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Key indicators

Single-crystal X-ray study
 $T = 150\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.039
 wR factor = 0.101
Data-to-parameter ratio = 10.6

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

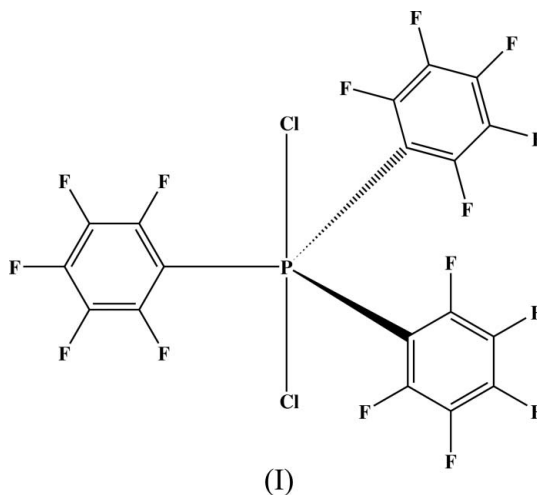
An orthorhombic polymorph of dichlorotris-(pentafluorophenyl)phosphorane

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An orthorhombic form of dichlorotris(pentafluorophenyl)-phosphorane, $\text{C}_{18}\text{Cl}_2\text{F}_{15}\text{P}$, has been obtained as the product of the reaction between PhSeCl and $(\text{C}_6\text{F}_5)_3\text{P}$, and is a polymorph of the previously reported monoclinic form obtained from the reaction of $(\text{C}_6\text{F}_5)_3\text{P}$ with Cl_2 . The molecule displays nearly perfect trigonal-bipyramidal geometry, and features a number of intermolecular $\text{F}\cdots\text{F}$ contacts, which lead to fluorine domains in the crystal packing.

Comment

Compounds of formula $R_3\text{PCl}_2$ are usually ionic in the solid state (Dillon *et al.*, 1976; Godfrey *et al.*, 1996, 1997; Ruthe *et al.*, 1997) and solution (Beveridge *et al.*, 1966; Wiley & Stine, 1967; Harris & Ali, 1968; Godfrey *et al.*, 1997); however, molecular five-coordinate trigonal-bipyramidal structures have been observed for $R_3 = \text{Ph}_3$, $(\text{C}_6\text{F}_5)_2\text{Ph}$ and $(\text{C}_6\text{F}_5)_3$ (Godfrey *et al.*, 1997; Godfrey, McAuliffe, Pritchard & Sheffield, 1998). Whilst the trigonal-bipyramidal form of Ph_3PCl_2 ionizes in solution, the analogous compounds containing highly electron withdrawing C_6F_5 groups retain their trigonal-bipyramidal geometry in solution. We have previously described the structure of the monoclinic form of $(\text{C}_6\text{F}_5)_3\text{PCl}_2$ (space group $P2_1/c$), prepared from $(\text{C}_6\text{F}_5)_3\text{P}$ and dichlorine (Godfrey *et al.*, 1997). We now report that the same compound is also formed when phenylselenenyl chloride is reacted with $(\text{C}_6\text{F}_5)_3\text{P}$; however the crystals obtained were an orthorhombic polymorph of $(\text{C}_6\text{F}_5)_3\text{PCl}_2$, (I) (see Fig. 1 and Table 1).



Compound (I) displays nearly perfect trigonal-bipyramidal geometry, although neither of the two polymorphs of $(\text{C}_6\text{F}_5)_3\text{PCl}_2$ display crystallographically imposed D_3

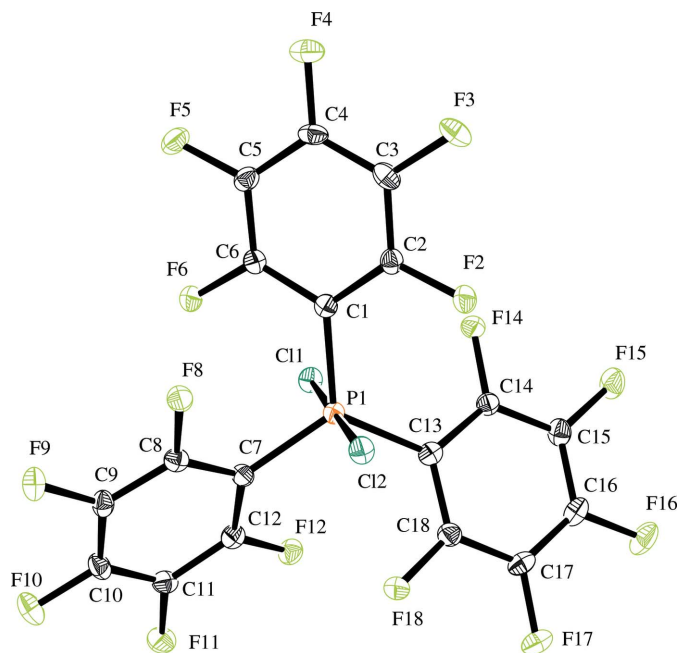


Figure 1
The structure of (I). Displacement ellipsoids are shown at the 30% probability level.

symmetry, unlike the analogous trigonal-bipyramidal $(\text{C}_6\text{F}_5)_3\text{PBr}_2$, space group $R\bar{3}c$ (Godfrey, McAuliffe, Mushtaq *et al.*, 1998). The P–Cl bonds in (I) are nearly equivalent and slightly shorter than observed in the monoclinic polymorph [P–Cl = 2.211 (2) Å; Godfrey *et al.*, 1997]. However, the P–Cl bonds are rather shorter than observed for $(\text{C}_6\text{F}_5)_2\text{Ph}_2\text{PCl}_2$ [P–Cl = 2.244 (2) and 2.241 (3) Å; Godfrey *et al.*, 1997] and Ph_3PCl_2 [P–Cl = 2.225 (1)–2.280 (2) Å; Godfrey, McAuliffe, Pritchard & Sheffield, 1998), reflecting the increased net electron-withdrawing capability of three C_6F_5 groups. The Cl–P–Cl angle is essentially linear, and the remaining angles around the P atom are close to ideal trigonal-bipyramidal geometry. The C–F bonds in the molecule vary in distance between 1.329 (3) and 1.349 (3) Å, with the C–F bonds to the *para*-F atoms being the shortest in each C_6F_5 group. A number of intermolecular $\text{F} \cdots \text{F}$ interactions, shorter than the sum of the van der Waals radii of two F atoms, (2.94 Å), are observed, which vary in length between 2.700 (2) Å and 2.900 (2) Å. The extended structure thus features extensive aggregation of the fluorous domains.

Experimental

The title compound was prepared by addition of $(\text{C}_6\text{F}_5)_3\text{P}$ (Aldrich) (0.273 g, 5.0×10^{-4} mol) to a freshly distilled diethyl ether solution (50 ml) containing PhSeCl (Aldrich) (0.196 g, 1.0×10^{-3} mol). The colour of the solution gradually changed from orange to yellow over several days. The solvent was reduced in volume to 10 ml, and colourless crystals of (I) formed at 273 K over several weeks. The spectroscopic data of (I) match the literature values (Godfrey *et al.*, 1997).

Crystal data

$\text{C}_{18}\text{Cl}_2\text{F}_{15}\text{P}$
 $M_r = 603.05$
Orthorhombic, $Pbca$
 $a = 16.7367$ (5) Å
 $b = 11.3713$ (2) Å
 $c = 19.9214$ (5) Å
 $V = 3791.40$ (16) Å³

$Z = 8$
 $D_x = 2.113$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.58$ mm⁻¹
 $T = 150$ (2) K
Prism, colourless
 $0.2 \times 0.15 \times 0.1$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
Absorption correction: multi-scan
(Blessing, 1995)
 $T_{\min} = 0.893$, $T_{\max} = 0.944$

19042 measured reflections
3458 independent reflections
2634 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$
 $\theta_{\max} = 25.3^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.101$
 $S = 1.02$
3458 reflections
325 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 3.0443P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38$ e Å⁻³
 $\Delta\rho_{\min} = -0.54$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1–P1	1.820 (3)	P1–Cl2	2.1995 (10)
C7–P1	1.819 (3)	P1–Cl1	2.2005 (10)
C13–P1	1.821 (3)		
C7–P1–C1	118.64 (13)	C13–P1–Cl2	89.51 (9)
C7–P1–C13	121.49 (13)	C7–P1–Cl1	90.12 (9)
C1–P1–C13	119.86 (13)	C1–P1–Cl1	90.01 (9)
C7–P1–Cl2	90.26 (9)	C13–P1–Cl1	89.74 (9)
C1–P1–Cl2	90.37 (9)	Cl2–P1–Cl1	179.25 (5)

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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