Diphosphonio-1,2-diphospholes: Structural P^{III}/P^{V} Hybrids

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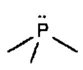
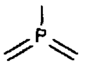
P-Methylation of the 3,5-bis(triphenylphosphonio)-1,2-diphospholide **1** leads to the dicationic diphosphole **3a**. A crystal of its bis(triflate) was used for a structure analysis. It indicates that in contrast to the known phospholes the cyclic π^6 system is preserved in **3a**. The coordination geometry of the methylated phosphorus atom shows a flat pyramid with a sum of angles of 339°. Therefore, **3a** represents a state that is intermediate between a phosphane and a bis(methylene)phosphorane, i.e. between P^{III} and P^{V}.

Geometries of Tricoordinated Phosphorus

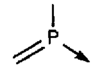
Tricoordinated phosphorus can be pyramidal or planar. The pyramidal coordination **A** is associated with the tervalent state and with a stereochemically active lone pair of electrons. In the case of the planar coordination these electrons are shared with the substituents in π bonds or are lost in an oxidation and are thus no longer of influence on the coordination geometry.



A

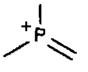


B^1

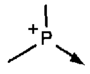


B^2

B^3



C^1



C^2

Planar phosphorus coordination is characteristically found in pentavalent tricoordinated phosphorus compounds of type **B^1** with two doubly bonded non-metal substituents[1a,2,3]. Type **B^2** with one double and one dative bond designates the wide field of dicoordinated phosphorus metal complexes of planar geometry (phosphaalkene, iminophosphane, diphosphene, phosphinine, heterophosphole complexes)[1b,4], and type **B^3** covers the field of the planar phosphinidene complexes[1c,5].

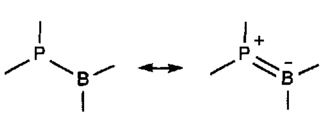
Cationic species of this type include methylene, imino, and chalcogenoxo phosphonium ions **C^1**[1b,6] and phosphenium complexes **C^2**[1b].

In accord with the clear distinction between pyramidal and planar coordination as suggested by **A** on the one hand and **B**, **C** on the other hand, the great majority of more than thousand tricoordinated phosphorus compounds which so far have been investigated by X-ray crystal structure analysis[7] fall in either one of the two categories with a sum of bond angles at phosphorus <325 and >355°. Only a small fraction (roughly 6–7%) shows a sum of bond angles in the range between the two extremes and represents the exception from the rule. Most of these structures belong to phosphanes and can still be described by type **A**. Their reduced pyramidal character may result from the steric demand or from the low electronegativity of one or several of their substituents.

Examples of the former type have been reported by using *tert*-butyl[8], *ortho*-disubstituted phenyl[9,10] and anthracenyl[11] substituents with sums of bond angles up to 344°.

The second type involves substituents with an electronegativity equal to or below that of phosphorus for which ligand-ligand repulsion becomes more important than the electron pair repulsion according to the VSEPR model[12]. In contrast to the small sum of angles in trihalophosphanes (PF_3 293°, PCl_3 301°, PBr_3 303°, PI_3 306°[12]) and trialkylphosphanes (PMe_3 296°[12]), the sum rises up to typically 330–345° in phosphanyl-, silyl- and gallylphosphanes or to even higher values where – in addition – bulky substituents are involved[13]. Metallophosphanes (metal phosphides, phosphido-metal complexes) often show a similarly reduced pyramidal coordination at P^{III} and may even reach almost planarity[14].

Of special interest are the borylphosphanes (phosphanylboranes). They often exhibit a sum of angles at the phosphorus atom of 330–350°[15], but also include cases of strict planarity, for which a double bond type **C^1** between the phosphorus and the boron of is assumed. The flat pyramides of other boryl phosphanes may thus be looked at as intermediate between **A** and **C^1**[15].



For sp^2 carbon substituents a situation intermediate between **A** and **B^1** could be expected but no definite example seems to be known. As suggested by formulas **D^1** and **D^2** phospholes could be candidates to verify this concept.

[+] X-ray structure analysis.

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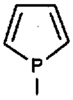
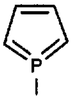
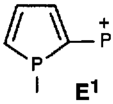
Phospholes are, however, non-aromatic with a decidedly pyramidal coordination of phosphorus[16-18] and obviously very little contribution of D^2[19]. Formula D^2 may gain importance when appropriate substituents at the carbon ring members hold the electrons in the cyclic π system and prevent a lone pair to be singled out by the phosphorus atom. Triphenylphosphonio groups in 2- or 3-position may play this role as indicated by formulas **E** and **F**[18].



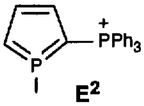
D^1



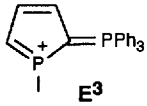
D^2



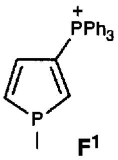
E^1



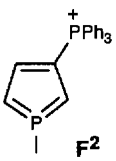
E^2



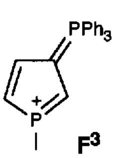
E^3



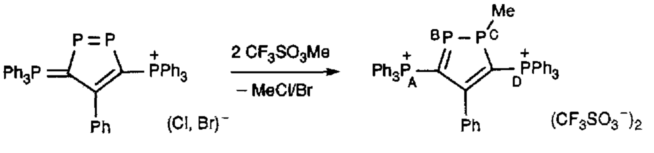
F^1



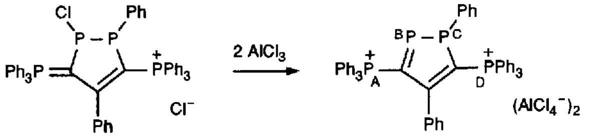
F^2



F^3



1 **3a**



2 **3b**

A first example of a twofold type **E** was achieved by protonation of 1,3-bis(triphenylphosphonio)isophosphindolide[20]. For the phosphorus atom of the protonated species a planar coordination was assumed on the basis of NMR data but could not be corroborated by an X-ray structure analysis. We now can report on the structure of an example of a type **E**/**F** combination.

Formation of 3,5-Diphosphonio-1,2-diphospholes

Recently we synthesized salts of the 3,5-bis(triphenylphosphonio)-1,2-diphospholide cation **1** and some of its dihydro derivatives such as **2**[21]. Cation **1** could not be protonated by triflic acid nor ethylated by ethyl triflate. However, it was methylated at a dicoordinated phosphorus atom to give a dication. Its bis(triflate) **3a** was isolated as yellow crystals suitable for an X-ray structure analysis. The corresponding phenyl dication **3b** resulted by chloride abstraction from **2**. The reaction is not unambiguous, however, and **3b** was identified only by means of its NMR spectrum.

A comparison of the ^{31}P-NMR data of **3** with those of the bis(phosphonio)diphospholide **1** (Table 1) reveals that the attachment of the substituent to P_C has only an insignificant or no effect at all on the still dicoordinated P_B atom: δ_{AB}, J_{AB} and most importantly J_{BC}[22] are essentially unchanged. The bonding system of the ring in **1** must thus be preserved in **3**. This is in contrast to the usual behavior of a phospholide which loses its aromatic character on protonation or alkylation[16]. Compared to the chemical shift of tricoordinated phosphorus atoms with a similar substitution, δ_C is found at rather low field and indicates a reduced pyramidal character[23]. The relatively small coupling J_{CD} and the relatively large coupling J_{AC} point more to a P^V than to a P^{III} character of P_C[21].

Molecular Structure of 3a

An X-ray structure analysis of compound **3a** shows the cation and triflate anions as expected in a 1:2 ratio. In Table 2 the relevant structural data of the dication **3a** are compared to those of the cation **1** from which it originates by methylation.

The outstanding structural feature of **3a** (Figure 1) is the flat pyramidal coordination of P4 with a sum of bond angles of 339°. A planar coordination would mean that the lone pair of P4 of **1** were used for bonding the methyl group, while a steep pyramidal coordination would mean that the electron pair were taken from the cyclic π system. **3a** seems to be closer to the first alternative. In a typical phosphole the sum of bond angles at phosphorus is 303°[16] but it may decrease to 295°[16] or 292°[24] where substituents further diminish the cyclic electron delocalization which is already very weak[25].

Each of the three carbon ring members in **3a** has maintained its planar coordination as in compound **1**, and the diphosphole ring as a whole has remained essentially planar

Table 1. ^{31}P-NMR data of **3a** and **3b** (ABCD spin systems) and of **1** (AA'BB' spin system)[18] for comparison; dichloromethane solution, coupling constants J in Hz

	δ_A	δ_B	δ_C	δ_D	$^2J_{AB}$	$^3J_{AC}$ AB'	$^4J_{AD}$ AA'	$^1J_{BC}$ BB'	$^3J_{BD}$	$^2J_{CD}$
3a	18.7	279.0	141.8	11.7	102.2	27.5	<5	468.5	9.1	30.5
3b	19.1	267.3	147.2	12.1	99.2	24.4	<10	483.7	<10	24.4
1	15.6	285.7			80.0	6.7	2.7	465.6		

Figure 1. Molecular structure of the dication of **3a** (25% probability ellipsoids, hydrogen atoms omitted for clarity)

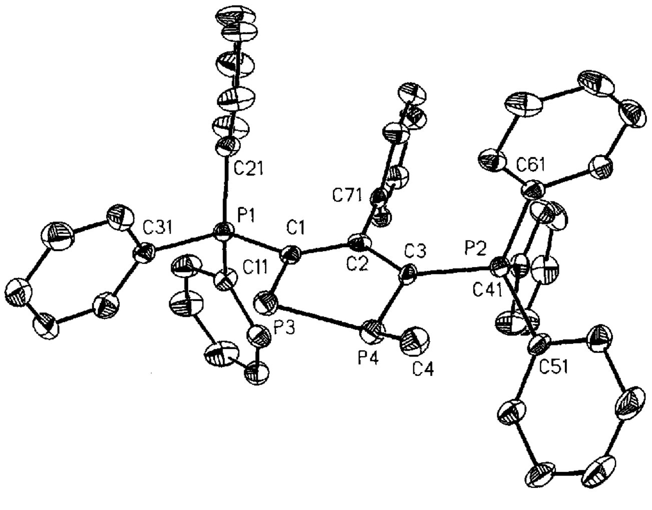
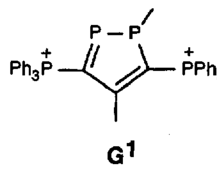


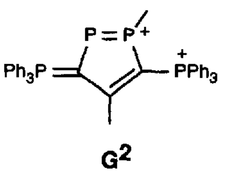
Table 2. Relevant bond lengths [pm] and bond angles [°] of the dication **3a** and of the cation **1**[18] for comparison

	3a	**1**		**3a**	**1**
P1–C1	178.5(6)	177.8(3)	C1–C2–C3	114.9(6)	114.8(3)
P2–C3	181.0(7)	177.9(3)	C1–C2–C71	123.0(6)	123.5(3)
C1–C2	141.4(10)	141.7(5)	C3–C2–C71	122.0(6)	121.6(3)
C2–C3	139.4(8)	141.2(5)	P3–C1–C2	120.6(5)	117.6(3)
P3–C1	176.0(7)	177.0(3)	P1–C1–P3	115.0(4)	119.0(2)
P4–C3	173.0(7)	177.3(3)	P1–C1–C2	124.3(5)	123.3(3)
P3–P4	207.4(3)	207.7(1)	P4–C3–C2	114.0(5)	117.6(3)
P4–C4	179.8(7)		P2–C3–P4	120.6(3)	117.1(2)
C2–C71	149.2(9)	150.8(5)	P2–C3–C2	125.3(5)	125.3(3)
			P4–P3–C1	87.7(2)	95.0(1)
			P3–P4–C3	99.4(2)	94.9(1)
			P3–P4–C4	119.7(3)	
			C3–P4–C4	119.9(3)	

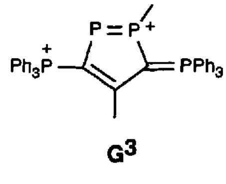
(sum of endocyclic angles 538.6° in **3a** as compared to 539.9° in **1**). Also the bond lengths have remained the same with two exceptions: The bond from the methylated P4 to the ylidic carbon atom C3 is 4 pm shorter, and the bond of the latter to the phosphonio center P2 is 3 pm longer. The endocyclic PC π bond is thus strengthened on methylation instead of being greatly reduced as in the case of normal phospholide ions.



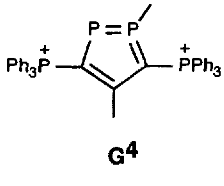
G^1



G^2



G^3



G^4

The bonding situation in **3** may consequently be described in terms of the resonance formulas **G^1**–**G^4** with special emphasis on **G^4**, and the tricoordinated phosphorus ring member of **3** may be understood as being intermediate between P^{III} (as in **A**) and P^{V} (as in **B^1** and **C^1**).

The flat pyramidal coordination of the phosphorus atoms of a 1,3-diphosphetanediyl (sum of bond angles: 338°) was recently interpreted similarly[10].

Experimental

All manipulations were carried out in flame-dried glassware under dry argon by using Schlenk technique. Dry dichloromethane and benzene were used as obtained (Fluka). – NMR: Jeol GSX 270 (^{31}P), Jeol EX 400 (^{1}H) with Me$_4$Si (int.) and 85% H$_3$PO$_4$ (ext.) as standards. – ^{31}P-NMR data are compiled in Table 1.

4-Phenyl-3,5-bis(triphenylphosphonio)-1,2-diphospholide Chloride/Bromide (**1**) *and 1-Chloro-2,4-diphenyl-3,5-bis(triphenylphosphonio)-1,2-dihydro-1,2-diphospholide Chloride/Bromide* (**2**) were prepared as described[18].

1-Methyl-4-phenyl-3,5-bis(triphenylphosphonio)-1,2-diphosphole Bis(triflate) (**3a**): To a stirred solution of **1** (2.15 g, 2.8 mmol) in 10 ml of dichloromethane methyl trifluoromethanesulfonate (0.90 g, 5.6 mmol) was added at room temp. After stirring of the resulting yellow solution for 30 min and addition of 5 ml of benzene, yellow crystals of **3a** precipitated. They were filtered off, washed twice with benzene/dichloromethane (1:1) and dried under argon. Concentration of the filtrate afforded a second crop. Yield 2.20 g (78%), m.p. 241–243 °C, (dec., sealed capillary, uncorrected). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.76 (dd, $^2J_{PH}$ = 11.8, $^3J_{PH}$ = 6.4 Hz, 3H, PMe), 6.11–6.20 (m, 4H, *o,m*-H, C-Ph), 6.62 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *p*-H, C-Ph), 7.55–7.83 (m, 30H, *o,m,p*-H, P-Ph). – C$_{48}$H$_{38}$F$_6$O$_6$P$_4$S$_2$ (1012.8): calcd. C 56.92, H 3.78; found C 56.66, H 3.92.

1,4-Diphenyl-3,5-bis(triphenylphosphonio)-1,2-diphosphole Bis(tetrachloroaluminate) (**3b**): In an NMR tube 122 mg (0.1 mmol) of **2** was dissolved in 0.5 ml of dichloromethane; then 34 mg (0.2 mmol) of aluminium trichloride was added at −78 °C. After 10 min a ^{31}P-NMR spectrum was recorded at room temp.

Crystal Structure Analysis of **3a**: C$_{48}$H$_{38}$F$_6$O$_6$P$_4$S$_2$, M = 1012.78, crystal size: 0.45 × 0.3 × 0.28 mm^3, yellow block, triclinic, space group $P\bar{1}$, a = 10.474(3), b = 12.230(4), c = 18.941(13) Å, α = 75.49(3), β = 82.65(3), γ = 83.48(2)°, V = 2321(2) Å^3, Z = 2, $d_{calcd.}$ = 1.449 Mg/m^3, μ = 0.326 mm^{-1}, $F(000)$ = 1040. Siemens P4 diffractometer, Mo-K_α, λ = 0.71073 Å, ω scans, T = 293(2) K, 2Θ range = 3.46 to 48.08° in $0 \leq h \leq 11$, $-13 \leq k \leq 13$, $-20 \leq l \leq 21$, reflections collected: 7513, independent reflections: 7042 (R_{int} = 0.0644), observed reflections: 4186 [$F > 4\sigma(F)$], scan speed: 4 to 60.0°/min in ω, scan range (ω): 1.8°. Structure solution program: XS (Siemens), direct methods, data-to-parameter ratio: 11.2:1 (6.7:1 [$F > 4\sigma(F)$]), final R indices [$F > 4\sigma(F)$]: $R1$ = 0.0931, $wR2$ = 0.2909 (all data), GOF on F^2 = 1.029, largest and mean Δ/σ: −0.760, 0.033, largest difference peak/hole: 0.895, −0.530 eÅ^{-3}, program used: SHELXL (Sheldrick 1993). Three fluorine atoms showed large thermal ellipsoids. They were refined with restraints for C–F distances to comply with the C_{3v} symmetry of the triflate group. Further details are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405327.

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