Diphosphonio Dihydrophosphetide and 1,2-Diphospholide Cations

Georg Jochem, Alfred Schmidpeter* and Heinrich Nöth

Dedicated to Professor Rolf Appel on the occasion of his 75th birthday

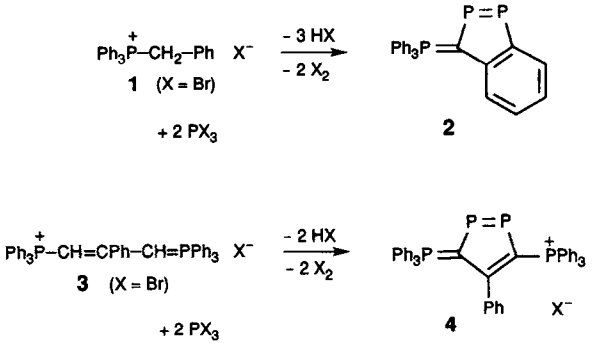
Abstract: Condensation of a 1,3-diphosphoniopropenide cation at its reactive 1,3-positions with a dichlorophosphine in the presence of triethylamine provides a route to 2,4-diphosphoniodihydrophosphetide cations. An excess of dichlorophosphine in the presence of an additional reducing agent results in a ring expansion and yields 3,5-diphosphoniodihydro-1,2-diphospholide cations. The chlorosubstituted cation derived from PCl_3 can be further reduced to the hydrolytically stable 3,5-diphosphonio-1,2-diphospholide cation. It adds halogen to the P=P bond and can easily be regained from the halogen adduct. Structural comparison of the 1,2-diphenyl- and 1,2-dichlorodihydro-1,2-diphospholide cation with the 1,2-diphospholide cation shows three stages of interaction of the C_3 and the P_2 entities of the ring: no conjugation in the first case, hyperconjugative extension of the allylic system to include the phosphorus atoms in the second case and cyclic π conjugation in the third.

Keywords
heterocycles · organic syntheses · phospholes · phosphorus ylides · ring expansions

Introduction

In contrast to 1,3-diphospholes, little is known about 1,2-diphospholes. The first examples were metal-coordinated.[1, 2] Recently we reported the first noncoordinated representative, the phosphoranylidene-substituted and benzanellated 1,2-diphosphole **2**. It resulted from the unintentional and unexpected formation of the five-membered ring in the reaction of benzyl triphenylphosphonium bromide **1** and phosphorus trichloride and its subsequent reduction (Scheme 1),[3] or simply from the sulfide-initiated disproportionation of the primary product of this reaction.[4] Assuming similar reactivity we hoped to obtain the diphosphonio-1,2-diphospholide **4** from the 2-phenyl-1,3-bis(triphenylphosphonio)propenide bromide **3**.[5] At the same time we expected that these investigations would throw light on the pathway by which the five-membered ring is formed. The intended synthesis may furthermore be compared to that of the first monocyclic and noncoordinated 1,2-diphospholide ion which was reported by F. Mathey et al.[6] very recently.

The phosphonio-substituted phospholides merit special interest for the unusual behaviour of their phosphorus ring member(s) as already discussed for the diphosphonio isophosphindolide cation.[7, 8]



Scheme 1.

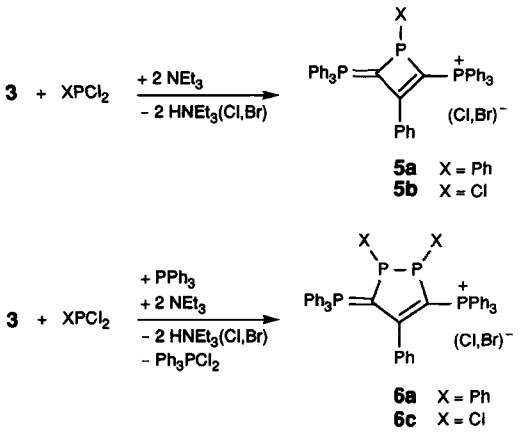
Results and Discussion

Synthesis: Chlorophosphines react with benzyl triphenylphosphonium halides in the presence of triethylamine to give phosphino-substituted phosphonium ylides.[9] In the same way, one equivalent of phenyl dichlorophosphine or phosphorus trichloride and two equivalents of triethylamine react with compound **3**. Both positions adjacent to the phosphonio centres are substituted, yielding the 2,4-bis(triphenylphosphonio)-3-phenyl dihydrophosphetide halide **5** (Scheme 2). This reaction is complete within some minutes at room temperature. Besides **5** as the principal product, the reaction mixture always contains a small amount of the respective 3,5-bis(triphenylphosphonio)-4-phenyl-1,2-dihydro-1,2-diphospholide halide **6** (molar ratio 5:1 in the case of **5a** and **6a**), which can be identified by its characteristic AA'BB' signal pattern in the $^{31}P\{^1H\}$ NMR spectrum. The isolated products **5a** and **b** therefore also contain small amounts of **6**. The compounds **6** can be understood to be formed from the primary product **5** and a second molecule of the chlorophosphine by reductive P–P coupling and expansion of the four-membered ring; compound **5** must serve in this instance as the reducing agent. Consequently, if compound **3** is made to react with two equivalents of the dichlorophosphine $XPCl_2$, one equivalent of triphenyl phosphine as reducing agent[10] and again two equivalents of triethylamine, compound **6** becomes

[*] Prof. Dr. A. Schmidpeter, Dr. G. Jochem, Prof. Dr. H. Nöth[+]
Institut für Anorganische Chemie der Universität
Meiserstrasse 1, D-80333 München (Germany)
Telefax: Int. code +(89) 5902-578
e-mail: ui161aa@sunmail.lrz-muenchen.de

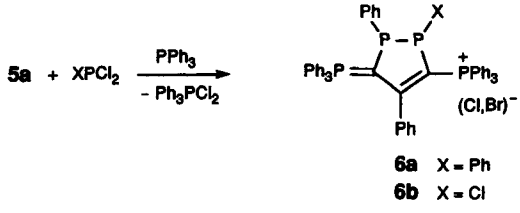
[+] X-ray stucture investigations.

  0947-6539/96/0202-0221 $ 10.00+.25/0



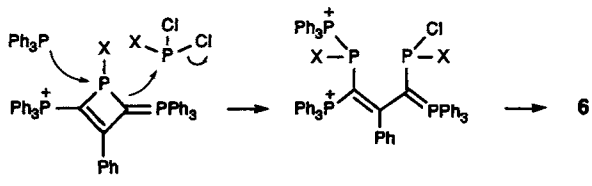
Scheme 2.

the main product. Monitoring the reaction by $^{31}P\{^1H\}$ NMR reveals that **6** in fact forms from **5** as the intermediate. The latter is generated in a rapid first step of the reaction and is then slowly converted to **6**. Compound **6a** is also formed when one equivalent each of $PhPCl_2$ and PPh_3 are added to a solution of **5a**. Furthermore, compound **5a** reacts with PCl_3 and PPh_3 to give selectively the mixed substituted representative **6b** (Scheme 3). No subsequent exchange of the two phosphorus ring members (PCl and PPh) can be observed.



Scheme 3.

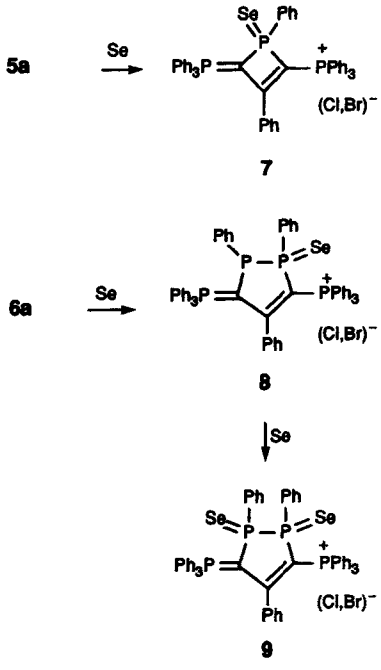
These results clearly identify the compounds **5** as intermediates in the reaction sequence leading from **3** to **6**. The second step from **5** to **6** corresponds in principle to the conversion of a 1,2-dihydrophosphete to a 2,3-dihydro-1,2-diphosphole in the synthesis of the 1,2-diphospholide.[6] It is probably formed by a different mechanism, however, as **5** can attack the dichlorophosphine by its nucleophilic ylidic carbon atom. The resulting ring opening will be followed by the addition of triphenylphosphine (or in its absence by the addition of the phosphine moiety of a second molecule of **5**) and by the elimination of a chlorophosphonium ion, closing the ring again (Scheme 4).



Scheme 4.

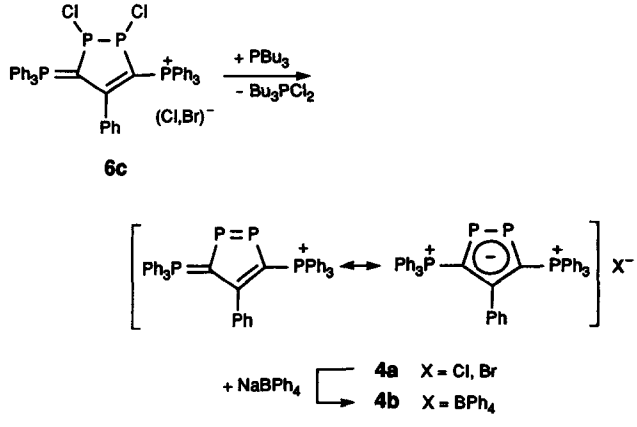
In the same way the synthesis of the bromo derivative **6d** has been attempted from **3**, PBr_3, PPh_3 and NEt_3. Indeed, it can be identified by its ^{31}P NMR spectrum (Table 1), but it is heavily contaminated by the polymeric phosphorus subbromides known to result from reduction of PBr_3 by PPh_3.[10]

To obtain **5** and **6** as pure products they must be separated from the triethylammonium halides. This was possible for **6** by recrystallization from a dichloromethane/benzene mixture leading to isolation as mixed chloride/bromides. They form air-sensitive yellow crystals which are readily soluble in dichloromethane or chloroform and insoluble in nonpolar solvents like benzene. Attempts to isolate pure **5a** and **b** were unsuccessful. Compound **5a** can, however, be oxidized with grey selenium to give the phosphine selenide **7** (Scheme 5), which is stable towards water; this allows easy removal of the triethylammonium salts. Analogously, **6a** forms the monoselenide **8**, characterized only in solution, and the diselenide **9**.



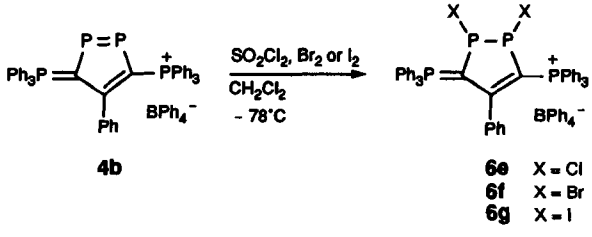
Scheme 5.

Reduction of **6c** with tri-*n*-butylphosphine yields a mixed chloride/bromide of the expected 1,2-diphospholide cation; its salt **4a** (Scheme 6) can be isolated as colourless crystals, which



Scheme 6.

are stable towards air and water. By metathesis, the halide ions in **4a** can be exchanged for the tetraphenylborate anion to give **4b**. Halogenation of **4b** yields the 1,2-dihalodiphospholide tetraphenylborates **6e–g** (Scheme 7). This reaction complements



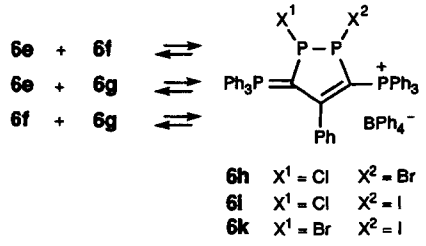
Scheme 7.

0947-6539/96/0202-0222 $ 10.00+.25/0 Chem. Eur. J. 1996, 2, No. 2

the direct synthesis of compounds **6** by which the dibromo and diiodo derivatives are not accessible. The addition can easily be reversed, in the case of the diiododiphospholide **6g**, for example, by treating its dichloromethane solution with elemental mercury. Even without a reducing agent added the ^{31}P NMR spectra of **6e–g** in dichloromethane solution always contain the signals of **4b** and some others which could not be assigned. Their intensities increase with time and are higher in the case of the iodo derivative **6g** than of the chloro derivative **6e**. Obviously compounds **6** are self-reductive. This is in accord with the observation that they can take up more halogen, the ring system being destroyed in the reaction.

^{31}P NMR Spectra: The $^{31}P\{^1H\}$ NMR spectra (Table 1) of the four-membered-ring compounds **5** and **7** reveal A_2B spin systems for the phosphorus nuclei. The spectra of the five-membered-ring compounds **4**, **6**, **8** and **9** represent AA'BB' spin systems in the case of the symmetrically substituted derivatives, and ABCD spin systems in the case of the unsymmetrically substituted derivatives. Although with regard to the substituents at P1 and P2 in **6**, **8** and **9** *cis* and *trans* isomers would be possible, only signals of the latter (see below) are observed. The signals of the triphenylphosphonio groups of the four-membered compounds **5** and **7** ($\delta_A \approx 7$) are characteristically found at higher field than those of the five-membered-ring compounds **4**, **6**, **8** and **9** ($\delta_{A,D} \approx 16$). The chemical shift of the ring phosphorus atoms varies with their coordination number and the nature of their substituents. A value of $\delta = 286$ found for the two-coordinate phosphorus atoms in **4** is in agreement with the shift of those atoms in other five-membered-ring compounds and in particular in compounds of type **2**. The phosphorus atom next to the triphenylphosphonio group gives rise to a signal at $\delta = 309-317$ and the other at $\delta = 219-229$.[3] In diphospholides not influenced by phosphonio groups this signal is found at considerably higher field: $\delta = 152-206$.[6] The phosphorus–phosphorus coupling constants confirm the structures of **4–9**: $^1J_{PP} = -466$ Hz for **4** clearly indicates a cyclic diphosphene group; values of the coupling constants from -460 to -500 Hz were found for five-membered-ring compounds with this structural moiety such as 1,2-diphospholides[3, 6] or 1,2,3-triphospholides.[13, 14] Coupling constants $^1J_{PP}$ for **6** are typical for diphosphines, especially cyclophosphines, and point to a *trans* position of the substituents at the phosphorus atoms. The constants $^2J_{PP}$ for the coupling between the substituent phosphonio group and the tervalent phosphorus atom in the five-membered rings of **4** and **6** lie in the usual range[3, 7] and as expected[15] are considerably smaller in the four-membered rings of **5**.

Halogen Exchange: The ^{31}P NMR spectra of equimolar mixtures of **6e** and **f**, **6e** and **g** and **6f** and **g** in dichloromethane solution show very broad and unstructured signals for P1 and P2 and an averaged signal for 3,5-PPh_3 instead of the signals of the individual compounds. They indicate a rapid exchange of halogen substituents (resulting in **6h**, **6i** and **6k**, respectively; Scheme 8). This can be demonstrated by adding halide, which



Scheme 8.

increases the rate of exchange: the signals of PCl and PBr in the spectrum of the equilibrium mixture of **6e** and **f** (shown in Fig. 1, top) recorded at ambient temperature merge into one at an averaged position on addition of a catalytic amount of benzyl triphenylphosphonium bromide.

At $-80\,^\circ C$ in the ^{31}P NMR spectra of each of the above mixtures, separate signals are observed for the two symmetrical dihalodiphospholides and for the mixed substituted species **6h**, **6i** or **6k**, respectively, formed by halogen exchange. The molar ratio of the three compounds in each equilibrium mixture is nearly statistical (1:1:2). In the case of the Cl/Br (Fig. 1, bottom) and the Cl/I systems the exchange rate at $-80\,^\circ C$ is slow enough to allow the recording of well-resolved spectra of the three components, including the spectra of ABCD spin type of

Table 1. ^{31}P NMR data of compounds **4–11** in CD_2Cl_2. δ_D refers to the PPh_3 group at C3, δ_A to other PPh_3 groups; δ_B refers to P1 or to P1,2 if equivalent, δ_C to P2. Coupling constants J are given in Hz; where signs are given they originate from a simulation of the spectrum by LAOCOON [11] and refer to $J_{BC} = {}^1J_{PP}$ taken as negative [12].

	Substituents P1	P2	Anion	Spin system [a]	δ_A	δ_B	δ_C	δ_D	$^2J_{AB}$	$^3J_{AC,AB'}$	$^4J_{AD,AA'}$	$^1J_{BC,BB'}$	$^3J_{BD}$	$^2J_{CD}$
5a	Ph		Br,Cl	A_2B	6.6	20.3			36.6					
5b	Cl		Br,Cl	A_2B	7.1	97.2			37.4					
5c	Br		Br	A_2B	6.9	96.0			36.6					
7 [b]	Ph, Se		Br,Cl	A_2B	6.7	46.3			18.3					
4a [c]			Br,Cl	$[AB]_2$	15.6	285.7			+80.0	−6.7	+2.7	−465.6		
4b [c]			BPh_4	$[AB]_2$	15.6	285.8			+80.2	−6.5	+2.7	−465.5		
6a [c]	Ph	Ph	Br,Cl	$[AB]_2$	15.3	−2.9			+86.1	−5.8	+1.6	−237.4		
6b	Cl	Ph	Br,Cl	ABCD	17.6	132.3	2.4	15.0	87.0	<5	<5	280.0	4.4	85.5
6c [c]	Cl	Cl	Br,Cl	$[AB]_2$	16.9	101.9			+85.3	−5.2	+0.8	−260.9		
6d [c]	Br	Br	Br	$[AB]_2$	16.4	97.7			+83.7	−7.4	<1	−246.6		
6e [c]	Cl	Cl	BPh_4	$[AB]_2$	16.7	101.9			+85.8	−4.7	+1.0	−261.2		
6f [c]	Br	Br	BPh_4	$[AB]_2$	16.4	97.9			+83.3	−7.0	+0.1	−247.3		
6g [c]	I	I	BPh_4	$[AB]_2$	16.5	92.1			+80.7	−9.0	+0.2	−231.9		
6h [d]	Cl	Br	BPh_4	ABCD	16.4	102.1	96.5	16.2	78.6	<5	<5	254.4	<5	78.6
6i [d]	Cl	I	BPh_4	ABCD	16.3	108.0	71.7	15.6	80.9	8.4	<2	244.1	6.1	81.6
6k [d,e]	Br	I	BPh_4	ABCD		107	77							
8 [f]	Ph, Se	Ph	Br,Cl	ABCD	15.8	51.0	1.1	15.9	25.6	6.1	3.5	222.8	32.3	68.3
9 [g]	Ph, Se	Ph, Se	Br,Cl	$[AB]_2$	16.6	38.6								

[a] Relating to ^{31}P nuclei only. [b] $^1J_{SeP} = 777.0$ Hz, $\delta^{77}Se = -292.7$. [c] Coupling constants obtained from simulation. [d] At $-80\,^\circ C$. [e] Broad signals; coupling constants and δ_A and δ_D were not obtained. [f] $^1J_{SeP} = 756.6$ Hz, $^2J_{SeP} < 10$ Hz. [g] $\delta^{77}Se = -129.7$; because of superposition of the ^{77}Se satellites in the ^{31}P NMR spectrum, coupling constants were not obtained, except $N_{AB} = 52.1$ Hz.

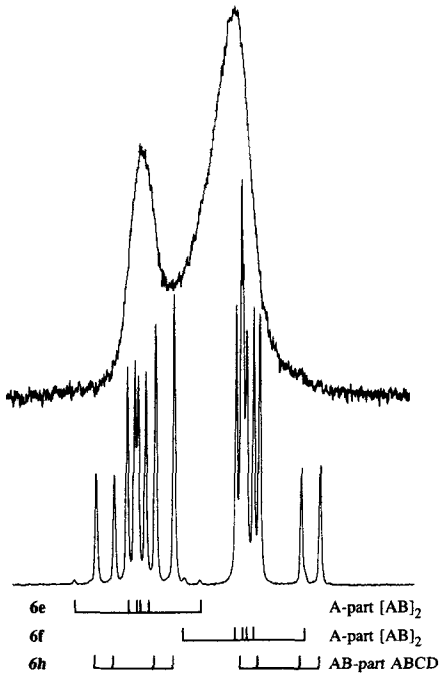


Fig. 1. Low-field part of the $^{31}P\{^1H\}$ NMR spectrum of the equilibrium mixture of equimolar amounts of **6e** and **6f**, top: at 25 °C; bottom: at −80 °C showing superimposed one half each of the AA'BB' spectra of the symmetric compounds **6e** and **6f** and of the ABCD spectrum of the mixed substituted compound **6h**.

6h and **6i**. However, the signals stay broad for the Br/I system.

It seems noteworthy that the phosphorus chemical shifts of PX^1 and PX^2 in any mixed substituted dihalodiphospholide **6** deviate more from each other than the shifts of the two symmetric parent compounds. This is most pronounced for the combination Cl/I in **6i**. As a rule, the phosphorus nucleus in a bromophosphine is a little more shielded and in an iodophosphine considerably more shielded than in the corresponding chlorophosphine.[16] This is also true for compounds **6**. However, as shown in Figure 2, the chemical shift also depends on the halogen at the neighbouring phosphorus, but in the opposite sense and somewhat less. This may be explained by the electronic effect of the allylic part of the ring for which the two phosphorus atoms compete (see Molecular Structures). As a consequence of the counteracting influences in the symmetric compounds **6e**, **f** and **g**, the chemical shifts of the latter are rather similar (Table 1). Also consistent with this picture is the low-field signal of the PCl group in compound **6b**.

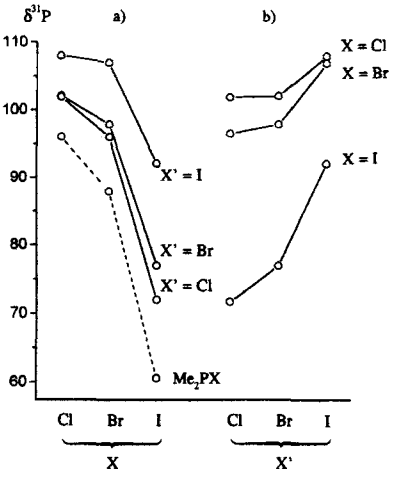


Fig. 2. Dependence of δ(PX) of compounds **6**: a) on the nature of halogen X with the halogen X' at the neighbouring phosphorus atom kept constant, b) on the nature of the halogen X' at the neighbouring phosphorus atom for a constant PX group. In a) $\delta(Me_2PX)$ is shown for comparison [16].

Molecular Structures: Single-crystal X-ray investigations of the compounds **4a**, **6c** and **6a** prove them to be ionic also in the solid state. The compounds result from the synthesis as mixtures of chloride and bromide and the crystals also represent mixed chloride/bromides. The ratio of chloride to bromide and the amount of cocrystallizing solvent found by elemental and structural analyses do not always correspond. Figures 3, 4 and 5 show the molecular structures of the three cations. In the diphosphoniodiphospholide cation of **4a** the ring is almost perfectly planar with the four phosphorus atoms hardly (5 pm at the most) deviating from the plane C1-C2-C3. In the dichloro-

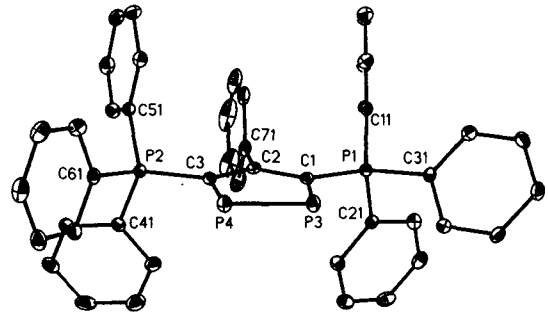


Fig. 3. Molecular structure of the cation in **4a** (thermal ellipsoids with 25% probability).

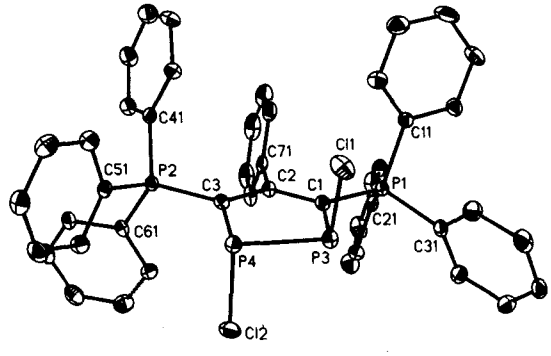


Fig. 4. Molecular structure of the cation in **6c** (thermal ellipsoids with 25% probability).

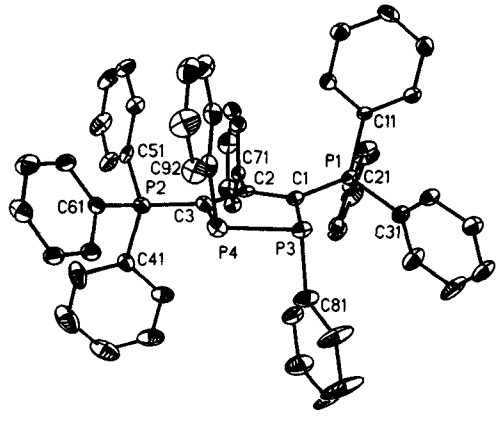


Fig. 5. Molecular structure of the cation in **6a** (thermal ellipsoids with 25% probability).

0947-6539/96/0202-0224 $ 10.00+.25/0 Chem. Eur. J. 1996, 2, No. 2

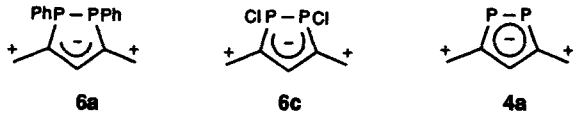
and diphenyl-substituted cations of **6c** and **6a** the substituents at P3 and P4 (corresponding to P1 and P2 in heterocyclic nomenclature) are in the *trans* position. The ring members P3 and P4 deviate significantly (up to 14 pm) from the plane C1-C2-C3 in the corresponding directions; this results in a flat half-chair conformation of the ring. In each case the phenyl ring at C2 stands roughly perpendicular to this plane (Table 2).

Table 2. Relevant bond lengths (pm) and bond and dihedral angles (°) of **4a**, **6c** and **6a**.

	4a	6c	6a
P1–C1	177.8(3)	176.8(5)	174.2(6)
P2–C3	177.9(3)	177.3(5)	174.4(6)
C1–C2	141.7(5)	141.0(7)	142.2(7)
C2–C3	141.2(5)	141.0(6)	141.2(7)
C1–P3	177.0(3)	179.4(5)	183.2(5)
C3–P4	177.3(3)	179.4(5)	183.8(6)
P3–P4	207.7(1)	221.6(2)	219.3(2)
C2–C71	150.8(5)	150.7(7)	149.1(7)
P3–Cl, C81	–	212.3(2)	184.4(7)
P4–Cl2, C91	–	212.6(2)	184.3(7)
C1-C2-C3	114.8(3)	118.9(4)	118.6(5)
C1-C2-C71	123.5(3)	120.1(4)	120.5(5)
C3-C2-C71	121.6(3)	121.0(4)	120.9(5)
P1-C1-C2	123.3(3)	124.8(4)	128.4(4)
P1-C1-P3	119.0(2)	118.2(3)	115.1(3)
C2-C1-P3	117.6(3)	117.0(4)	116.2(4)
P2-C3-C2	125.3(3)	125.3(4)	127.0(4)
P2-C3-P4	117.1(2)	117.6(3)	115.8(3)
C2-C3-P4	117.6(3)	117.1(4)	117.2(4)
C1-P3-P4	95.0(1)	93.4(2)	94.1(2)
C1-P3-Cl1, C81		103.2(2)	101.0(3)
P4-P3-Cl1, C81		94.2(1)	98.5(3)
C3-P4-P3	94.92(12)	93.2(2)	93.0(2)
C3-P4-Cl2, C91		102.6(2)	103.1(3)
P3-P4-Cl2, C91		93.1(1)	102.7(2)
P1-C1-P3-Cl1,C81		87.5	−94.4
P2-C3-P4-Cl2,C91		92.3	−87.7
C2-C1-P3-Cl1,C81		− 90.5	91.2
C2-C3-P4-Cl2,C91		− 87.5	96.2
Cl1,C81-P3-P4-Cl2,C91		−159.4	161.8

The cations may be viewed as being composed of the phosphocyanine system P1-C1-C2-C3-P2[17] and the diphosphene or diphosphine group P3–P4 bridging C1 and C3. The way in which the two fragments interact is in fact the most interesting aspect of the comparison of the three structures: in the phenyl derivative **6a** they behave rather independently. The distances in the phosphocyanine part (d_{PC} = 174.3(6), d_{CC} = 142.2(7) pm, averaged values) are similar to those in an acyclic analogue (d_{PC} = 172,5(4), d_{CC} = 139.1(5) pm[18]) and the bonds C1–P3 and C3–P4 as well as P3–P4 are normal single bonds.[19] The differences observed when the phenyl substituents are replaced by chlorine atoms in **6c** indicate an electron shift from C1 and C3 to P3 and P4, respectively. This is expressed by elongation of the ylidic P–C bonds (3 pm), a shortening of the endocyclic P–C bonds (4 pm) and—again—an elongation of the P–P bond (2 pm). Furthermore, the P–Cl bonds are longer than normal (PCl_3: 204 pm[19]), indicating that electron density from the allylic π system C1-C2-C3 is transferred to the antibonding PCl orbitals. This transfer is possible as the dihedral angles are close to 90° (Table 2) and the two interacting orbitals are thus roughly parallel, a prerequisite for this kind of interaction (negative hyperconjugation).[20]

On reduction of **6c** to **4a** the P–P bond becomes 14 pm shorter. The distance of 207.7(1) pm is now characteristic of a double bond. The bond is, however, still somewhat longer than in acyclic *trans* diphosphenes (202–204 pm[21]) but is comparable to that in 1,2,3-azadiphospholes (205.5(9)[22] or 206.3 (1) pm[23]), where it is part of a cyclic π conjugated system. It seems most remarkable that the P–C bond lengths change less in going from **6c** to **4a** than from **6a** to **6c**, although the three-coordinated phosphorus atoms in **6** prevent cyclic π conjugation: the ylidic bonds remain almost unchanged and the endocyclic P–C bonds are only 2 pm shorter in **4a** than in **6c**. This means that the structural effect of the negative hyperconjugation in **6c** is almost as strong as the effect of π conjugation in **4a**.



6a **6c** **4a**

The three cations may thus be described and distinguished in short by the symmetric formulae with two positively charged phosphonio substituents and a negatively charged ring. In **6a** this surplus of electrons in the ring is restricted to the allylic system and no conjugation to the phosphorus atoms of the ring is observed. The delocalized system extends by negative hyperconjugation to the two phosphorus atoms of the ring in **6c** and eventually includes all ring members and becomes "aromatic" by π conjugation in **4a**.

Experimental Procedure

All operations were carried out in flame-dried glassware under dry argon by Schlenk techniques. Tetrahydrofuran was dried by refluxing it with sodium/benzophenone and distillation. Pentane was dried over a molecular sieve (4 Å). Dry dichloromethane and benzene were used as obtained (Fluka). Triethylamine was dried by refluxing with sodium/benzophenone and distillation. The chlorophosphines were distilled prior to use. Triphenyl methylenephosphorane [24] was prepared from methyl triphenylphosphonium bromide (Merck) and sodium bis(trimethylsilyl)amide [25] in benzene. Phenylethinyl triphenylphosphonium bromide [26] was obtained from the alkylation of triphenylphosphine with bromophenyl acetylene [27] in tetrahydrofuran. Melting points were measured in sealed capillaries and are uncorrected. NMR: Jeol GSX270 (^{31}P, ^{77}Se), Jeol EX400 (^{1}H, ^{13}C) with TMS (int.), 85% H_3PO_4 (ext.) and Me_2Se (ext.) as standards. ^{31}P and ^{77}Se NMR data are given in Table 1. The atoms of Ph_3P groups are identified as *o,m,p*-H and *i,o,m,p*-C, the atoms of *C*-phenyl groups as 2,3,4-H and C-1,2,3,4, the atoms of *P*-phenyl groups as C-5,6,7,8.

1,3-Bis(triphenylphosphonio)propenide bromide (3): (ref. [5], without detailed procedure.)] To a magnetically stirred solution triphenyl methylenephosphorane (45.28 g, 127.1 mmol) in THF (300 mL), solid phenylethinyl triphenylphosphonium bromide (56.21 g, 127.1 mmol) was added at room temperature. A dark red solution and a yellow precipitate were formed instantaneously; the reaction mixture was stirred for 15 h at room temperature. The yellow precipitate was filtered off, washed with 3 × 50 mL of THF and dried in vacuo. Yield 67.7 g (74%). $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2): δ = 10.3 (s), 11.4 (s); ^{1}H NMR (CH_2Cl_2): δ = 3.50 (d, $^{2}J_{PH}$ = 15.2 Hz, 1H, PCH), 3.59 (dd, $^{2}J_{PH}$ = 22.7 Hz, $^{4}J_{PH}$ = 7.1 Hz, 1H, PCH), 6.78–6.84 (m, 4H, arom. H), 6.95–7.01 (m, 7H, arom. H), 7.31 (m, 6H, *m*-H), 7.48 (m, 3H, *p*-H), 7.59–7.74 (m, 15H, arom. H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 59.4 (dd, $^{1}J_{PC}$ = 121.3 Hz, $^{3}J_{PC}$ = 6.9 Hz, C-PPh_3), 60.9 (dd, $^{1}J_{PC}$ = 102.2 Hz, $^{3}J_{PC}$ = 16.8 Hz, C-PPh_3), 123.1 (d, $^{1}J_{PC}$ = 88.5 Hz, *i*-C), 125.3 (d, $^{1}J_{PC}$ = 90.1 Hz, *i*-C), 127.4 (s), 127.8 (s), 127.8 (s, C-4), 129.0 (d, $^{3}J_{PC}$ = 12.2 Hz, *m*-C), 129.8 (d, $^{3}J_{PC}$ = 12.2 Hz, *m*-C), 132.3 (d, $^{2}J_{PC}$ = 9.2 Hz, *o*-C), 132.6 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-C), 132.8 (d, $^{2}J_{PC}$ = 10.7 Hz, *o*-C), 133.6 (s, *p*-C), 142.7 (dd, $^{3}J_{PC}$ = 16.8 Hz, $^{3}J_{PC}$ = 6.1 Hz, C-1), 171.0 (t, $^{2}J_{PC}$ = 6.8 Hz, C-Ph).

4-Phenyl-3,5-bis(triphenylphosphonio)-1,2-diphospholide chloride/bromide (4a): To a magnetically stirred solution of crude **6c** (20.50 g, ca. 21 mmol, contaminated by about 10% by weight of triethylammonium chloride) in dichloromethane (60 mL), tributylphosphine (4.39 g, 21.7 mmol) was added through a syringe. The colour of the solution turned from dark yellow to pale yellow. After 3 h of stirring at room temperature, benzene (100 mL) was added. After 5 d pale yellow crystals had separated. They were filtered off, washed twice with a 2:1 mixture of benzene and dichloromethane and dried in vacuo. A solution of these crystals in dichloro-

methane (100 mL) was washed with 4 × 20 mL of water to remove the ammonium salts, then the solvent was removed in vacuo and the pale yellow residue was recrystallized from dichloromethane/benzene. Yield 15.1 g (ca. 90%), pale yellow crystals of **4a**·0.5 C_6H_6, decomp. above 285 °C. $[C_{45}H_{35}P_4]Br_{0.5}Cl_{0.5}\cdot 0.5\,C_6H_6 = C_{48}H_{38}Br_{0.5}Cl_{0.5}P_4$ (796.4): calcd C 72.39 H 4.81, found C 72.32 H 4.88; ^{1}H NMR ($CDCl_3$): δ = 5.84 (d, $^3J_{HH}$ = 7.3 Hz, 2H, 2-H), 6.00 (t, $^3J_{HH}$ = 7.3 Hz, 2H, 3-H), 6.47 (t, $^2J_{HH}$ = 7.3 Hz, 1H, 4-H), 7.20 (s, 3H, C_6H_6), 7.30–7.42 (m, 24H, *o,m*-H), 7.55 (m, 6H, *p*-H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 122.0 (d, $^1J_{PC}$ = 89.3 Hz, *i*-C), 126.3 (s, C-2/3) 126.4 (s, C-4), 126.4 (m, *C*-PPh_3), 127.5 (s, C-2/3), 128.6 (m, *m*-C), 129.2 (s, C_6H_6), 133.0 (s, *p*-C), 133.1 (m, *o*-C), 134.4 (t, $^3J_{PC}$ = 3.1 Hz, C-1), 164.6 (tt, $^2J_{PC}$ = 16.8 Hz, $^2J_{PC}$ = 3.1 Hz, C-Ph).

1,3-Diphenyl-2,4-bis(triphenylphosphonio)-1,2-dihydrophosphetide chloride/bromide (5a): To a magnetically stirred solution of **3** (11.80 g, 16.4 mmol) in dichloromethane (30 mL) were added triethylamine (3.33 g, 32.8 mmol) and phenyldichlorophosphine (2.94 g, 16.4 mmol) through syringes. The orange-red solution was stirred for 15 h at room temperature. After addition of benzene (20 mL) the colourless precipitate was filtered off. After addition of further benzene (40 mL), yellow crystals precipitated at room temperature. These were filtered off, washed twice with a 2:1 mixture of benzene and dichloromethane and dried in vacuo. By concentration of the filtrate, two more fractions of **5a** together with various amounts of triethylammonium halides and **6a** were obtained. These impurities could not be removed by recrystallization from dichloromethane/benzene; therefore **5a** was used without further purification.

1,2,4-Triphenyl-3,5-bis(triphenylphosphonio)-1,2-dihydro-1,2-diphospholide chloride/bromide (6a): To a magnetically stirred solution of **3** (7.82 g, 10.9 mmol) and triphenylphosphine (2.85 g, 10.3 mmol) in dichloromethane (40 mL) were added phenyldichlorophosphine (3.89 g, 21.7 mmol) and triethylamine (2.20 g, 21.7 mmol) through syringes at room temperature. The reaction mixture was stirred for 3 d at room temperature, then benzene (20 mL) was added. After 1 d, the colourless precipitate was filtered off. Benzene (50 mL) was added to the orange filtrate. On standing at room temperature, yellow crystals precipitated, which were filtered off after 3 d, washed twice with benzene and dried in vacuo. By concentration of the filtrate, an additional crop was obtained. The combined fractions were recrystallized from dichloromethane/benzene. Yield 8.45 g yellow crystals (ca. 85%, contaminated by about 5% triethylammonium halides). A small amount of this product was recrystallized four more times from dichloromethane/benzene to obtain a pure sample, M.p. 260–263 °C, decomp. $[C_{57}H_{45}P_4]Br_{0.7}Cl_{0.3}\cdot CH_2Cl_2\cdot 1.5\,C_6H_6 = C_{67}H_{56}Br_{0.7}Cl_{2.3}P_4$ (1122.5): calcd C 71.69 H 5.03 Br 4.98 Cl 7.26, found C 71.75 H 5.08 Br 4.93 Cl 7.17; ^{1}H NMR ($CDCl_3$): δ = 6.22 (m, 2H, 3-H), 6.35 (m, 2H, 2-H), 6.51 (m, 1H, 4-H), 7.12–7.17 (m, 30H, arom. H), 7.35–7.38 (m, 12H, arom. H), 7.47 (m, 4H, arom. H); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 73.3 (m, C-PPh_3) 124.3 (d, $^1J_{PC}$ = 89.6 Hz, *i*-C), 128.0 (s), 128.2 (s, C_6H_6), 128.3 (s), 128.5 (m, C-7), 128.6 (s), 128.7 (m, *m*-C), 129.1 (s), 131.4 (m, C-6), 132.8 (m, *p*-C), 133.7 (m, *o*-C), 135.9 (t, $^3J_{PC}$ = 3.8 Hz, C-1), 138.7 (m, C-5), 181.2 (t, $^2J_{PC}$ = 16.6 Hz, C-Ph); the multiplets m represent the X parts of AA'BB'X spin systems which were, however, not analyzed.

1-Chloro-2,4-diphenyl-3,5-bis(triphenylphosphonio)-1,2-dihydro-1,2-diphospholide chloride/bromide (6b): To a magnetically stirred solution of **5a** (3.56 g, ca. 3.9 mmol, contaminated by about 10% by weight of triethylammonium halides) in dichloromethane (20 mL) were added triphenylphosphine (1.02 g, 3.9 mmol) and phosphorus trichloride (0.54 g, 3.9 mmol) at room temperature. After 5 h stirring at room temperature the yellow solution was concentrated in vacuo to half of its former volume, and benzene (20 mL) was added. After 15 h colourless crystals of chlorotriphenylphosphonium halides were filtered off. All volatiles were removed from the filtrate and the yellow residue was dissolved again in dichloromethane (3 mL) and benzene (15 mL). On standing at room temperature, yellow crystals precipitated, which were filtered off after 3 d, washed twice with benzene and dried in vacuo. By concentration of the filtrate, one more crop was obtained. The combined fractions were recrystallized from dichloromethane/benzene. Yield 2.74 g (ca. 80%) of yellow crystals of **6b**. A small amount of this product was recrystallized four more times from dichloromethane/benzene to obtain a pure sample; decomp. above 130 °C. $[C_{51}H_{40}ClP_4]Br_{0.7}Cl_{0.3} = C_{51}H_{40}Br_{0.7}Cl_{1.3}P_4$ (878.8), calcd C 69.70 H 4.59, found C 69.90 H 4.63.

1,2-Dichloro-4-phenyl-3,5-bis(triphenylphosphonio)-1,2-dihydro-1,2-diphospholide chloride/bromide (6c): As described for **6a**, **3** (45.00 g, 62.5 mmol), triphenylphosphine (16.40 g, 62.5 mmol), phosphorus trichloride (17.18 g, 125.1 mmol) and triethylamine (12.66 g, 125.1 mmol) were allowed to react in dichloromethane (100 mL). Recrystallization from dichloromethane/benzene yielded a crude product (yield 50.90 g, ca. 90%) containing about 10% triethylammonium halides. This product was used to synthesize **4**. A small amount of the mixture was recrystallized four more times to obtain an analytically pure sample of **6c**; yellow crystals, decomp. above 120 °C. $[C_{45}H_{35}Cl_2P_4]Br_{0.75}Cl_{0.25}\cdot 2\,C_6H_6 = C_{57}H_{47}Br_{0.75}Cl_{2.25}P_4$ (995.6): calcd C 68.77 H 4.76 Br 6.02 Cl 8.01, found C 68.42 H 4.84 Br 6.02 Cl 8.07; ^{1}H NMR ($CDCl_3$): δ = 5.82 (m, 2H, 2-H), 5.94 (m, 2H, 3-H), 6.41 (m, 1H, 4-H), 7.19 (s, 6H, C_6H_6), 7.40–7.43 (m, 24H, *o,m*-H), 7.56–7.60 (m, 6H, *p*-H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 86.9 (m, C-PPh_3), 122.2 (d, $^1J_{PC}$ = 91.5 Hz, *i*-C), 126.8 (s), 127.1 (s), 127.7 (s), 127.8 (s, C_6H_6), 129.2 (m, *m*-C), 132.8 (t, $^3J_{PC}$ = 2.9 Hz, C-1), 133.3 (m, *o*-C), 133.5 (s, *p*-C), 183.6 (t, $^2J_{PC}$ = 16.8 Hz, C-Ph).

1,3-Diphenyl-1-selenoxo-2,4-bis(triphenylphosphonio)-1,2-dihydrophosphetide chloride/bromide (7): To a magnetically stirred solution of crude **5a** (1.89 g), containing about 15% by weight of triethylammonium halides in dichloromethane (14 mL), grey selenium (0.20 g, 2.5 mmol) was added at room temperature. After stirring for 5 d, the excess selenium was filtered off and the orange filtrate was extracted four times with 5 mL water each time to remove the ammonium salts. Afterwards, all volatiles were removed in vacuo from the dichloromethane solution and the yellow residue was recrystallized from dichloromethane/benzene. Yield 1.22 g of **7**, yellow needles, decomp. above 210 °C; $[C_{51}H_{40}P_3Se]Br_{0.2}Cl_{1.8}\cdot 0.5\,CH_2Cl_2\cdot 0.5\,C_6H_6 = C_{54.5}H_{44}Br_{0.2}Cl_{1.8}P_3Se$ (950.5): calcd C 68.87 H 4.67 Br 1.66 Cl 6.71, found C 68.65 H 4.94 Br. 1.67 Cl 6.77; ^{1}H NMR ($CDCl_3$): δ = 6.65–6.71 (m, 4H, 2-H +3-H), 6.90 (m, 1H, 4-H), 7.22 (s, 3H, C_6H_6), 7.36–7.54 (m, 27H, arom. H), 7.58 (m, 6H, *p*-H), 7.92 (m, 2H, 6-H).

1,2,4-Triphenyl-1,2-diselenoxo-3,5-bis(triphenylphosphonio)-1,2-dihydro-1,2-diphospholide chloride/bromide (9): A solution of **6a** (0.51 g, 0.6 mmol) in dichloromethane (5 mL) was treated with grey selenium (135 mg, 1.7 mmol). The reaction mixture was stirred for 3 d at ambient temperature. The excess of selenium was removed by filtration and the filtrate treated with benzene (10 mL). The pale yellow precipitate was filtered off, washed twice with a mixture of dichloromethane/benzene (3:1) and dried in vacuo. Yield 0.59 g (95%), pale yellow needles, m.p. 317–319 °C. $[C_{57}H_{45}P_4Se_2]Br_{0.7}Cl_{0.3}\cdot CH_2Cl_2 = C_{58}H_{47}Br_{0.7}Cl_{2.3}P_4Se_2$ (1163.3): calcd C 59.88 H 4.07, found C 59.67 H 4.46.

4-Phenyl-3,5-*bis*(triphenylphosphonio)-1,2-diphospholide tetraphenylborate (4b): A solution of sodium tetraphenylborate (3.45 g, 10.1 mmol) in methanol (20 mL) was added dropwise over 10 min at room temperature to a magnetically stirred solution of **4a** (7.65 g, 9.6 mmol) in methanol (50 mL). A colourless precipitate formed instantaneously, and the reaction mixture was stirred for 30 min at room temperature. The precipitate was filtered off, washed three times with methanol (50 mL) and dried in vacuo. Yield 9.52 g (97%) of **4b**, colourless, microcrystalline powder, m.p. 208–212 °C. $[C_{45}H_{35}P_4]C_{24}H_{20}B = C_{69}H_{55}BP_4$ (1018.9): calcd C 81.34 H 5.44, found C 80.87 H 5.46; ^{1}H NMR ($CDCl_3$): cation, δ = 5.97 (m, 2H, 2-H), 6.09 (m, 2H, 3-H), 6.51 (m, 1H, 4-H), 7.38–7.43 (m, 24H, *o,m*-H), 7.56–7.61 (m, 6H, *p*-H); anion, δ = 6.89 (m, 4H, *p*-H), 7.04 (m, 8H, *m*-H), 7.47–7.50 (m, 8H, *o*-H).

1,2-Dichloro-4-phenyl-3,5-bis(triphenylphosphonio)-1,2-dihydro-1,2-diphospholide tetraphenylborate (6e): To a magnetically stirred solution of **4b** (1.57 g, 1.5 mmol) in dichloromethane (10 mL), a solution of sulfuryl chloride (208 mg, 1.5 mmol) in dichloromethane (3 mL) was added dropwise over 10 min at −78 °C. The resulting yellow solution was concentrated in vacuo to half of its former volume, then benzene (15 mL) was added. On standing at room temperature, orange crystals precipitated, which were filtered off, washed with benzene and recrystallized from dichloromethane/benzene. Yield 1.45 g (86%) of **6e**, orange crystals, decomp. above 150 °C. $[C_{45}H_{35}Cl_2P_4]C_{24}H_{20}B = C_{69}H_{55}BCl_2P_4$ (1089.8): calcd C 76.05 H 5.09, found C 75.55 H 5.15.

1,2-Dibromo-4-phenyl-3,5-bis(triphenylphosphonio)-1,2-dihydro-1,2-diphospholide tetraphenylborate (6f): As described above, from **4b** (2.20 g, 2.2 mmol) in dichloromethane (20 ml) and bromine (0.35 g, 2.2 mmol) in dichloromethane (5 ml). Yield 2.34 g (92%) of **6f**, orange crystals, decomp. above 160 °C. $[C_{45}H_{35}Br_2P_4]C_{24}H_{20}B = C_{69}H_{55}BBr_2P_4$ (1178.7): calcd C 70.31 H 4.70, found C 70.35 H 4.79.

1,2-Diiodo-4-phenyl-3,5-bis(triphenylphosphonio)-1,2-dihydro-1,2-diphospholide tetraphenylborate (6g): As described above, from **4b** (0.59 g, 0.6 mmol) in dichloromethane (5 mL) and iodine (146 mg, 0.6 mmol) in dichloromethane (3 mL). Yield 0.59 g (80%) of **6g**, red crystals, decomp. above 150 °C. $[C_{45}H_{35}I_2P_4]C_{24}H_{20}B\cdot C_6H_6 = C_{75}H_{61}BI_2P_4$ (1350.8): calcd C 66.69 H 4.55 I 18.79, found C 67.68 H 4.38 I 18.98.

Crystal Structure Determination: Crystals suitable for X-ray diffraction were grown from mixtures of dichloromethane and benzene. X-ray data were recorded on a Siemens P4 diffractometer with low-temperature equipment and graphite-monochromated $Mo_{K\alpha}$ radiation. Cell constants were determined from the setting angles of 20–30 centred reflexions. Data were collected in the ω-scan mode with variable scan speed. They are summarized together with other relevant data in Table 3. Structure solutions were performed with SHELXTL PLUS software; the SHELX93 program package was used for refinement. Semiempirical absorption corrections based on psi-scans were applied for compounds **4a** and **6a** besides Lorentz and polarization corrections. Non-hydrogen atoms were refined anisotropically; hydrogen-atom positions were revealed by difference Fourier synthesis. However, they were first placed in calculated positions and then finally fully refined with fixed U_i values.

The following points should be noted. Compound **4a**: Refinement of the compound as the bromide resulted in an anomalously large U_{eq} which led to a nonpositive definite value in anisotropic refinement. An unacceptable U_{eq} also resulted when Br^- was replaced by Cl^-. This pointed to the conclusion that the halide position was occupied by Cl^- and Br^-. On this assumption the site occupancy factor converged close to 0.75 for Cl and 0.25 for Br, and the final refinement used these as fixed SOF

0947-6539/96/0202-0226 $ 10.00+.25/0 Chem. Eur. J. 1996, 2, No. 2

Table 3. Crystal and data collection parameters for compounds **4a**, **6b** and **6a**.

	4a	**6c**	**6a**
formula	$C_{45}H_{35}Br_{0.25}Cl_{0.75}P_4 \cdot 0.5C_6H_6$	$C_{45}H_{35}Br_{0.75}Cl_{2.25}P_4 \cdot 2C_6H_6$	$C_{57}H_{45}Br_{0.5}Cl_{0.5}P_4 \cdot 0.5C_6H_6 \cdot 0.6CH_2Cl_2$
molar mass	785.2	995.52	1001.2
colour, habit	yellow block	yellow prism	yellow prism
crystal size (mm)	$0.40 \times 0.32 \times 0.29$	$0.4 \times 0.3 \times 0.22$	$0.4 \times 0.36 \times 0.2$
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (no. 1)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a (Å)	10.094(3)	11.519(2)	11.192(2)
b (Å)	12.373(3)	14.856(3)	20.495(3)
c (Å)	17.841(4)	15.750(3)	22.965(8)
α (Å)	107.79(1)	110.51(1)	90
β (Å)	97.82(2)	90.39(1)	102.18(2)
γ (Å)	105.92(2)	94.33(1)	90
V (Å^3)	1980.6(9)	2515.6(8)	5149(2)
Z	2	2	4
F(000)	815	1036	2076
ρ_{calcd} (Mg m^{-3})	1.317	1.329	1.292
μ (mm^{-1})	–	1.088	0.662
T (K)	198	223	293
2θ range (°)	2.5–49	2.8–50	2.7–48
index ranges h,k,l	0/11, −13/13, −20/20	−13/0, −16/16, −18,18	−12/0, −23/0, −25/26
refl. coll.	6894	9064	8517
refl. indep.	6447	8596	8059
R(int)	0.085	0.035	0.094
refl. observ. [a]	4530 [b]	5606 [c]	4131
scan speed (° min^{-1})	4–60	3–60	6.5–60
scan range (°)	1.2	0.9	1.1
variables	601	577	649
restraints	0	0	30
$R(F>4\sigma F)$	0.049	0.050	0.069
w$R2$ (F^2)	0.090	0.106	0.137
GOOF on F^2	1.054	1.041	1.013
largest diff. peak (e Å^{-3})	0.734	0.438	0.369

[a] $F>4\sigma(F)$. [b] Semiempirical absorption correction, min./max. transmission: 0.885/0.957. [c] Semiempirical absorption correction, min./max. transmission: 0.685/0.878.

values. Compound **6c**: A problem similar to that for **4a** was noted for the anionic halide, and in the final refinement SOF was fixed at 0.25 for Cl^- and 0.75 for Br^-, while data for the Cl atoms attached to P atoms refined normally and there was no residual electron density at these Cl atoms to suggest Cl/Br exchange, although the U_{ij} values of atom Cl1 are noticeable larger than for atom Cl2. Two benzene molecules were found for each **6c** molecule. Their parameters refined normally, suggesting no splitting of the C positions. Compound **6a**: Once again the position of the free halide is occupied by Cl^- and Br^- (SOF 0.5 for each atom in the final refinement) and SOFs converged in the refinement close to 0.5. The thermal parameters of the crystal solvent benzene are fairly large, and the SOF was not refined. However, the SOF for the CH_2Cl_2 molecule was refined. It converged close to 0.6 and this value was kept fixed in the final stages. Moreover, U_{ij} values of the carbon atoms of the phenyl group at P3 (C81–C86) suggested splitting of 3 positions (C82, 83, 84) resulting in additional positions (C87, 88, 89). SOFs of 0.5 were assumed. Fig. 5 represents only one of the two orientations of this phenyl group. In the lattice of **6a** the voluminous cations leave a cavity which is filled by molecules of dichloromethane and benzene and into which the phenyl group at P3 also extends. The positions of the solvent molecules are occupied only in part, however, with the consequence that this phenyl group aligns in a different way depending on whether the local dichloromethane position is filled or not.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59035.

Acknowledgement: Thanks are due to Martin Schmidt for his contributions to the structure investigations of **6a**, and to the Fonds der Chemischen Industrie for financial support.

Received: May 26, 1995 [F139]

[1] L. Weber, R. Kirchhoff, R. Boese, H.-G. Stammler, *J. Chem. Soc. Chem. Commun.* **1991**, 1293–1295.
[2] E. Niecke, D. Schmidt, *J. Chem. Soc. Chem. Commun.* **1991**, 1659–1660.
[3] G. Jochem, A. Schmidpeter, M. Thomann, H. Nöth, *Angew. Chem.* **1994**, *106*, 708–711; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 663–665.
[4] G. Jochem, A. Schmidpeter, F. Kulzer, S. Dick, *Chem. Ber.* **1995**, *128*, 1015–1020.
[5] H. J. Bestmann, L. Kisielowski, *Tetrahedron Lett.* **1990**, *31*, 3301–3304.
[6] N. Maigrot, N. Avarvari, C. Charrier, F. Mathey, *Angew. Chem.* **1995**, *107*, 623–625; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 590–592.
[7] A. Schmidpeter, M. Thiele, *Angew. Chem.* **1991**, *103*, 333–335; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 308–310.
[8] D. Gudat, M. Nieger, M. Schrott, *Chem. Ber.* **1995**, *128*, 259–266.
[9] A. Schmidpeter, H. Nöth, J. Jochem, H.-P. Schrödel, K. Karaghiosoff, *Chem. Ber.* **1995**, *128*, 379–393.
[10] In contrast to trialkyl phosphines, triphenylphosphine does not reduce PCl_3 or $PhPCl_2$. It does, however, reduce PBr_3. A. Schmidpeter, S. Lochschmidt, W. S. Sheldrick, *Angew. Chem.* **1985**, *97*, 214–215; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 226–227.
[11] L. Cassidei, O. Sciacorelli, QCPE program No. 440.
[12] C. J. Jameson in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis* (Eds.: J. G. Verkade and L. D. Quin), VCH, Deerfield Beach, **1987**, pp. 205–229.
[13] N. Maigrot, M. Sierra, C. Charrier, F. Mathey, *Bull. Soc. Chim. Fr.* **1994**, *131*, 397–399.
[14] M. Baudler, J. Hahn, *Z. Naturforsch. B* **1990**, *45*, 1139–1142.
[15] H.-P. Schrödel, G. Jochem, A. Schmidpeter, H. Nöth, *Angew. Chem.* **1995**, *107*, 2006–2010; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1853–1856.
[16] S. G. Kleemann, E. Fluck, J. C. Tebby in *Handbook of Phosphorus-31 NMR Data* (Ed.: J. C. Tebby), CRC, Boca Raton, **1991**, pp. 49–63.
[17] A. Schmidpeter, G. Jochem, *Tetrahedron Lett.* **1992**, *33*, 471–474, ref. [8].
[18] H. Schmidbaur, Ch. Paschalidis, O. Steigelmann, G. Müller, *Angew. Chem.* **1989**, *101*, 1739–1740; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1700–1701.
[19] D. E. C. Corbridge, *The Structural Chemistry of Phosphorus*, Elsevier, Amsterdam, **1974**.
[20] The dependence of the PCl bond length on the dihedral angle has been investigated in detail for other ylidyl chlorophosphines (ref. [9]).
[21] M. Yoshifuji in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz and O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 321–337.
[22] G. Märkl, S. Dietl, M. L. Ziegler, B. Nuber, *Tetrahedron Lett.* **1988**, *29*, 5867–5870.
[23] W. Güth, T. Busch, W. W. Schoeller, E. Niecke, B. Krebs, M. Dartmann, P. Rademacher, *New J. Chem.* **1989**, *13*, 309–313.
[24] H.-J. Bestmann, R. Zimmermann in *Houben–Weyl: Methoden der organischen Chemie* (Ed.: M. Regitz), Thieme, Stuttgart, **1982**, pp. 616–782.
[25] U. Wannagat, H. Niederprüm, *Chem. Ber.* **1959**, *94*, 1540–1547.
[26] H. G. Viehe, E. Franchimont, *Chem. Ber.* **1962**, *95*, 319–327.
[27] S. I. Miller, C. R. Ziegler, R. Wieleseck, *Org. Synth.* **1965**, *45*, 86–88; *Org. Synth. Coll., Vol. 5*, **1973**, 921–923.