oxygen [O(3)] is the acceptor for the two shortest hydrogen bonds [to O(5), 2·750 (2) Å and to N(3), 2·815 (2) Å]. The chloride ion is the acceptor for five hydrogen bonds with $X\cdots\mathrm{Cl}$ from 3·207 (2) to 3·375 (2) Å. All Y—H$\cdots X$ angles are reasonable [range 148 (1) to 177 (1)°].

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Structure of a Complex of *trans*-Dichlorobis(triphenylphosphine)palladium(II) with *p*-Dichlorobenzene, $[PdCl_2\{P(C_6H_5)_3\}_2].\frac{1}{2}(p\text{-}C_6H_4Cl_2)$

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Abstract. $M_r = 775{\cdot}39$, monoclinic, $P2_1/n$, $a = 16{\cdot}565$ (1), $b = 18{\cdot}692$ (2), $c = 11{\cdot}676$ (1) Å, $\beta = 105{\cdot}39$ (3)°, $V = 3485{\cdot}6$ Å^3, $Z = 4$, $D_m = 1{\cdot}470$, $D_x = 1{\cdot}478$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5405$ Å, $\mu = 7{\cdot}58$ mm^{-1}, $F(000) = 1572$, $T = 298$ K. The final R was 0·057 for 5308 independent reflections. The crystal structure analysis showed that *p*-dichlorobenzene is selectively incorporated into the cavity formed by two $PdCl_2\{P(C_6H_5)_3\}_2$ from the mixed solution of *ortho* and *para* isomers to form the stable title complex. The Pd atom possesses an essentially *trans* square-planar coordination with mean Pd—Cl 2·289 (1), and Pd—P 2·349 (1) Å.

Introduction. By the recrystallization of dichlorobis(triphenylphosphine)palladium(II) from a mixed solution of *o*- and *p*-dichlorobenzene, a new crystalline complex has been obtained in high yield (Kajimoto & Hara, 1983). The analysis of the complex suggested that one mole of dichlorobenzene was apparently incorporated per two $PdCl_2\{P(C_6H_5)_3\}_2$ in this complex. This structural analysis confirmed that a *p*-dichlorobenzene is trapped in the cavity formed by two $PdCl_2\{P(C_6H_5)_3\}_2$.

Experimental. Needle-like hexagonal orange-yellow prisms of a size suitable for X-ray analysis obtained by recrystallization of $PdCl_2\{P(C_6H_5)_3\}_2$ from hot *o*-dichlorobenzene which contained about 20% of *para* isomer. Density measured by flotation in an ethyl iodide–toluene mixture at 298 K. Data collection: Rigaku automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation; single crystal, $0{\cdot}12 \times 0{\cdot}05 \times 0{\cdot}20$ mm, mounted with c coincident with the goniostat axis; unit-cell dimensions determined by least-squares refinement of angular settings of 15

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reflections; 2θ–ω scan, scan rate 15° min^{-1} with $\Delta\omega = (1{\cdot}0 + 0{\cdot}145 \tan\theta)°$; three standard reflections measured after every 100 reflections, no significant change in intensities; 5618 reflections ($2\theta_{\max} = 120°$, $\pm h, +k, +l$) measured, 5308 (4879 non-zero) unique; corrected for usual Lorentz and polarization factors but not for absorption. Usual Patterson and Fourier methods applied and refinement was by the block-diagonal least-squares procedure (*HBLS*VI, Ashida, 1981), anisotropic temperature factors for non-H atoms, isotropic for H. H atoms found at or near the expected positions in a difference Fourier map after a few cycles of anisotropic refinement. Function minimized: $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + a|F_o| + b|F_o|^2]^{-1}$ for $F_o \neq 0$, and $w = c$ for $F_o = 0$, where $\sigma(F_o)$ is the standard deviation based on counting statistics; mean shift in the last cycle of refinement $0{\cdot}2\sigma$. Final refinement ($a = 0{\cdot}0112$, $b = 0{\cdot}0031$, $c = 0{\cdot}1034$) gave $R = 0{\cdot}0567$ ($wR = 0{\cdot}0956$) for all reflections and $R = 0{\cdot}0548$ for non-zero reflections; no residual detectable electron density peak obtained in the final difference Fourier map. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); *Universal Crystallographic Computing System* (1981) used for calculations.

Table 1. *Fractional atomic coordinates* ($\times 10^4$; *for* Pd $\times 10^5$), *and* B_{eq} *values for non-*H *atoms* ($\times 10^2$) *with e.s.d.'s in parentheses*

The equivalent isotropic temperature factors are defined by Hamilton (1959).

	x	y	z	B_{eq}(Å^2)
Pd	20272 (2)	17322 (1)	94896 (3)	231
Cl(1)	2174 (1)	519 (1)	9778 (1)	377
Cl(2)	1826 (1)	2931 (1)	9178 (1)	339
P(1)	1989 (1)	1849 (1)	11474 (1)	239
P(2)	1947 (1)	1640 (1)	7453 (1)	216
C(11)	1559 (2)	2689 (2)	11880 (4)	298
C(12)	1992 (4)	3326 (2)	11878 (5)	366
C(13)	1659 (4)	3970 (3)	12142 (5)	513
C(14)	890 (4)	3991 (3)	12393 (5)	556
C(15)	469 (4)	3347 (3)	12406 (5)	495
C(16)	789 (3)	2715 (3)	12164 (4)	386
C(21)	3015 (3)	1772 (2)	12527 (4)	294
C(22)	3236 (3)	2162 (3)	13558 (4)	353
C(23)	4033 (3)	2109 (3)	14335 (5)	438
C(24)	4610 (4)	1660 (3)	14078 (6)	523
C(25)	4391 (3)	1251 (3)	13070 (5)	467
C(26)	3616 (3)	1310 (3)	12271 (4)	427
C(31)	1356 (3)	1143 (2)	11879 (4)	308
C(32)	1633 (3)	766 (3)	12922 (5)	420
C(33)	1144 (4)	212 (3)	12170 (5)	518
C(34)	383 (4)	65 (3)	12421 (6)	547
C(35)	92 (3)	435 (3)	11365 (5)	455
C(36)	578 (3)	988 (3)	11072 (5)	379
C(41)	2333 (2)	2425 (2)	6837 (3)	259
C(42)	1869 (3)	2758 (3)	5808 (4)	378
C(43)	2187 (4)	3341 (3)	5357 (6)	466
C(44)	2984 (4)	3580 (3)	5896 (5)	462
C(45)	3458 (4)	3254 (2)	6902 (6)	436
C(46)	3123 (3)	2681 (2)	7374 (4)	343
C(51)	840 (3)	1574 (2)	6657 (4)	277
C(52)	579 (3)	1195 (3)	5571 (4)	409
C(53)	−265 (3)	1167 (3)	4982 (5)	463
C(54)	−833 (3)	1497 (3)	5450 (5)	486
C(55)	−589 (3)	1859 (3)	6511 (6)	434
C(56)	250 (3)	1890 (3)	7121 (5)	361
C(61)	2450 (2)	900 (2)	6870 (3)	255
C(62)	2206 (3)	193 (2)	7048 (4)	311
C(63)	2591 (3)	−371 (2)	6592 (4)	373
C(64)	3176 (3)	−238 (2)	5988 (5)	427
C(65)	3414 (3)	454 (3)	5851 (5)	411
C(66)	3055 (3)	1024 (2)	6271 (6)	363
Cl(3)	4568 (1)	1614 (1)	9979 (2)	600
C(71)	4815 (3)	709 (3)	10000 (4)	398
C(72)	4270 (3)	249 (3)	9271 (6)	548
C(73)	4477 (3)	−476 (3)	9289 (6)	545

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

A prime denotes an atom at $-x, -y, 1-z$.

Pd–Cl(1)	2·296 (1)	Pd–Cl(2)	2·281 (1)
Pd–P(1)	2·345 (1)	Pd–P(2)	2·353 (1)
Cl(3)–C(71)	1·740 (6)	P(1)–C(11)	1·836 (4)
P(1)–C(21)	1·820 (5)	P(1)–C(31)	1·824 (5)
P(2)–C(41)	1·823 (4)	P(2)–C(51)	1·827 (5)
P(2)–C(61)	1·835 (4)	C(71)–C(72)	1·367 (8)
C(72)–C(73)	1·399 (9)	C(71)–C(73′)	1·368 (8)
Mean of C(*n*1)–C(*n*2) and C(*n*1)–C(*n*6)	1·393 (7)*		
Mean of C(*n*2)–C(*n*3) and C(*n*5)–C(*n*6)	1·386 (8)		
Mean of C(*n*3)–C(*n*4) and C(*n*4)–C(*n*5)	1·373 (9)		
Mean of C–H	1·08 (7)		
Cl(1)–Pd–Cl(2)	177·76 (5)	P(1)–Pd–P(2)	175·23 (4)
Cl(1)–Pd–P(1)	88·66 (5)	Cl(1)–Pd–P(2)	92·95 (5)
Cl(2)–Pd–P(1)	91·40 (4)	Cl(2)–Pd–P(2)	86·81 (4)
Pd–P(1)–C(11)	116·7 (2)	Pd–P(1)–C(21)	113·2 (2)
Pd–P(1)–C(31)	110·9 (2)	Pd–P(2)–C(41)	114·1 (1)
Pd–P(2)–C(51)	107·4 (2)	Pd–P(2)–C(61)	121·4 (1)
C(11)–P(1)–C(21)	104·5 (2)	C(21)–P(1)–C(31)	105·4 (2)
C(31)–P(1)–C(11)	105·2 (2)	C(41)–P(2)–C(51)	105·3 (2)
C(51)–P(2)–C(61)	104·7 (2)	C(61)–P(2)–C(41)	102·7 (2)
C(71)–C(72)–C(73)	118·8 (6)	C(72)–C(73)–C(71′)	120·1 (6)
C(72)–C(71)–C(73′)	121·1 (6)	Cl(3)–C(71)–C(72)	119·3 (4)
Cl(3)–C(71)–C(73′)	119·6 (5)		
Mean of C(*n*2)–C(*n*1)–C(*n*6)	119·3 (4)*		
Mean of C(*n*1)–C(*n*2)–C(*n*3) and C(*n*1)–C(*n*6)–C(*n*5)	119·8 (5)		
Mean of C(*n*2)–C(*n*3)–C(*n*4) and C(*n*4)–C(*n*5)–C(*n*6)	120·5 (6)		
Mean of C(*n*3)–C(*n*4)–C(*n*5)	120·0 (6)		

* Mean values of the lengths and angles of equivalent bonds within the phenyl rings bonded to phosphines (n = 1–6).

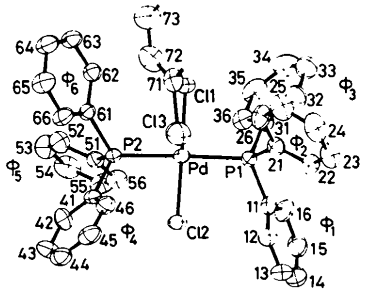

Fig. 1. A perspective view of an asymmetric unit of the complex viewed along the metal coordination plane normal, with the atomic numbering. The thermal ellipsoids correspond to 50% probability level and φ's designate the phenyl-ring planes.

Discussion. The final atomic parameters are in Table 1.* A perspective view of an asymmetric unit of the complex, with the numbering of atoms, as viewed along the metal coordination plane normal is shown in Fig. 1. Fig. 2 represents the stereopairs of the crystal structure viewed along **a**. The principal interatomic distances and angles are listed in Table 2. Further details of the molecular geometry have been deposited. The coordination geometries around the Pd atom are essentially

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, atomic parameters for H atoms, least-squares planes, and dihedral angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38548 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

identical with those recently found in $PdCl_2\{P(C_6H_5)_3\}_2$ (Ferguson, McCrindle, McAlees & Parvez, 1982, and references therein). The central Pd atom is 0·071 (4) Å above the coordination plane formed by two Pd and Cl atoms and is somewhat distorted from a square plane, the major distortion being the Cl(2)—Pd—P(2) angle of 86·81 (4)°. The triphenylphosphine groups, which are *trans*, display a staggered conformation with respect to the P—P axis. The mean Pd—P value of 2·349 Å is in good agreement with the values found in *trans*-$Pd(COOCH_3)(OCOCH_3)\{(C_6H_5)_3P\}_2$ (2·339 Å) (Del Piero & Cesari, 1979), *trans*-$PdI_2\{P(CH_3)_2C_6H_5\}_2$ (2·333 Å) (Bailey & Mason, 1968), and the mean Pd—Cl value of 2·289 Å is essentially identical with the value of 2·287 Å in *trans*-$PdCl_2(dmso)_2$ (Bennett, Cotton, Weaver, Williams & Watson, 1967). The P—C distances within the triphenylphosphine ligand range from 1·820 (5) to 1·836 (4) Å and the average is 1·828 Å. These results are in good agreement with the mean distances of 1·831 Å in $Pd(COOCH_3)(OCOCH_3)\{(C_6H_5)_3P\}_2.\frac{1}{2}C_6H_6$ (Manojlović-Muir, Muir & Walker, 1979) and also with the average value of 1·828 Å in the free triphenylphosphine molecule (Daly, 1964). The average value of 104·6 (2)° for the C—P—C angles is significantly smaller than the regular tetrahedral angle, but resembles the values generally found in triphenylphosphine–transition-metal complexes (Miki, Kai, Yasuoka & Kasai, 1979; Kobayashi, Iitaka & Yamazaki, 1972; Churchill & O'Brien, 1968, and references therein), or even in triphenylphosphine itself. Within the triphenylphosphine ligands the C—C distances in the phenyl rings agree well with the expected value [mean C—C 1·381 (8) Å] and the angles within the ring are all normal with an average value of 119·6 (6)°. The C atoms in the phenyl rings show no significant deviations from the least-squares planes.

The most interesting structural feature in $PdCl_2\{P(C_6H_5)_3\}_2.\frac{1}{2}(p\text{-}C_6H_4Cl_2)$ is the presence of the dichlorobenzene molecule in the complex. As may be seen in Fig. 2, *p*-dichlorobenzene at a crystallographic center of symmetry is trapped in the cavity formed by the two $PdCl_2\{P(C_6H_5)_3\}_2$ moieties and is sandwiched by one pair of phenyl rings (φ_6's) of the triphenylphosphine ligands. This mode of packing may probably contribute to the stability of the complex. The dichlorobenzene-ring plane is nearly perpendicular to the phenyl-ring (φ_6) plane (the dihedral angle of the dichlorobenzene-ring plane and the φ_6 plane being 106·8°), and the C(72) atom in the dichlorobenzene is the nearest to the φ_6 plane with a length of 3·531 Å. The Cl(3)—Cl(3′) (a prime denotes the atom at $-x$, $-y$, $1-z$) axis of the dichlorobenzene is almost parallel to the *b* axis of the crystal, but is inclined to the central Pd atom in such a way that Cl(3) comes closer to Pd [Pd—Cl(3) 4·10 Å]. The dihedral angle of the dichlorobenzene-ring plane is 60·2° to the coordination plane and the Cl(3) atom is 4·085 Å above the coordination plane. The nearest approaches of the dichlorobenzene to the phenyl-ring C atoms and to the coordinated Cl atom are as follows: C(72)—C(62) 3·705 (8), C(72)—C(61) 3·734 (8), C(72)—C(63) 3·775 (8), C(73)—C(63) 3·807 (8), C(72)—Cl(1) 3·709 (6) Å.

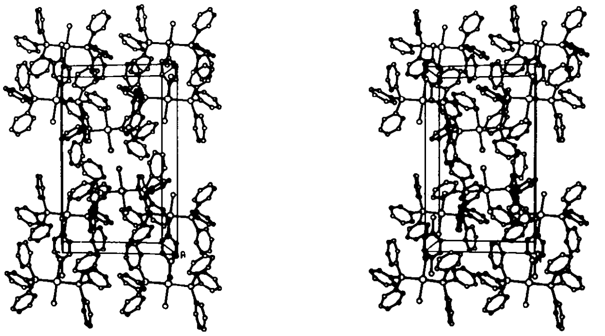

Fig. 2. A stereopair of the crystal structure viewed along **a** with **b** vertical and **c** horizontal. Dichlorobenzenes at $(0,\frac{1}{2},\frac{1}{2})$ and $(1,\frac{1}{2},\frac{1}{2})$ are omitted for clarity.

As far as the *o*-dichlorobenzene is concerned, although it was the main portion of the crystallization solvent, it is concluded that there is no evidence for the existence of the *o*-isomer in the crystal as no detectable peaks of structural significance were found on the final difference synthesis.

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