

Structure of Tetraphenylphosphonium Hexafluorophosphate

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Abstract. $[P(C_6H_5)_4][PF_6]$, $M_r = 484.36$, tetragonal, $I\bar{4}$, $a = 12.207(2)$, $c = 7.173(3)$ Å, $V = 1068.9$ Å³, $Z = 2$, $D_x = 1.505$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.66$ cm⁻¹, $F(000) = 496$, $T = 293$ K, $R = 0.037$ for 500 unique observed reflections. Both ions possess $\bar{4}$ (S_4) point symmetry. For the cation, the coordination about phosphorus is approximately tetrahedral with P–C 1.805 (4) Å. The anion is octahedral to within the limits of experimental accuracy, with P–F 1.555 (5) and 1.556 (3) Å. The title compound was obtained as an unknown by-product in the reaction of $[P(C_6H_5)_4][\text{ReOCl}_4]$ and *N*-(3-diphenylphosphinopropyl)salicyclideneamine in the presence of ammonium hexafluorophosphate, in an attempt to obtain a cationic Schiff base complex with rhenium.

Experimental. A crystal of size 0.5 × 0.1 × 0.2 mm was selected for X-ray analysis. Measurements were made on an Enraf–Nonius CAD-4 diffractometer with Mo *K*α radiation. Lattice parameters were determined from the setting angles of 25 reflections ($10 \leq \theta \leq 16^\circ$). Intensity data were measured with ω -2 θ scans within $2 \leq \theta \leq 25^\circ$ (h 0 to 14, k 0 to 14, l 0 to 8). Three standard reflections measured every 2 h showed no significant variation over the period of data collection. 565 reflections were scanned of which 558 were unique, $R_{\text{int}} = 0.01$, and 500 were considered observed [$F > 5\sigma(F)$] and were used in the analysis. No absorption correction was applied. The structure was solved by Patterson and Fourier methods. The H atoms were

located in a difference Fourier map and included in the refinement. Coordinates were refined for all atoms using full-matrix least squares on F values with weights $w = 1/[\sigma^2(F) + 0.00025F^2]$. All non-H atoms were assigned anisotropic thermal parameters. H atoms were assigned isotropic temperature factors. The refinement was terminated when all shift/e.s.d. rates were less than 0.001 and $R = 0.037$, $wR = 0.044$ for the 500 observed reflections. The residual electron density in a final difference map was within ± 0.38 e Å⁻³. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974); computations were carried out on the University of Birmingham Honeywell computer and on the CDC 7600 at the University of Manchester Regional Computer Centre with *SHELX78* (Sheldrick, 1978) and *PLUTO78*

Table 1. Fractional atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses and equivalent isotropic temperature factors (Å² × 10³)

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
P(1)	5000	0	2500	31
C(1)	5659 (3)	991 (3)	1007 (6)	35
C(2)	5470 (3)	2110 (3)	1189 (7)	40
C(3)	5982 (3)	2824 (3)	-27 (9)	49
C(4)	6666 (4)	2438 (4)	-1393 (7)	50
C(5)	6877 (4)	1328 (4)	-1548 (7)	51
C(6)	6366 (4)	607 (4)	-368 (6)	43
P(2)	0	0	0	41
F(1)	0	0	-2168 (6)	134
F(2)	1151 (3)	548 (3)	0 (9)	111

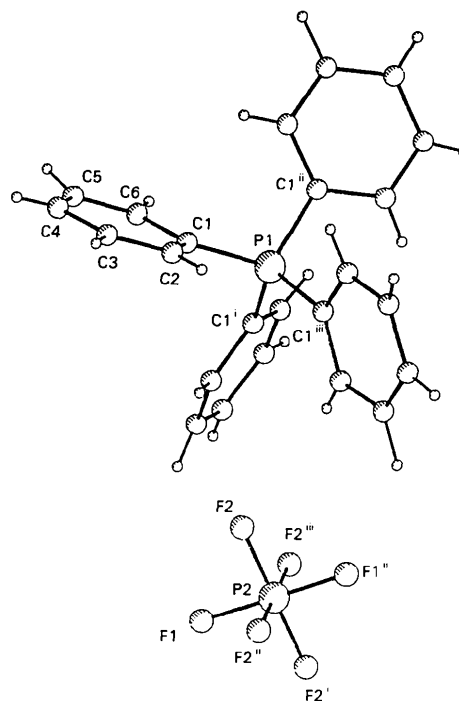


Fig. 1. View of the title compound. Symmetry codes are (a) for the tetraphenylphosphonium cation: (i) $1-x, -y, z$; (ii) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$; (iii) $\frac{1}{2} - y, -\frac{1}{2} + x, \frac{1}{2} - z$; (b) for the hexafluorophosphate anion: (i) $-x, -y, z$; (ii) $y, -x, -z$; (iii) $-y, x, -z$.

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

Symmetry codes are defined in the figure caption.

P(1)—C(1)	1.805 (4)	C(4)—C(5)	1.384 (7)
C(1)—C(2)	1.390 (6)	C(5)—C(6)	1.371 (7)
C(1)—C(6)	1.393 (6)	P(2)—F(1)	1.555 (5)
C(2)—C(3)	1.383 (7)	P(2)—F(2)	1.556 (3)
C(3)—C(4)	1.371 (8)		
P(1)—C(1)—C(2)	122.0 (3)	C(3)—C(4)—C(5)	120.5 (4)
P(1)—C(1)—C(6)	118.1 (3)	C(4)—C(5)—C(6)	119.7 (5)
C(2)—C(1)—C(6)	120.0 (4)	C(1)—C(6)—C(5)	120.2 (4)
C(1)—P(1)—C(1 ⁱ)	107.2 (3)	F(1)—P(2)—F(2)	90.0 (2)
C(1)—P(1)—C(1 ⁱⁱ)	110.6 (1)	F(1)—P(2)—F(1 ⁱⁱ)	180.0
C(1)—P(1)—C(1 ⁱⁱⁱ)	110.6 (1)	F(2)—P(2)—F(2 ⁱ)	180.0 (1)
C(1)—C(2)—C(3)	119.1 (5)	F(2)—P(2)—F(2 ⁱⁱ)	90.0 (1)
C(2)—C(3)—C(4)	120.6 (4)	F(2)—P(2)—F(2 ⁱⁱⁱ)	90.0 (1)

Related literature. The title compound consists of two much used counterions. A search of the Cambridge Structural Database (Allen *et al.*, 1979) during February 1988 shows that the PPh_4^+ cation and the PF_6^- anion have been determined in 252 and 580 different crystal structures, respectively, with mean P—C bond length 1.798 Å, and mean P—F 1.551 Å.

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(Motherwell & Clegg, 1978). Atomic parameters are in Table 1,* bond lengths and angles in Table 2. The atomic numbering is shown in Fig. 1.

* Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51019 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 9,10-Dihydro-10,9-propenoanthracene

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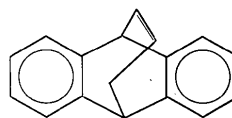
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Abstract. $\text{C}_{17}\text{H}_{14}$, $M_r = 218.30$, orthorhombic, *Iba*2, $a = 22.796$ (5), $b = 14.145$ (4), $c = 7.477$ (2) Å, $V = 2411$ (1) Å³, $Z = 8$, $D_x = 1.203$ g cm⁻³, $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å), $\mu = 0.63$ cm⁻¹, $F(000) = 928$, $T = 298$ K, $R = 0.0352$ for 1128 reflections [$F_o \geq 6\sigma(|F_o|)$]. The molecule consists of a dihydroanthracene unit bridged by a propeno unit between C(9) and C(10). The dihedral angle between the two phenyl rings is 134.6° and they form almost equal dihedral angles, 67.9 and 67.1°, with the plane of atoms C(9), C(10), C(11), C(12) and C(13). Angles C(10)—C(11)—C(12), C(11)—C(12)—C(13) and C(9)—C(13)—C(12) are larger than the expected sp^2 and sp^3 angles of 120 and 109.5°, indicating that the molecule in this region is under angular strain.

Experimental. This compound (1) was isolated as the sole product (m.p. 441–443 K; 60%) of the attempted amination of 11-bromo-9,10-dihydro-9,10-propano-

anthracene (2) with 3-*N,N*-dimethylaminopropylamine, potassium iodide and potassium *tert*-butoxide in refluxing dioxane. Treatment of 10,11-dihydro-5,10-ethano-5*H*-dibenzo[*a,d*]cycloheptane (3) with *N*-bromosuccinimide and benzoyl peroxide in refluxing carbon tetrachloride for one hour in the presence of a strong light afforded (2) (b.p. 391 K, 6.7 Pa; 65%; structure consistent with ¹³C NMR and ¹H NMR) instead of the expected 11-bromo-10,11-dihydro-5,10-ethano-5*H*-dibenzo[*a,d*]cycloheptane. A modification of the cyclidehydration of *trans*-4-benzyl-1-tetralol by Low & Roberts (1973) was used to prepare (3).



(1)