

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1241). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(4-chlorophenyl)phosphine and Tris(4-fluorophenyl)phosphine

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Abstract

The crystal structures $C_{18}H_{12}Cl_3P$ (1) and $C_{18}H_{12}F_3P$ (2) have been determined. In (1) the average P—C distance and C—P—C angle are 1.834 (2) Å and 101.9 (1)°, respectively, while in (2) they are 1.825 (5) Å and 102.5 (2)°. Intermolecular C—H...F hydrogen bonds are observed in (2).

Comment

There have been numerous X-ray structural determinations of tertiary phosphines, PR_3 , which are widely used as ligands in organo-transition-metal chemistry. However, a search of the October 1995 release of the Cam-

bridge Crystallographic Database (Allen, Kennard & Taylor, 1983) revealed only ten entries for organometallic complexes containing the ligand (1), 16 entries for complexes of (2), and no reports on the structures of the free ligands. As part of our study of substitution of metal carbonyls by group 15 ligands, we have previously determined the structures of several tertiary phosphine ligands (Shawkataly, Chong, Fun & Sivakumar, 1996; Shawkataly, Sivakumar & Fun, 1996). We now report the structures of (1) and (2).

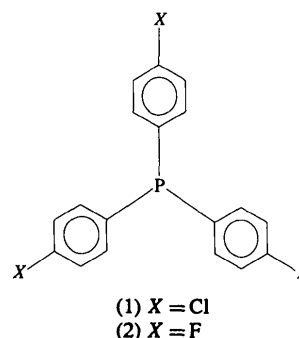
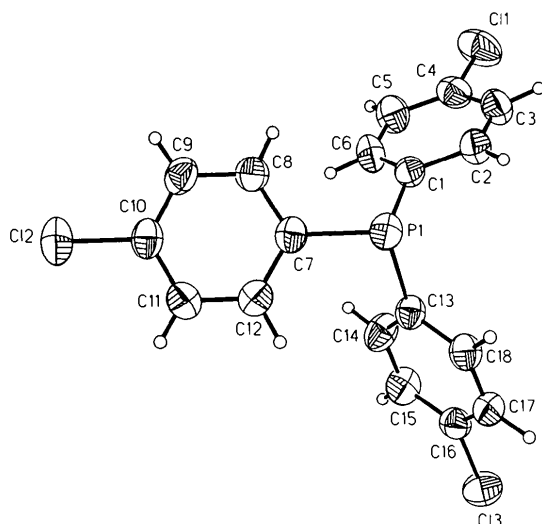


Fig. 1 shows the displacement-ellipsoid plots of the molecules of (1) and (2) with the numbering scheme. Both compounds have the expected geometry whereby the P atom is three coordinate with P—C(Ph) bonds folded back from the lone-pair site, giving a slightly distorted tetrahedral geometry and C—P—C angles less than 109.5°.

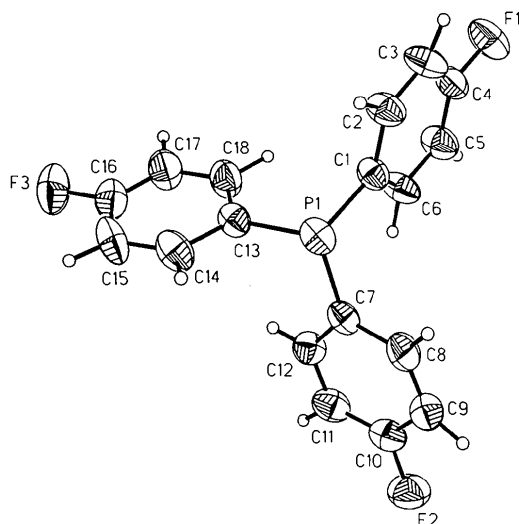
In (1) and (2) the mean P—C bond lengths of 1.834 (2) and 1.825 (5) Å are comparable with values of 1.828 (3) and 1.831 (2) Å reported for PPh_3 (Dunne & Orpen, 1991; Daly, 1964) and with the mean value of 1.828 Å for 2239 transition-metal complexes containing PPh_3 (Orpen *et al.*, 1989). The P—C distance in (2), however, is shorter than the corresponding distance of 1.835 (2) Å in *cis*-[Mo(CO)₄L₂], L = (2), which has significant Mo—P back bonding (Alyea, Ferguson, Gallagher & Song, 1994). While there are no appreciable differences between the three P—C bond lengths in (1), their variation in (2) may be significant. In (1) and (2) the mean C—P—C bond angles are 101.9 (1) and 102.5 (2)°, respectively. Since both structures were determined at room temperature, a detailed description of the distortion of the phenyl rings (see Domenicano, Vaciago & Coulson, 1975) is not presented. The dihedral angles between the planes of the phenyl rings are 129.40 (7), 92.57 (7) and 66.31 (7)° for (1) and 84.1 (2), 85.0 (2) and 93.6 (2)° for (2). In general, the dihedral angles in PPh_3 and other substituted PPh_3 structures are within 20° of 90° but in (1), an abnormal deviation of 40° is observed.

There are no short contacts observed in (1) but in (2) five possible intermolecular C—H...F hydrogen bonds attributable to the high electronegativity of fluorine have been observed (see Table 5).

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(a)



(b)

Fig. 1. Displacement-ellipsoid plots of (a) the chloro derivative (1), and (b) the fluoro derivative (2), with the numbering scheme. In (a) the 50% probability surface is shown, in (b) the 30% surface.

Experimental

Single crystals of both compounds were obtained by slow evaporation of ethanol solutions.

Compound (1)

Crystal data

C₁₈H₁₂Cl₃P

M_r = 365.60

Orthorhombic

Pbca

a = 14.654 (1) Å

b = 14.385 (1) Å

c = 15.897 (1) Å

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 39 reflections

θ = 8–25°

μ = 0.635 mm⁻¹

T = 293 (2) K

V = 3351.1 (4) Å³
Z = 8
D_x = 1.449 Mg m⁻³
D_m not measured

Prism

0.46 × 0.44 × 0.30 mm

Colourless

Data collection

Siemens *P4* diffractometer

θ/2θ scans

Absorption correction:
none

4759 measured reflections

3847 independent reflections

2282 observed reflections

[*I* > 2σ(*I*)]

*R*_{int} = 0.0296

θ_{max} = 27.50°

h = -1 → 19

k = -1 → 18

l = -20 → 1

3 standard reflections

monitored every 97

reflections

intensity decay: <3%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0402

wR(*F*²) = 0.1053

S = 0.881

3847 reflections

247 parameters

All H-atom parameters

refined

w = 1/[σ²(*F*_o²) + (0.0519*P*)²]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.26 e Å⁻³

Δρ_{min} = -0.25 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C11	0.42671 (5)	0.23783 (5)	0.10257 (6)	0.0790 (3)
C12	-0.13687 (5)	-0.15873 (6)	0.29247 (5)	0.0760 (2)
C13	0.48830 (4)	-0.13510 (5)	0.58247 (4)	0.0615 (2)
P1	0.18078 (4)	0.11056 (4)	0.41090 (4)	0.0440 (2)
C1	0.24636 (14)	0.14320 (15)	0.3167 (2)	0.0414 (5)
C2	0.3011 (2)	0.2219 (2)	0.3239 (2)	0.0520 (6)
C3	0.3565 (2)	0.2511 (2)	0.2588 (2)	0.0595 (7)
C4	0.3561 (2)	0.2025 (2)	0.1851 (2)	0.0527 (6)
C5	0.3022 (2)	0.1250 (2)	0.1747 (2)	0.0559 (7)
C6	0.2487 (2)	0.0959 (2)	0.2413 (2)	0.0502 (6)
C7	0.09486 (14)	0.0287 (2)	0.37245 (14)	0.0406 (5)
C8	0.0453 (2)	0.0459 (2)	0.2994 (2)	0.0467 (6)
C9	-0.0254 (2)	-0.0112 (2)	0.2745 (2)	0.0504 (6)
C10	-0.04835 (15)	-0.0859 (2)	0.3238 (2)	0.0478 (6)
C11	-0.0029 (2)	-0.1042 (2)	0.3981 (2)	0.0505 (6)
C12	0.0689 (2)	-0.0471 (2)	0.4211 (2)	0.0487 (6)
C13	0.26489 (14)	0.0333 (2)	0.46001 (14)	0.0405 (5)
C14	0.2962 (2)	-0.0490 (2)	0.4237 (2)	0.0524 (6)
C15	0.3637 (2)	-0.1013 (2)	0.4609 (2)	0.0537 (6)
C16	0.40126 (15)	-0.0705 (2)	0.53515 (15)	0.0446 (6)
C17	0.3734 (2)	0.0103 (2)	0.57228 (15)	0.0461 (5)
C18	0.3033 (2)	0.0614 (2)	0.5350 (2)	0.0453 (6)

Table 2. Selected geometric parameters (Å, °) for (1)

C11—C4	1.746 (3)	P1—C7	1.829 (2)
C12—C10	1.741 (2)	P1—C13	1.834 (2)
C13—C16	1.749 (2)	P1—C1	1.840 (2)
C7—P1—C13	102.39 (10)	C12—C7—P1	120.5 (2)
C7—P1—C1	104.60 (10)	C8—C7—P1	121.6 (2)
C13—P1—C1	98.63 (10)	C18—C13—P1	117.7 (2)
C6—C1—P1	126.5 (2)	C14—C13—P1	124.0 (2)
C2—C1—P1	116.2 (2)		

Compound (2)*Crystal data*C₁₈H₁₂F₃P $M_r = 316.25$

Trigonal

P3₁ $a = 12.428 (1) \text{ \AA}$ $c = 8.753 (1) \text{ \AA}$ $V = 1170.8 (2) \text{ \AA}^3$ $Z = 3$ $D_x = 1.346 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 36 reflections

 $\theta = 8-25^\circ$ $\mu = 0.200 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Rod-like

 $0.52 \times 0.22 \times 0.22 \text{ mm}$

Colourless

Data collection

Siemens P4 diffractometer

 $\theta/2\theta$ scansAbsorption correction:
none

1975 measured reflections

1604 independent reflections

1076 observed reflections

 $[I > 2\sigma(I)]$ $R_{\text{int}} = 0.0202$ $\theta_{\text{max}} = 24.99^\circ$ $h = -1 \rightarrow 14$ $k = -14 \rightarrow 1$ $l = -1 \rightarrow 10$

3 standard reflections

monitored every 97

reflections

intensity decay: <3%

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.0359$ $wR(F^2) = 0.0791$ $S = 0.907$

1604 reflections

247 parameters

All H-atom parameters
refined $w = 1/[\sigma^2(F_o^2) + (0.0341P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.11 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*
for *Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Absolute configuration:

Flack (1983)

Flack parameter = 0.20 (13)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)

	x	y	z	U_{eq}
P1	0.20654 (10)	0.45958 (10)	0.0112 (2)	0.0717 (4)
F1	0.5995 (3)	0.4296 (3)	-0.3396 (5)	0.1265 (12)
F2	0.1205 (3)	0.1236 (3)	0.5357 (4)	0.1221 (11)
F3	-0.2473 (3)	0.2182 (3)	-0.3714 (5)	0.1396 (13)
C1	0.3244 (4)	0.4430 (4)	-0.0961 (5)	0.0661 (12)
C2	0.4010 (5)	0.5383 (4)	-0.1899 (7)	0.0873 (15)
C3	0.4928 (5)	0.5345 (5)	-0.2741 (7)	0.098 (2)
C4	0.5089 (4)	0.4356 (5)	-0.2587 (6)	0.0845 (15)
C5	0.4356 (5)	0.3387 (6)	-0.1672 (7)	0.095 (2)
C6	0.3419 (5)	0.3418 (5)	-0.0859 (6)	0.0859 (15)
C7	0.1731 (4)	0.3499 (4)	0.1661 (5)	0.0647 (12)
C8	0.2539 (4)	0.3898 (5)	0.2891 (7)	0.0818 (14)
C9	0.2392 (5)	0.3157 (6)	0.4134 (7)	0.0899 (15)
C10	0.1375 (5)	0.1976 (5)	0.4120 (6)	0.0869 (14)
C11	0.0527 (6)	0.1530 (5)	0.2966 (7)	0.087 (2)
C12	0.0712 (5)	0.2292 (4)	0.1735 (7)	0.0743 (14)
C13	0.0689 (4)	0.3803 (4)	-0.1093 (5)	0.0676 (12)
C14	-0.0325 (5)	0.3939 (5)	-0.0745 (8)	0.091 (2)
C15	-0.1380 (5)	0.3400 (5)	-0.1594 (9)	0.101 (2)
C16	-0.1422 (5)	0.2729 (5)	-0.2834 (8)	0.096 (2)
C17	-0.0473 (6)	0.2554 (6)	-0.3254 (8)	0.104 (2)
C18	0.0598 (5)	0.3109 (5)	-0.2374 (7)	0.091 (2)

Table 4. Selected geometric parameters (\AA , $^\circ$) for (2)

P1—C7	1.817 (5)	F1—C4	1.364 (5)
P1—C13	1.823 (5)	F2—C10	1.367 (6)
P1—C1	1.836 (5)	F3—C16	1.368 (6)
C7—P1—C13	103.0 (2)	C8—C7—P1	117.3 (4)
C7—P1—C1	101.2 (2)	C12—C7—P1	125.7 (4)
C13—P1—C1	103.2 (2)	C18—C13—P1	124.6 (4)
C2—C1—P1	117.4 (4)	C14—C13—P1	118.1 (4)
C6—C1—P1	124.5 (4)		

Table 5. Hydrogen-bonding geometry (\AA , $^\circ$) for (2)

$D-H\cdots A$	$D\cdots A$	$D-H\cdots A$
C15—H15 ⁱ ···F3 ⁱ	3.221 (9)	127 (4)
C11—H11 ⁱ ···F2 ⁱⁱ	3.243 (8)	116 (4)
C18—H18 ⁱⁱⁱ ···F2 ⁱⁱⁱ	3.420 (8)	125 (4)
C15—H15 ⁱ ···F1 ^{iv}	3.426 (6)	128 (4)
C5—H5 ^v ···F1 ^v	3.565 (9)	149 (5)

Symmetry codes: (i) $-y, 1+x-y, \frac{1}{3}+z$; (ii) $-x+y, -x, z-\frac{1}{3}$; (iii) $x, y, z-1$; (iv) $-y, x-y, \frac{1}{3}+z$; (v) $1-y, x-y, \frac{1}{3}+z$.The computer program *PARST* (Nardelli, 1983) was used for geometrical calculations.For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL93*.

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