Isolation and Structural Characterisation of Monoprotonated 1,2-Bis(diphenylphosphino)benzene in its Tetrabromogallate(III) Salt

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Hydrolysis of gallium tribromide complexes of 1,2-bis(diphenylphosphino)benzene in toluene solvent affords crystals of the mono-phosphonium salt $[1,2-Ph_2P-(C_6H_4)-PPh_2H]^+$ [GaBr₄]⁻. The structure analysis by single crystal X-ray diffraction allows an internal comparison of Ph₂P phosphino and Ph₂PH⁺ phosphonium functions.

Introduction

In a recent study of the coordination chemistry of gallium and indium trihalides with chelating ditertiary phosphines a rich series of 1:1 and 1:2 complexes has been isolated and structurally characterised [1]. The metals appear in a tetra-, penta- and hexacoordinated state both in neutral molecules and in ionic crystals. The compounds are often fluctional in solution and various sets of isomers have been discovered [2].

These compounds show tailored Lewis acid reactivity depending on the nature of the metal (Ga, In), the halogen (Cl, Br, I), and the phosphine ligand [3]. They are also sensitive to hydrolysis, and this is particularly true for the gallium(III) complexes [4]. It therefore was of no surprise that in many experiments small amounts of the corresponding hydrolysis products have also been observed even if moisture was rigorously excluded. A typical example has been the title salt, which appeared whenever gallium tribromide was reacted with 1,2-bis-(diphenylphosphino)benzene. After its identity had been confirmed by standard methods, the compound was prepared deliberately by controlled hydrolysis as described below (eq. (1)). Following the same procedure, but using gallium triiodide, the analogous tetraiodogallate(III) has also been obtained. A protonation of both phosphorus atoms was never observed. The formation of a second onium centre in cis position seems to be hindered by electrostatic repulsion.



The tetra*bromo*gallate crystallizes very well from chloroform. Its structure has been studied because the salt provides a unique chance for an internal comparison of phosphino and phosphonium functions at a common *ortho*-phenylene unit.

Structural Results

The title compound crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. The lattice is composed of independent tetrabromogallate anions and P-protonated ligand cations (Fig. 1).

The anion has a tetrahedral geometry with all angles close to the 109.48° standard [106.75(5) - 111.96(4)°]. The Ga-Br distances are in the narrow range 2.3044(2) - 2.3345(11) Å. The data compare well with literature values [1]. The cation shows no symmetry element, because the P-H bond is not in the potential mirror plane of the central phenylene ring. The P-C₆H₅/C₆H₄ bond lengths are significantly different for the protonated and non-protonated phosphorus atoms P1 and P2, respectively. The former bonds:

[P1-C1, -C111, -C121 = 1.790(7), 1.783(7), 1.7787(7) Å]

are consistently shorter than the corresponding data of the latter:

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Fig. 1. Molecular structure of [1,2-(diphenylphosphino)-(diphenylphosphonio)benzene](+)[tetra-bromo-gallate(III)](-) with atomic numbering (ORTEP drawing,

50% probability ellipsoids, hydrogen atoms of the phenyl groups omitted for clarity).

[P2-C2, -C211, -C221 = 1.845(7), 1.8825(7), 1.8840(7) Å].

In a similar way all C-P-C angles are smaller for the Ph_2P group (P2) as compared to the Ph_2PH^+ group (P1):

C1-P1-C111 111.5(3), C1-P1-C121 112.4(3), C111-P1-C121 109.5(3)°;

C2-P2-C211 102.4(3), C2-P2-C221 102.1(3), C211-P2-C221 105.9(3)°.

Protonation thus widens the C-P-C angles by an average of 7.3° and shortens the P-C bonds by 0.020 Å. There are no significant changes in the dimensions of the phenyl and phenylene groups. The conformation of the cation is such that the P1-H1 bond has a dihedral angle C2-C1-P1-H1 = 40.3° relative to the phenylene plane. It appears that the vector of the lone pair of electrons at P2 has roughly the same orientation, i.e. it is directed to the same side of the phenylene plane. However, the distance P1—P2 is too long for P1-H1–P2 hydrogen bonding.

Experimental Section

All experiments were carried out using standard equipment. For the preparation of the ligand see Ref. [5].

[1,2-(Diphenylphosphino)(diphenylphosphonio)benzene](+)[tetrabromogallate(III)](-)

A solution of 1,2-bis(diphenylphosphino)benzene (122 mg, 0.27 mmol) in 10 ml of toluene is treated with anhy-

drous GaBr₃ (83 mg, 0.27 mmol) without rigorous exclusion of moisture for 2 h at 20°C. A heavy pale yellow oil separates, which is taken up with chloroform and layered with pentane. Colourless crystals (147 mg, 64% yield) are collected and dried in a vacuum (m.p. 169° C).

C30H25Br4GaP2 (836.81)

Calcd C 43.06, H 3.01%, Found C 42.78, H 2.95%.

¹H NMR (CDCl₃, -60°C): δ 9.77, d [¹*J*(PH) = 528 Hz], 1H, PH; 6.94 - 7.82, m, 20H, C₆H_{5/4}. ³¹P{¹H}: δ 17.4, d; -0.9, d [³*J*(PP) = 80 Hz]. ¹³C{¹H}: δ 131.1, 135.2, 135.6, 136.4, 137.0, 143.1, all m, C₆H₄; 129.4, s and 131.9, d [⁴*J*(PC) = 4 Hz], C_{para}; 133.3, d [²*J*(PC) = 19 Hz] and 133.5, d [²*J*(PC) = 9 Hz], C_{ortho}; 128.7, d [³*J*(PC) = 7 Hz] and 130.3, d [³*J*(PC) = 13 Hz], C_{meta}; 114.6, dd [¹*J*(PC) = 88, ⁴*J*(PC) = 6 Hz] and 121.1, dd [¹*J*(PC) = 91, ⁴*J*(PC) = 36 Hz], C_{ipso}.

The analogous tetraiodogallate(III) was prepared similarly, m.p. 164°C, 66% yield.

$C_{30}H_{25}I_4GaP_2$ (1024.81)

Calcd C 35.16, H 2.46%, Found C 34.69, H 2.33%.

Crystal structure determination

A specimen of suitable quality and size (0.40 x 0.25 x 0.20 mm) was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å) with ω scan mode at -90°C. Lp correction was applied but data were not corrected for absorption effects. The structure was solved by Patterson methods and completed by full-matrix least-squares refinement against F².

 $C_{30}H_{25}Br_4GaP_2$, $M_r = 836.80$, monoclinic, a = $10.585(1), b = 23.490(2), c = 12.752(1) \text{ Å}, \beta = 106.25(1)^{\circ},$ space group $P 2_1/n$ [No. 14], Z = 4, $D_{calc} = 1.826$ g cm⁻³, $F(000) = 1624 \text{ e}, \ \mu(\text{Mo-K}_{\alpha}) = 62.8 \text{ cm}^{-1}.7189 \text{ inten-}$ sity data were measured up to $(\sin\theta/\lambda)_{max} = 0.64 \text{ Å}^{-1}$, of which 5515 independent structure factors were considered "observed" $[F_o \ge 4\sigma(F_o)]$ and used for refinement. All non-H atoms were refined with anisotropic displacement parameters; C-H-atoms were placed in idealized calculated positions and allowed to ride on their carbon atoms. The P-H atom was located and refined isotropically. The function minimized was $wR2 = \{ [\Sigma w (F_o^2 F_{\rm c}^{2}^{2}/\Sigma[w(F_{\rm o}^{2})^{2}]^{1/2}; w = 1/[\sigma^{2}(F_{\rm o}^{2})+(ap)^{2}+bp]; p =$ $(F_0^2 + 2F_c^2)/3$; a = 0.1027, b = 0.000. The final R and R_w values were 0.0590 and 0.1392, respectively, for 338 refined parameters; residual electron densities: +1.196/ -1.767 $e^{A^{-3}}$. Important bond lengths and angles are given

in the Figure Caption. Further information on the Xray structure determination can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 410067, the names of the authors, and the journal citation.

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