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trans-Dichlorobis[tris(pentafluorophenyl)phosphane]palladium(II)

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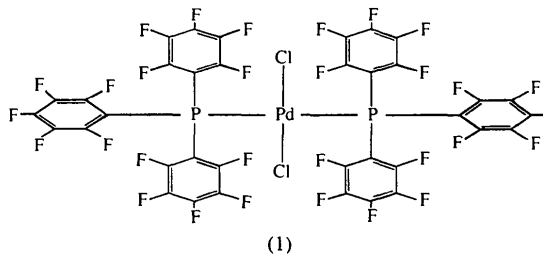
Abstract

The crystal structure of the title compound, *trans*-[{$(C_6F_5)_3P$}$_2PdCl_2$], was determined from single-crystal X-ray diffraction data. Owing to the steric requirements of the bulky phosphane ligands, the centrosymmetric molecule shows a considerable angle distortion at the square-planar coordinated Pd atom [Cl—Pd—P 95.23 (4)°]. Pd—Cl and Pd—P distances are 2.291 (1) and 2.305 (1) Å, respectively. The metal–phosphorus distance is significantly shorter than in *trans*-dichlorobis(triphenylphosphane)palladium(II).

Comment

trans-[{$(C_6F_5)_3P$}$_2PdCl_2$], (1), is a catalyst for the synthesis of hydrogen peroxide from the elements (Dyer & Moseley, 1981). In the course of a study of the catalytic behavior of the compound, we were interested in comparing its structure with that of the corresponding triphenylphosphane derivative, *trans*-[{$(C_6H_5)_3P$}$_2PdCl_2$], (2) [(2) (Ferguson, McCrindle, McAlees & Masood, 1982); (2).0.5*p*-$C_6H_4Cl_2$ (Kitano, Kinoshita, Nakamura & Ashida, 1983)].

(1)

The crystals of (1) consist of discrete centrosymmetric molecules (Fig. 1) separated by van der Waals distances. The packing is like that of the isotypic platinum compound *trans*-[{$(C_6H_5)_3P$}$_2PtCl_2$] (Schaefer, Lyon, Labinger & Bercaw, 1992). The Pd—Cl distance lies in the middle of the range of values collected by Ferguson *et al.* (1982) for *trans*-dichlorobis(phosphane)palladium complexes [2.267–2.326 Å], whereas the Pd—P distance is slightly shorter than the shortest value given

by those authors [2.310(5) Å for the dimethyl(neo-menthyl)phosphane derivative] and significantly shorter than in (2) [2.337(1) Å] and (2).0.5p-$C_6H_4Cl_2$ [2.345(1) and 2.353(1) Å]. With respect to the Pd—P bond strength, this shows that the lower basicity and therefore weaker σ-donor ability of tris(perfluorophenyl)-phosphane compared with triphenylphosphane is over-compensated by its better π-acceptor properties. The P—C, C—C and C—F bond lengths in the molecule agree with established values.
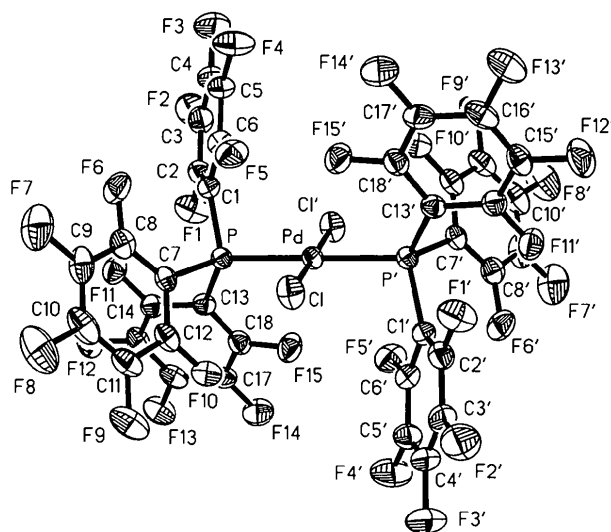

Fig. 1. Diagram of trans-[{(C_6F_5)$_3$P}$_2$PdCl$_2$] showing the atom-numbering scheme (displacement ellipsoids are at the 40% proba-bility level; symmetry code: (') $-x$, $-y$, $-z$]. Some C-atom labels are omitted for clarity.

The conformational arrangement of the linear $PdCl_2$ fragment with respect to the pentafluorophenyl groups at the P atom can be described by the torsion angle Cl—Pd—P—C7 [2.7(1)°], i.e. the ipso C atom of one phenyl ring is in an eclipsed position with respect to the Cl atom. The Cl—Pd—P angle in (1) [95.23(4)°] shows a much greater deviation from 90° than the corresponding angle in (2) [92.0(1)°]. Together with the variance of the C—P—C angles [99.2(2)–109.4(2)° for (1); 104.0(1)–106.3(1)° for (2)] this reflects the enhanced intramolecular crowding effects in (1). Two of the pentafluorophenyl rings are oriented such that an ortho F atom of each ring is directed towards the Pd atom [Pd···F5 3.13, Pd···F15 3.16 Å]. As these values coincide with the sum of the van der Waals radii of Pd and F (3.10–3.20 Å; Bondi, 1964), a bonding interaction can be excluded.

Experimental

The compound was synthesized according to procedures given in the literature (Kemmitt, Nichols & Peacock, 1968). Thin orange plates were grown from acetone solution at room temperature.

Crystal data

[PdCl$_2$(C$_{18}$F$_{15}$P)$_2$]	Mo $K\alpha$ radiation
M_r = 1241.60	λ = 0.71069 Å
Triclinic	Cell parameters from 33
$P\bar{1}$	reflections
a = 9.502(2) Å	θ = 9.8–11.8°
b = 11.252(2) Å	μ = 0.837 mm^{-1}
c = 11.602(2) Å	T = 293(2) K
α = 102.98(2)°	Transparent plate
β = 113.68(2)°	0.35 × 0.19 × 0.02 mm
γ = 106.92(2)°	Orange
V = 1000.9(3) Å^3	
Z = 1	
D_x = 2.060 Mg m^{-3}	

Data collection

Stoe Siemens AED-2 four-circle diffractometer	3029 observed reflections [$I > 2\sigma(I)$]
ω/θ scans	θ_{max} = 27.49°
Absorption correction:	h = $-12 \rightarrow 10$
ψ scan (EMPIR; Stoe & Cie, 1988b)	k = $-14 \rightarrow 14$
	l = $0 \rightarrow 15$
T_{min} = 0.594, T_{max} = 0.788	1 standard reflection frequency: 60 min
4590 measured reflections	intensity decay: none
4590 independent reflections	

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.464 e Å^{-3}
$R[F^2 > 2\sigma(F^2)]$ = 0.0516	$\Delta\rho_{min}$ = -0.459 e Å^{-3}
$wR(F^2)$ = 0.0727	Extinction correction: none
S = 1.239	Atomic scattering factors
4590 reflections	from International Tables
322 parameters	for Crystallography (1992,
w = $1/\sigma^2(F_o^2)$	Vol. C, Tables 4.2.6.8 and
$(\Delta/\sigma)_{max}$ = 0.37	6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd	0	0	0	0.03441(13)
P	0.23433(11)	0.04717(9)	0.20264(9)	0.0347(2)
Cl	$-0.09738(13)$	0.13214(11)	0.09805(10)	0.0537(3)
F1	0.4759(3)	$-0.1050(2)$	0.2264(3)	0.0715(7)
F2	0.3942(4)	$-0.3603(3)$	0.1969(3)	0.0933(9)
F3	0.0913(4)	$-0.5151(3)$	0.1595(3)	0.1023(10)
F4	$-0.1330(4)$	$-0.4088(3)$	0.1524(3)	0.1006(10)
F5	$-0.0513(3)$	$-0.1502(2)$	0.1867(2)	0.0633(7)
F6	0.2026(3)	$-0.0020(3)$	0.4553(2)	0.0642(7)
F7	0.2103(3)	0.1732(3)	0.6551(3)	0.0926(9)
F8	0.2736(4)	0.4303(3)	0.6731(3)	0.1007(10)
F9	0.3188(3)	0.5063(2)	0.4800(3)	0.0805(8)
F10	0.3036(3)	0.3291(2)	0.2740(2)	0.0561(6)
F11	0.5688(3)	0.1260(2)	0.4497(2)	0.0566(6)
F12	0.8830(3)	0.2803(3)	0.5105(2)	0.0732(8)
F13	0.9314(3)	0.3803(2)	0.3317(2)	0.0719(7)
F14	0.6610(3)	0.3189(2)	0.0862(3)	0.0728(7)
F15	0.3490(3)	0.1735(2)	0.0273(2)	0.0644(7)
C1	0.2174(5)	$-0.1151(4)$	0.2131(3)	0.0385(9)
C2	0.3256(5)	$-0.1744(4)$	0.2133(4)	0.0489(10)

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C3	0.2843 (6)	−0.3075 (5)	0.1963 (4)	0.0589 (12)
C4	0.1314 (7)	−0.3855 (4)	0.1778 (4)	0.0653 (13)
C5	0.0189 (6)	−0.3328 (4)	0.1741 (4)	0.0609 (12)
C6	0.0619 (5)	−0.2000 (4)	0.1928 (4)	0.0478 (10)
C7	0.2502 (4)	0.1557 (4)	0.3547 (3)	0.0378 (9)
C8	0.2274 (5)	0.1217 (4)	0.4554 (4)	0.0488 (10)
C9	0.2326 (5)	0.2123 (5)	0.5605 (4)	0.0590 (12)
C10	0.2644 (5)	0.3409 (5)	0.5680 (5)	0.0647 (13)
C11	0.2894 (5)	0.3802 (4)	0.4720 (5)	0.0547 (11)
C12	0.2783 (4)	0.2872 (4)	0.3661 (4)	0.0451 (10)
C13	0.4469 (4)	0.1384 (4)	0.2335 (4)	0.0368 (9)
C14	0.5888 (5)	0.1722 (4)	0.3569 (4)	0.0428 (9)
C15	0.7501 (5)	0.2492 (4)	0.3896 (4)	0.0482 (10)
C16	0.7747 (5)	0.2993 (4)	0.2986 (5)	0.0505 (11)
C17	0.6391 (5)	0.2696 (4)	0.1760 (4)	0.0484 (10)
C18	0.4768 (5)	0.1912 (4)	0.1440 (4)	0.0437 (10)

Table 2. *Selected geometric parameters (Å, °)*

Pd—Cl	2.2907 (10)	P—C7	1.827 (4)
Pd—P	2.3051 (12)	P—C13	1.819 (4)
P—C1	1.821 (4)		
Cl—Pd—P	95.23 (4)	C2—C1—P	127.8 (3)
C1—P—C13	107.4 (2)	C6—C1—P	115.9 (3)
C1—P—C7	109.4 (2)	C8—C7—P	128.4 (3)
C13—P—C7	99.2 (2)	C12—C7—P	115.7 (3)
C1—P—Pd	106.01 (12)	C18—C13—P	122.9 (3)
C13—P—Pd	119.98 (12)	C14—C13—P	120.6 (3)
C7—P—Pd	114.43 (11)		
Cl—Pd—P—C1	123.42 (13)	Pd—P—C1—C2	116.0 (3)
Cl—Pd—P—C13	−114.93 (14)	Pd—P—C7—C8	109.1 (3)
Cl—Pd—P—C7	2.75 (14)	Pd—P—C13—C14	177.4 (2)

Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography*, (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2).

Data collection: *DIF4* (Stoe & Cie, 1988*a*). Cell refinement: *DIF4*. Data reduction: *EMPIR, REDU4* (Stoe & Cie, 1988*b*,*c*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

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Tetraphenylphosphonium Pentachlorostannat, PPh$_4$[SnCl$_5$], und Tetraphenylphosphonium Pentachlorostannat Monohydrat, PPh$_4$[SnCl$_5$.H$_2$O]

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Abstract

Tetraphenylphosphonium pentachlorostannate contains trigonal-bipyramidal [SnCl$_5$]$^-$ ions. It is isotypic with PPh$_4$[Sn(CH$_3$)Cl$_4$]; however, the published space group of the latter is corrected from $P2$ to $P2/n$. In the hydrate the [SnCl$_5$(H$_2$O)]$^-$ ions have a distorted octahedral configuration. The packing principle is the same for both compounds and corresponds to the known arrangement in tetraphenylphosphonium compounds with PPh$_4^+$ ions stacked in columns in the c direction.

Kommentar

Bei Hauptgruppenelementen ist die trigonale Bipyramide das normale Koordinationspolyeder für die Koordinationszahl fünf. Dies gilt auch für das SnCl$_5^-$-Ion in den wenigen bekannten Strukturen von Pentachlorostannaten (Freedman & Young, 1964; Ginzburg *et al.*, 1977; Shamir, Lusti, Bino, Cohen & Gibson, 1985). Auch das InCl$_5^{2-}$-Ion im (PPh$_4$)$_2$[InCl$_5$].CH$_3$CN hat trigonal-bipyramidale Struktur (Bubenheim, Frenzen & Müller, 1995), während das quadratisch-pyramidale InCl$_5^{2-}$-Ion im (NEt$_4$)$_2$[InCl$_5$] eine der wenigen Ausnahmen ist (Brown, Einstein & Tuck, 1969). Für Tetraphenylphosphonium-Ionen

PPh$_4$[SnCl$_5$.H$_2$O]