)

supplementary materials

C13—C14—C15—C16	-0.6 (4)	C36—C31—C32—C33	-2.4 (3)
C11—C14—C15—C16	179.15 (18)	P—C31—C32—C33	176.56 (18)
C12—C11—C16—C15	1.0 (3)	C31—C32—C33—C34	0.2 (3)
P—C11—C16—C15	178.56 (17)	C32—C33—C34—C35	2.4 (3)
C14—C15—C16—C11	0.5 (3)	C32—C33—C34—C13	-175.38 (17)
C11—P—C21—C26	78.41 (19)	C33—C34—C35—C36	-2.7 (3)
C31—P—C21—C26	-30.3 (2)	C13—C34—C35—C36	175.00 (18)
Pd—P—C21—C26	-158.34 (15)	C32—C31—C36—C35	2.0 (3)
C11—P—C21—C22	-99.40 (19)	P—C31—C36—C35	-176.87 (17)
C31—P—C21—C22	151.87 (18)	C34—C35—C36—C31	0.5 (3)

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

Fig. 1

