

trans-Dichlorobis(tri-*m*-tolylphosphine)palladium(II)

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Key indicators

Single-crystal X-ray study
 T = 100 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 R factor = 0.027
 wR factor = 0.069
 Data-to-parameter ratio = 21.5

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

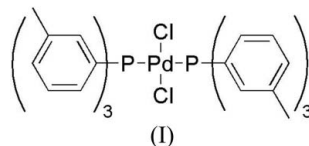
In the title compound, *trans*-[PdCl₂{P(C₇H₇)₃}₂], where P(C₇H₇)₃ is tri-*m*-tolylphosphine, the Pd atom is on an inversion centre, resulting in a *trans*-square-planar geometry. Selected geometric parameters are Pd–P and Pd–Cl distances of 2.3289 (4) and 2.2897 (4) Å, respectively, and a P–Pd–Cl angle of 87.77 (2)°. The effective cone angle for the tri-*m*-tolylphosphine is calculated to be 165°.

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Comment

Transition metal complexes containing phosphine, arsine and stibine ligands are being widely investigated in various fields of organometallic chemistry (Spessard & Miessler, 1996). As part of a systematic investigation involving complexes with the general formula *trans*-[MX₂(L)₂] (*M* is Pt or Pd, *X* is halogen, Me or Ph, and *L* is a group 15 donor ligand), crystals of the title compound, (I), were obtained.



[PdCl₂(L)₂] (*L* is tertiary phosphine, arsine or stibine) complexes can conveniently be prepared by the substitution of 1,5-cyclooctadiene (COD) from [PdCl₂(COD)]. The title compound, *trans*-[PdCl₂{P(C₇H₇)₃}₂], (I), crystallizes in the triclinic space group $P\bar{1}$ ($Z = 1$), with the Pd atom on an inversion centre and each pair of equivalent ligands in a mutually *trans* orientation. The geometry is, therefore, slightly distorted square planar and the Pd atom is not displaced from the coordination plane. All angles in the coordination of Pd are close to the ideal value of 90° (Table 1). Some weak interactions are observed and these are reported in Table 2.

The most widely used method for determining ligand steric behaviour at a metal centre is by calculating the cone angle, as described by Tolman (1977). For the current study, the actual *M*–P distances were used, resulting in effective cone angles, Θ_E (Otto *et al.*, 2000). The substituents of the phosphine may have different orientations, resulting in variations in cone angle sizes. For example, the cone angles for PPh₃ were reported to have a mean value of 148°, with a standard deviation of 5° and a spread from 129 to 168° (Bunten *et al.*, 2002). Data of this sort attest to the ability of phosphine ligands to adjust to their individual environment, specifically in the solid state. The value of 165° obtained from effective cone-angle calculations for (I) illustrates this point, when compared with the previously reported values of 155 and 160° for *trans*-[Rh(CO)Cl{P(C₇H₇)₃}₂] (Meijboom *et al.*, 2005).

In Table 3, the title compound is compared with other closely related Pd^{II} complexes from the literature containing two chloro and two tertiary phosphine ligands in a *trans* geometry. Compound (I), having a Pd–Cl bond length of 2.2897 (4) Å and a Pd–P bond length of 2.3289 (4) Å, fits well into the typical range for complexes of this kind.

Experimental

Dichloro(1,5-cyclooctadiene)palladium(II), [PdCl₂(COD)], was prepared according to the literature procedure of Drew & Doyle (1990). A solution of tri-*m*-tolylphosphine (28.6 mg, 0.2 mmol) in dichloromethane (2.0 ml) was added to a solution of [PdCl₂(COD)] (60.3 mg, 0.1 mmol) in dichloromethane (3.0 ml). Slow evaporation of the solvent gave yellow crystals of *trans*-[PdCl₂[P(C₇H₇)₃]₂], (I), suitable for X-ray analysis, in quantitative yield.

Crystal data

[PdCl ₂ (C ₂₁ H ₂₁ P) ₂]	$V = 938.17 (7) \text{ \AA}^3$
$M_r = 786$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.391 \text{ Mg m}^{-3}$
$a = 10.1864 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.4434 (3) \text{ \AA}$	$\mu = 0.75 \text{ mm}^{-1}$
$c = 11.1137 (5) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\alpha = 108.102 (2)^\circ$	Block, yellow
$\beta = 114.206 (2)^\circ$	$0.21 \times 0.15 \times 0.13 \text{ mm}$
$\gamma = 102.811 (2)^\circ$	

Data collection

Bruker X8 APEX-II area-detector diffractometer	44847 measured reflections
ω and φ scans	4673 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	4360 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.858, T_{\max} = 0.909$	$R_{\text{int}} = 0.032$
	$\theta_{\text{max}} = 28.4^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 1.0272P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 1.33 \text{ e \AA}^{-3}$
4673 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
217 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

C1–P	1.8189 (17)	P–Pd	2.3289 (4)
C8–P	1.8188 (19)	Cl–Pd	2.2897 (4)
C15–P	1.8215 (18)		
C8–P–Pd	114.66 (6)	Cl–Pd–P	87.772 (16)
C1–P–Pd	109.91 (6)	P ¹ –Pd–P	180
C15–P–Pd	113.96 (7)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C19–H19 ⁱⁱ –Cl ⁱⁱ	0.95	2.76	3.531 (2)	139
C21–H21 ⁱⁱ –Cl	0.95	2.82	3.467 (2)	126

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

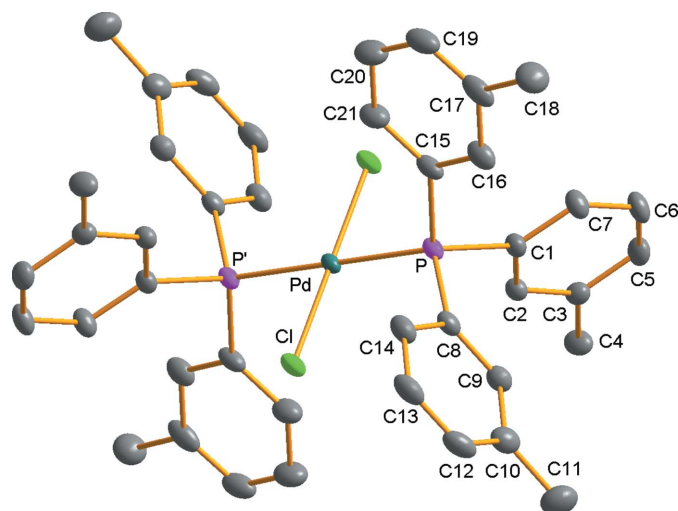


Figure 1

The structure of (I), showing the atom-numbering scheme and with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. The primed atom and the unlabelled atoms are generated by inversion ($1 - x, 1 - y, 1 - z$).

Table 3

Comparative geometric parameters (Å) for selected *trans*-[PdCl₂(L)₂] complexes (L is a tertiary phosphine ligand).

L	Pd–P	Pd–Cl	Reference
PPh ₃	2.337 (1)	2.290 (1)	(a)
PPh ₃	2.345 (1)	2.296 (1)	(b)
	2.353 (1)	2.281 (1)	
P(<i>m</i> -tol) ₃	2.3289 (4)	2.2897 (4)	(c)
PCy ₃ [†]	2.3628 (9)	2.3012 (9)	(d)
PPh(^t Bu) ₂	2.398 (2)	2.301 (2)	(e)
PPh ₂ Cy [†]	2.3257 (9)	2.2995 (9)	(f)
PPh ₂ [<i>p</i> -(^t BuNO)Ph]	2.3298 (6)	2.2865 (7)	(g)
PPh ₂ CHCO ₂ H	2.326 (1)	2.305 (1)	(h)
PPh ₂ (NC ₅ H ₁₀)	2.324 (2)	2.289 (2)	(i)

[†] Cy is cyclohexyl. References: (a) Ferguson *et al.* (1982); (b) Kitano *et al.* (1983); (c) this work; (d) Grushin *et al.* (1994); (e) DiMeglio *et al.* (1990); (f) Meij *et al.* (2003); (g) Leznoff *et al.* (1999); (h) Edwards *et al.* (1998); (i) Burrow *et al.* (1994).

The methyl and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.95–0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and $1.2U_{\text{eq}}(\text{C})$, respectively. The methyl groups were generated to fit the difference electron density and the groups were then refined as rigid rotors. The maximum electron-density peak is 0.48 Å from atom H20, presenting no physical meaning.

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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References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Release 3.0c. Crystal Impact GbR, Bonn, Germany.
- Bruker (2004). *SAINTE-Plus* (Version 7.12, including *XPREP*) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2005). *APEX2*. Version 1.0-27. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bunten, K. A., Chen, L., Fernandez, A. L. & Poë, A. J. (2002). *Coord. Chem. Rev.* **233–234**, 41–51.
- Burrow, R. A., Farrar, D. H. & Honeyman, C. H. (1994). *Acta Cryst.* **C50**, 681–683.
- DiMeglio, C. M., Luck, L. A., Rithner, C. D., Rheingold, A. L., Elcesser, W. L., Hubbard, J. L. & Bushweller, C. H. (1990). *J. Phys. Chem.* **94**, 6255–6263.
- Drew, D. & Doyle, J. R. (1990). *Inorg. Synth.* **28**, 346–349.
- Edwards, D. A., Mahon, M. F. & Paget, T. J. (1998). *Polyhedron*, **17**, 4121–4130.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Ferguson, G., McCrindle, R., McAlees, A. J. & Parvez, M. (1982). *Acta Cryst.* **B38**, 2679–2681.
- Grushin, V. V., Bensimon, C. & Alper, H. (1994). *Inorg. Chem.* **33**, 4804–4806.
- Kitano, Y., Kinoshita, Y., Nakamura, R. & Ashida, T. (1983). *Acta Cryst.* **C39**, 1015–1017.
- Leznoff, D. B., Rancurel, C., Sutter, J., Rettig, S. J., Pink, M. & Kahn, O. (1999). *Organometallics*, **18**, 5097–5102.
- Meij, A. M. M., Muller, A. & Roodt, A. (2003). *Acta Cryst.* **E59**, m44–m45.
- Meijboom, R., Muller, A. & Roodt, A. (2005). *Acta Cryst.* **E61**, m699–m701.
- Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spessard, G. O. & Miessler, G. L. (1996). *Organometallic Chemistry*, pp. 131–135. Upper Saddle River, New Jersey: Prentice Hall.
- Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.