Crystal and Molecular Structure of $P(C_6H_5)_5 \cdot 0.5$ THF

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Pentaphenylphosphorus crystallizes from tetrahydrofuran (THF) as $P(C_6H_5)_5 \cdot 0.5$ THF (triclinic space group: $P\bar{1}$, $a = 10.095(4)$, $b = 10.252(3)$, $c = 12.725(3)$ Å, $\alpha = 71.21(1)$, $\beta = 76.98(3)$, $\gamma = 87.12(1)^\circ$, $Z = 2$). Its molecular structure is an almost perfect trigonal bipyramid with significantly longer axial than equatorial P-C_{Ph} bonds (P-C_{ax} 1.982(2)/1.979(2), P-C_{eq} 1.853(2)/1.845(2)/1.847(2) Å). It differs from the well established structure of solvent-free $P(C_6H_5)_5$ (P. J. Wheatley, J. Chem. Soc. 2206 (1964)) in the relative orientation of the phenyl rings with respect to each other (axial rings) and with respect to the equatorial PC_3 plane (equatorial rings) but not in the trigonal-bipyramidal (tbp) geometry at phosphorus. Differences in the geometry around the central atom had been found previously for $Sb(C_6H_5)_5$ (square pyramid) and $Sb(C_6H_5)_5 \cdot 0.5C_6H_{12}$ (tbp) but not in $As(C_6H_5)_5$ and $As(C_6H_5)_5 \cdot 0.5\ C_6H_{12}$ (both tbp).

Key words: Phosphorus, Structural Chemistry, Pentacoordination, Structure Determination

Introduction

The coordination number five is the first one (starting from low coordination numbers) where two alternative structures differ only very little in energy, the trigonal bipyramid (tbp) and the square or tetragonal pyramid (sp) [1]. The trigonal bipyramid is generally considered to be slightly lower in energy which is also born out from the vast number of structurally characterized trigonal-bipyramidal pentacoordinated main group element compounds [1, 2]. The easy energetic availability of an alternative structure, the square pyramid, gives rise, *inter alia*, to a pathway for the interconversion of trigonal-bipyramidal structures thus allowing for stereochemical non-rigidity [3, 4].

Probably the first pentacoordinated main group element whose structure was fully characterized by diffraction methods was pentaphenylantimony, $Sb(C_6H_5)_5$ [5]. It unambiguously showed a square-pyramidal geometry at antimony. Parallel work on pentaphenylphosphorus, $P(C_6H_5)_5$, and pentaphenylarsenic, $As(C_6H_5)_5$, showed them to be isostructural having trigonal-bipyramidal geometries, however [5, 6]. This and subsequent work on the homologous series of group 15 pentaphenyl compounds allows now a fairly concise picture to be drawn of this intriguing chapter of main group element structural chemistry. Table 1 summarizes the key structural features of the pentaaryl compounds of phosphorus [5, 6], arsenic [5, 7], antimony [8 – 11], and bismuth [12 – 15] which have been structurally characterized to date.

As can be seen from the table, the unsubstituted penta*phenyl* compounds of phosphorus and arsenic have trigonal-bipyramidal molecular geometries, while those of antimony and bismuth have square-pyramidal ones in the solid state. Most surprising is the situation encountered for antimony. Solvent-free $Sb(C_6H_5)_5$ is the already mentioned square pyramid [8, 9] but in the cyclohexane-containing crystals $Sb(C_6H_5)_5 \cdot 0.5\,C_6H_{12}$ antimony has a trigonal-bipyramidal geometry [10]. This geometry is also encountered for penta-*p*-tolylantimony, $Sb(4\text{-}CH_3C_6H_4)_5$ [11].

The recent structural work on pentarylbismuth compounds (Table 1) including heteroleptic ones (not having five equal substituents) adds even more variations to the theme [12 – 15]. While the square pyramidal geometry is clearly dominant, $Bi(4\text{-}CH_3C_6H_4)_3(2\text{-}FC_6H_4)_2$ was found to be a trigonal bipyramid. Noticeable deviations from the ideal geometries were observed in the solid state in some cases, and, even more important, the conspicuous bright colors of the pentaarylbismuth species allowed clues as to the structures in solution. For the first time it became evident that

Table 1. Crystal structure determinations and molecular geometries of group 15 pentaaryl compounds.

Compound	Molecular structure	Reference
$P(C_6H_5)_5$	trigonal bipyramid (isostructural with $As(C_6H_5)_5$)	[5, 6]
$P(C_6H_5)_5 \cdot 0.5$ THF	trigonal bipyramid	this work
$As(C_6H_5)_5$	trigonal bipyramid (inferred by analogy to $P(C_6H_5)_5$)	[5]
$As(C_6H_5)_5 \cdot 0.5\ C_6H_{12}$	trigonal bipyramid (isostructural with $Sb(C_6H_5)_5 \cdot 0.5\ C_6H_{12}$)	[7]
$Sb(C_6H_5)_5$	square pyramid	[8, 9]
$Sb(C_6H_5)_5 \cdot 0.5\ C_6H_{12}$	trigonal bipyramid	[10]
$Sb(4\text{-}CH_3C_6H_4)_5$	trigonal bipyramid	[11]
$Bi(C_6H_5)_5$	square pyramid	[12]
$Bi(4\text{-}CH_3C_6H_4)_5 \cdot LiCl \cdot 2$ THF	distorted square pyramid	[13]
$Bi(4\text{-}CH_3C_6H_4)_3(2,6\text{-}F_2C_6H_3)_2$	square pyramid	[13]
$Bi(C_6H_5)_3(2,6\text{-}F_2C_6H_3)_2$	square pyramid (2 crystallographically independent mol.)	[14]
$Bi(4\text{-}CH_3C_6H_4)_3(C_6F_5)_2$	square pyramid	[14]
$Bi(4\text{-}FC_6H_4)_3(C_6F_5)_2$	square pyramid	[14]
$Bi(C_6H_5)_3(2\text{-}FC_6H_4)_2$	square pyramid	[15]
$Bi(4\text{-}CH_3C_6H_4)_3(2\text{-}FC_6H_4)_2$	trigonal bipyramid	[15]

more than one structural isomer was present in solution [12 – 15].

With this body of information at hand it is now generally assumed that molecule packing forces in the crystal are responsible for the differences in molecular geometries encountered for the pentaarylantimony and -bismuth compounds in the solid state [16]. Especially for the pentaarylbismuth compounds the energy difference between the square-pyramidal and the trigonal-bipyramidal geometry should be close to nil, allowing for easy geometry variations as induced by the substituents and the environment [12 – 15].

On attempts to synthesize *ansa*-metallocenes af the alkali metals, we reacted $PhP(CR_2C_5H_4K)_2$ with $[PPh_4]^+Cl^-$. In addition to the desired *ansa*-potassocene $[PPh_4]^+[PhP(CR_2C_5H_4)_2K]^-$, which was obtained in 30% yield, we also isolated $P(C_6H_5)_5$ in 25% yield as crystalline THF solvate $P(C_6H_5)_5 \cdot 0.5$ THF [17]. The synthesis of the latter is believed to result from the reaction of K^+Ph^- (originating from P-Ph bond cleavage with potassium) with $[PPh_4]^+Cl^-$. We determined its crystal and molecular structure in order to have more precise molecular parameters of $P(C_6H_5)_5$, as compared to the original values obtained with film techniques, and to see if the presence of cocrystallized THF has an influence on the molecular geometry of this phosphorane.

Structure Determination

A single crystal of $P(C_6H_5)_5 \cdot 0.5$ THF suitable for X-ray diffraction was obtained as described above. It was mounted under nitrogen on a glass fiber in an inert oil drop at 183(2) K [18]. The crystal was examined directly on a four-circle diffractometer (Enraf-Nonius CAD4) with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71069$ Å). The crystal system indicated by preliminary search and indexing procedures was checked for higher metrical symmetry by reduced-cell calculations (DELOS [19], LePage [20]). Exact cell dimensions were determined by refinement of the Bragg angles of 25 selected high-angle re-

Table 2. Crystal structure data for $P(C_6H_5)_5 \cdot 0.5$ THF.

Formula	$C_{30}H_{25}P \cdot C_2H_4O_{0.5}$
M_r	452.56
T [K]	183(2)
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a [Å]	10.095(4)
b [Å]	10.252(3)
c [Å]	12.725(3)
α [deg.]	71.21(1)
β [deg.]	76.98(3)
γ [deg.]	87.12(1)
V [Å^3]	1214.4(7)
Z	2
D_{calcd} [gcm^{-3}]	1.238
μ(Mo-K$_\alpha$) [cm^{-1}]	1.31
$F(000)$ [e]	460
hkl Range	$+11, \pm11, \pm14$
Scan-type	ω
$((\sin\theta)/\lambda)_{max}$ [Å^{-1}]	0.595
Measured reflexions	4303
Unique reflexions	4049
R_{int}	0.014
Refined parameters	307
$R(F)/wR(F^2)$[a] (all reflexions)	0.054/0.139
GoF (F^2)[a]	1.06
$\Delta\rho_{fin}$ (max/min) [eÅ^{-3}]	0.74/−0.40

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_c|$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $GoF(F^2) = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflexions and p is the total number of parameters refined; $w = 1/[\sigma^2(F_o^2) + (0.0793 \cdot P)^2 + 0.7985 \cdot P)$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 3. Selected interatomic distances (Å) and angles (°) for $P(C_6H_5)_5$ in the crystals of $P(C_6H_5)_5 \cdot 0.5$ THF with estimated standard deviations in units of the last significant figure in parentheses. For atom numbering see Fig. 1.

P-C11	1.982(2)	P-C21	1.979(2)
P-C31	1.853(2)	P-C41	1.845(2)
P-C51	1.847(2)		
C11-P-C21	178.78(9)	C31-P-C41	120.2(1)
C31-P-C51	120.8(1)	C41-P-C51	119.0(1)
C11-P-C31	92.09(9)	C11-P-C41	86.38(9)
C11-P-C51	91.98(9)	C21-P-C31	88.76(9)
C21-P-C41	92.44(9)	C21-P-C51	88.34(9)

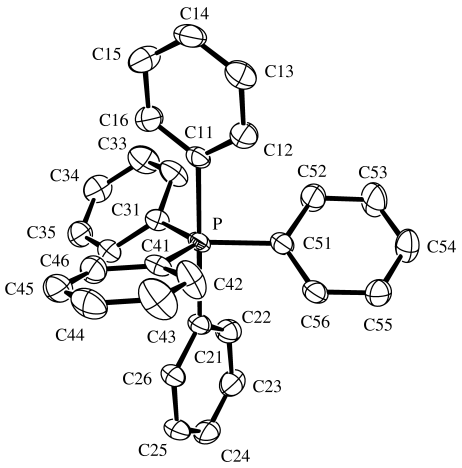

Fig. 1. Perspective view of the molecular structure of $P(C_6H_5)_5$ in the crystals of $P(C_6H_5)_5 \cdot 0.5$ THF and crystallographic numbering scheme used (ORTEP-III. Displacement ellipsoids at the 50% probability level; H atoms omitted for clarity).

flexions from various parts of reciprocal space carefully centered on the diffractometer. Lp and linear decay but no absorption corrections were applied. All H atoms were located in difference syntheses. They were included as fixed-atom contributions in final refinement cycles ($U_{iso} = 0.05$ Å^2). The cocrystallized molecule THF was found to be severly disordered around a center of inversion. As no reasonable model could be constructed, it was treated as one O atom with half occupacy and two C atoms bound to it with full occupancy. These atoms were refined freely with anisotropic displacement parameters. Refinement was done on F^2 of all reflexions with anisotropic displacement parameters for the non-H atoms. Programs used: SHELXS-/SHELXL-97 (structure solution and refinement) [21], PLATON (molecular geometry) [22], ORTEP-III (molecular drawings) [23]. Crystal structure data are summarized in Table 2, Table 3 contains the distances and angles involving phosphorus.

Results and Discussion

$P(C_6H_5)_5 \cdot 0.5$ THF crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. This implies that the THF molecule has to be disordered around a crystallographic center of inversion, while $P(C_6H_5)_5$ was found to have no crystallographic symmetry (Fig. 1). It adopts a nearly perfect trigonal-bipyramidal geometry at phosphorus as can be seen especially from the angles collected in Table 3. The axial P-C_{Ph} bonds are significantly longer than the equatorial ones (axial: P-C11/C21 1.982(2)/1.979(2); equatorial: P-C31/C41/C51 1.853(2)/1.845(2)/1.847(2) Å). The atom deviating most from the best plane through phosphorus and the *ipso*-carbon atoms of the equatorial phenyl rings is phosphorus with a distance of only 0.0040(9) Å.

A comparison with the structural parameters of the solvent-free $P(C_6H_5)_5$ structure [6], which was based on two-dimensional film data, reveals the remarkably good quality of the first structure determination. The average values of the P-C_{ax} and P-C_{eq} bond lengths of both structure determinations are virtually equivalent (P-C_{ax} 1.981 *vs.* 1.988 Å in the original structure determination; P-C_{eq} 1.848 *vs.* 1.850 Å [6]). There are noticeable differences in the relative orientation of the phenyl rings in the two crystal structures, however. While in $P(C_6H_5)_5 \cdot 0.5$ THF the dihedral angle between the axial phenyl rings C11-C16 and C21-C26 is 87.22(8)°, the respective value in $P(C_6H_5)_5$ is 71.5° [6]. The angles between the equatorial phenyl rings and the plane P, C31, C41, C51 are 43.03(8) (C31-C36), 5.17(7) (C41-C46), and 42.32(8)° (C51-C56) in our structure determination. That means that one of the rings (C41-C46) is almost coplanar with the equatorial PC_3 plane, while the other two (C31-C36 and C51-C56) are noticeably tilted with respect to P, C31, C41, C51. The tilt of these phenyl rings is in opposite direction, while the ring C41-C46 is tilted in the same sense as C51-C56 [24]. Thus, the equatorial phenyl rings are not oriented in a paddle-wheel fashion around phosphorus which can also be seen easily in Fig. 1. As was already found for the orientation of the axial phenyl rings, the relative orientation of the equatorial rings is noticeably different from that in solvent-free $P(C_6H_5)_5$. There the dihedral angles between the equatorial rings and the equatorial PC_3 plane are 53.9, 18.6, and 25.9° [6]. As in $P(C_6H_5)_5 \cdot 0.5$ THF, two of the rings are rotated in one direction, the third one (that rotated by 53.9°) in the opposite sense.

Our results clearly show that the cocrystallization of THF, *i.e.* the different crystalline environment of $P(C_6H_5)_5 \cdot 0.5$ THF as compared to solvent-free $P(C_6H_5)_5$, has no effect on the trigonal-bipyramidal geometry at phosphorus, nor does it effect bond lengths and angles. The major differences are in the relative orientations of the phenyl rings as they result from different rotations around the P-C_{ipso} bonds. Both molecular structures have a non-paddle-wheel arrangement of the equatorial phenyl rings in common.

The crystal and other structural data on the pentaaryl compounds of the group 15 elements phosphorus to bismuth accumulated so far (Table 1) strongly suggest that phosphorus and arsenic prefer trigonal-bipyramidal geometries while bismuth has a certain preference for a square-pyramidal structure. Antimony seems to be borderline [15]. A word of caution is appropriate, however, as the tiny energy differences involved, should not exclude *a priori* even major deviations from the expected geometries. This seems to be especially the case for bismuthpentaaryls [15].

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 250115. Copies of the data can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: (int. Code) +44 (1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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[24] When seen from the phosphorus center towards the *ipso*-carbon atoms of the phenyl rings, the plane C31-C36 is rotated counterclockwise out of a coplanar position with the equatorial PC_3 plane, the planes C41-C46 and C51-C56 are rotated clockwise. It should be noted that in the second, symmetry-equivalent molecule in the unit cell these rotation senses are opposite as is required by the crystallographic center of inversion.