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## Key indicators

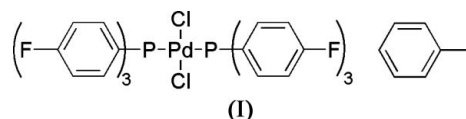
Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å  
 $R$  factor = 0.052  
 $wR$  factor = 0.150  
Data-to-parameter ratio = 19.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.*trans*-Dichlorobis[tris(4-fluorophenyl)-  
phosphine]palladium(II) toluene solvate

The title compound, *trans*-[PdCl<sub>2</sub>{P(C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>}<sub>2</sub>]·C<sub>7</sub>H<sub>8</sub>, where P(C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub> is tris(4-fluorophenyl)phosphine, crystallizes with both molecules in special positions. The *trans*-[PdCl<sub>2</sub>{P(C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>}<sub>2</sub>] molecule lies on an inversion centre, resulting in a distorted *trans* square-planar geometry. The Pd—P and Pd—Cl distances are 2.3398 (12) and 2.2955 (13) Å, respectively, and the P—Pd—Cl angle is 87.58 (5)°. The effective cone angle for the tris(4-fluorophenyl)phosphine group was calculated to be 152°. The toluene molecule lies on a twofold rotation axis.

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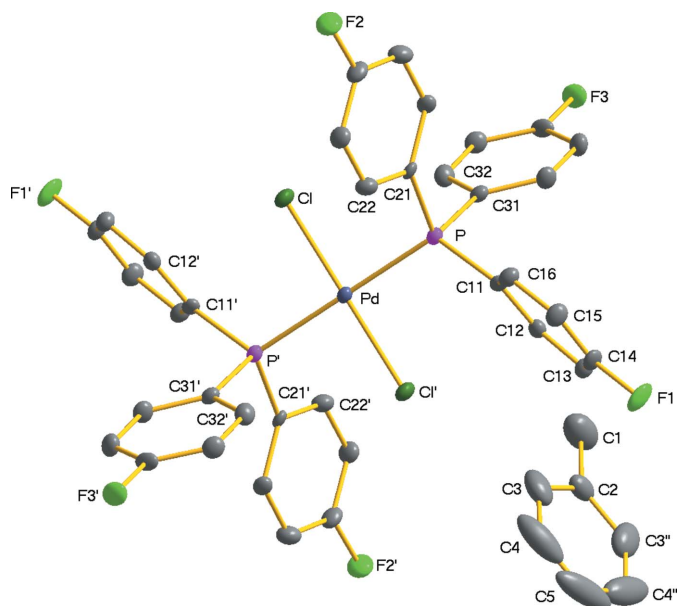
## Comment

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*-[MX<sub>2</sub>(L)<sub>2</sub>] ( $M = \text{Pt or Pd}$ ;  $X = \text{halogen, Me or Ph}$ ;  $L = \text{group 15 donor ligand}$ ), crystals of the title compound, (I), were obtained.



[PdCl<sub>2</sub>(L)<sub>2</sub>] ( $L = \text{tertiary phosphine, arsine or stibine}$ ) complexes can conveniently be prepared by the substitution of 1,5-cyclooctadiene (COD) from [PdCl<sub>2</sub>(COD)]. The title compound, *trans*-[PdCl<sub>2</sub>{P(C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>}<sub>2</sub>], (I), crystallizes in the orthorhombic space group *Pccn* ( $Z = 4$ ), 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 elevated out of the coordinating atom plane. All angles in the coordination polyhedron are close to the ideal value of 90° (see Table 1). The P—Pd—P<sup>i</sup> and Cl—Pd—Cl<sup>i</sup> [symmetry code: (i)  $-x + 2, -y + 1, z$ ] angles are 180°, as required by the crystallographic symmetry. Some weak intermolecular interactions were observed and are reported in Table 2. A crystallographic twofold axis passes through atoms C1, C2, C5 and H5 of the toluene molecule.

The most widely used method for determining ligand steric behaviour at a metal centre is by calculating the cone angle, as described previously (Tolman, 1977). For the current study, actual  $M$ —P distances were used, resulting in effective cone angles,  $\Theta_E$  (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 PPh<sub>3</sub> were reported to have a mean value of 148° with a standard



**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. [Symmetry codes: (i)  $2 - x, 1 - y, -z$ ; (ii)  $\frac{3}{2} - x, \frac{3}{2} - y, z$ .]

deviation of  $\pm 5^\circ$  and a spread from  $129$  to  $168^\circ$  (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  $152^\circ$  obtained from effective cone-angle calculations for (I) illustrates this point, when compared with the previously reported values of  $155$  and  $156^\circ$  for *trans*-[Rh(CO)Cl{P(C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>}<sub>2</sub>] (Meijboom *et al.*, 2006a).

In Table 3, the title compound is compared with other closely related Pd<sup>II</sup> 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  $2.2955$  (13) Å and a Pd–P bond length of  $2.3398$  (12) Å, fits well into the typical range for complexes of this kind.

## Experimental

Dichloro(1,5-cyclooctadiene)palladium(II), [PdCl<sub>2</sub>(COD)], was prepared according to the literature procedure of Drew & Doyle (1990). A solution of tris(4-fluorophenyl)phosphine (64.3 mg, 0.2 mmol) in dichloromethane (2.0 ml) was added to a solution of [PdCl<sub>2</sub>(COD)] (28.6 mg, 0.1 mmol) in dichloromethane (3.0 ml). Slow evaporation of the solvent gave yellow crystals of *trans*-[PdCl<sub>2</sub>{P(C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>}<sub>2</sub>] that slowly decomposed. Recrystallization from toluene gave crystals of the title compound, suitable for X-ray analysis, in quantitative yield.

### Crystal data

[PdCl<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>FP)<sub>2</sub>] $\cdot$ C<sub>7</sub>H<sub>8</sub>  
 $M_r = 901.93$   
 Orthorhombic, *Pccn*  
 $a = 29.215$  (5) Å  
 $b = 7.856$  (5) Å  
 $c = 17.051$  (5) Å  
 $V = 3913$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.531$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 6262 reflections  
 $\theta = 2.4$ – $24.2^\circ$   
 $\mu = 0.75$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 Plate, yellow  
 $0.32 \times 0.12 \times 0.04$  mm

### Data collection

Bruker X8 APEXII diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 SADABS (Bruker, 1998)  
 $T_{\min} = 0.795$ ,  $T_{\max} = 0.971$   
 52873 measured reflections  
 4842 independent reflections

3479 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.086$   
 $\theta_{\text{max}} = 28.2^\circ$   
 $h = -38 \rightarrow 38$   
 $k = -9 \rightarrow 10$   
 $l = -22 \rightarrow 22$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.15$   
 $S = 1.21$   
 4842 reflections  
 247 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 10.4167P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.009$   
 $\Delta\rho_{\text{max}} = 1.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.88$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cl–Pd	2.2955 (13)	P–Pd	2.3398 (12)
Cl–Pd–P	87.58 (5)	Cl <sup>i</sup> –Pd–P	92.42 (5)
Cl–Pd–P–C11	155.65 (16)	Cl–Pd–P–C31	–85.26 (15)
Cl–Pd–P–C21	32.06 (15)		

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

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H $\cdots$ <i>A</i>	<i>D</i> –H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> –H $\cdots$ <i>A</i>
C12–H12 $\cdots$ Cl <sup>i</sup>	0.93	2.82	3.177 (4)	104
C22–H22 $\cdots$ F3 <sup>ii</sup>	0.93	2.50	3.391 (5)	161
C33–H33 $\cdots$ Cl <sup>iii</sup>	0.93	2.83	3.714 (5)	160
C35–H35 $\cdots$ F1 <sup>iv</sup>	0.93	2.50	3.299 (5)	144

Symmetry codes: (i)  $-x + 2, -y + 1, -z$ ; (ii)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (iii)  $-x + 2, y + \frac{1}{2}, -z - \frac{1}{2}$ ; (iv)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .

**Table 3**

Comparative bond distances (Å) for selected *trans*-[PdCl<sub>2</sub>(L)<sub>2</sub>] (*L* = tertiary phosphine ligand) complexes.

<i>L</i>	Pd–P (Å)	Pd–Cl (Å)	Notes
PPh <sub>3</sub>	2.337 (1)	2.290 (1)	i
PPh <sub>3</sub>	2.345 (1)	2.296 (1)	ii
	2.353 (1)	2.281 (1)	
P(C <sub>6</sub> H <sub>4</sub> F) <sub>3</sub>	2.3398 (12)	2.2955 (13)	TW
P( <i>m</i> -tol) <sub>3</sub>	2.3289 (4)	2.2897 (4)	iii
PPh( <sup>t</sup> Bu) <sub>2</sub>	2.398 (2)	2.301 (2)	iv
PPh <sub>2</sub> Cy	2.3257 (9)	2.2995 (9)	v
PPh <sub>2</sub> [ <i>p</i> -( <sup>t</sup> BuNO)Ph]	2.3298 (6)	2.2865 (7)	vi
PPh <sub>2</sub> CHCO <sub>2</sub> H	2.326 (1)	2.305 (1)	vii
PPh <sub>2</sub> (NC <sub>5</sub> H <sub>10</sub> )	2.324 (2)	2.289 (2)	viii
PCy <sub>3</sub>	2.3628 (9)	2.3012 (9)	ix

Notes: Cy is cyclohexyl; TW is this work; (i) Ferguson *et al.* (1982); (ii) Kitano *et al.* (1983); (iii) Meijboom *et al.* (2006b); (iv) DiMeglio *et al.* (1990); (v) Meij *et al.* (2003); (vi) Leznoff *et al.* (1999); (vii) Edwards *et al.* (1998); (viii) Burrow *et al.* (1994); (ix) Grushin *et al.* (1994).

The methyl and aromatic H atoms were placed in geometrically idealized positions (C–H = 0.93–0.96 Å) and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$

respectively. The methyl H atoms were located in a difference Fourier map and they were then refined as a rigid rotor. The highest residual electron-density peaks are less than 1 Å from the Pd atom.

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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