1,2-Diphosphole and 1,4,7,10-Tetraphosphaphenalene Derivatives from the Reaction of Allylidenetriphenylphosphorane and PCl_3

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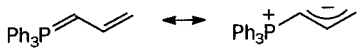
The equation 7 **1** + 11 PCl_3 → 2 **7** + **11** + 21 HCl describes in part the reaction of allylidenetriphenylphosphorane (triphenylphosphonium allylide) **1** with PCl_3. It involves the substitution of all α- and γ-hydrogen atoms of **1** and a concomitant disproportionation of the phosphorus. The reduction product **11** and its less highly substituted precursor **9** are new examples of the favoured family of 3-phosphonio 1,2-diphospholides and 1,2,4-triphospholides. The cation of the ionic oxidation product **7** has a phenalene structure with three peripheric PCl ring members and a chlorophosphonium center. In the crystal two of these bowl-shaped cations encapsulate a chloride anion. This is shown by an X-ray structure investigation. The structure of other products is elucidated by ^{31}P-NMR spectroscopy.

Allylidenetriphenylphosphorane [(prop-2-enediyl)triphenylphosphorane] (**1**) may be understood as phosphonio-substituted allyl anion and is expected to exhibit the reactivity of an asymmetric allyl anion[1][2][3][4].



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With phosphorus trichloride it consequently may interact at its α- or γ-carbon atom leading to compounds **2** or **3** as the primary substitution products and it also may interact at both sites with the same PCl_3 molecule or with two different of them to give compounds **4** or **5** as secondary products. All in all there are three hydrogen atoms of **1** that can be substituted. The different alternatives of this reaction were considered earlier[5]. The actual experiment (in benzene with an excess of **1**) gave a product which was assumed to be the hydrochloride of the "tris-ylene" **6**. It would be the result of the substitution of three molecules of **1** exclusively at the γ-position by the same PCl_3 molecule. Compound **6** was obtained from its hydrochloride by reaction with sodium amide. It is described as a deep red, very reactive, air-sensitive substance.

We repeated the reaction of **1** with PCl_3 in pyridine, which in similar cases had proved as a convenient solvent, able to take up the hydrogen chloride lost from the reaction partners in the substitution reaction[6].

Reaction and Products

The reaction of phosphorus trichloride with **1** in pyridine at 0°C was visually observable. ^{31}P-NMR spectroscopy was used to monitor several experiments with different molar ratios. The spectra always indicated complex mixtures of products. These mixtures at room temperature continued to change their composition for a long time (up to several months). At long reaction times the spectra tended to become simpler. Naturally the reaction of the three-functional PCl_3 with the three-functional partner **1** can be expected to take various pathways with numerous intermediates. In the course of the reaction more and more of the functions are used, and the number of alternatives should decrease.

With a 3:1 initial molar ratio of **1** and PCl_3, compound **7** becomes the main product after 2 d. Its identity follows from its $^{31}P\{^1H\}$-NMR spectrum of $[AB]_3D$ type. As only the two-bond coupling constants J_{AB} and J_{BD}, and the four-bond coupling constant J_{AD} are large enough to influence the signal splitting significantly ($J_{AA'}$, $J_{AB'}$ and $J_{BB'}$ are too small), the spectrum is rather simple in appearance (Figure 1). The chemical shifts δ_A, δ_B and δ_D are in the expected range, δ_D in particular is characteristic for a chlorophosphonium center (Table 1).

No intermediate on the way to **7** could be identified from the spectra. In particular compound **6** (or its hydrochloride) was not found; however, it cannot be excluded as an intermediate either. It would be expected to possess a highly reactive phosphane center which easily becomes oxidized.

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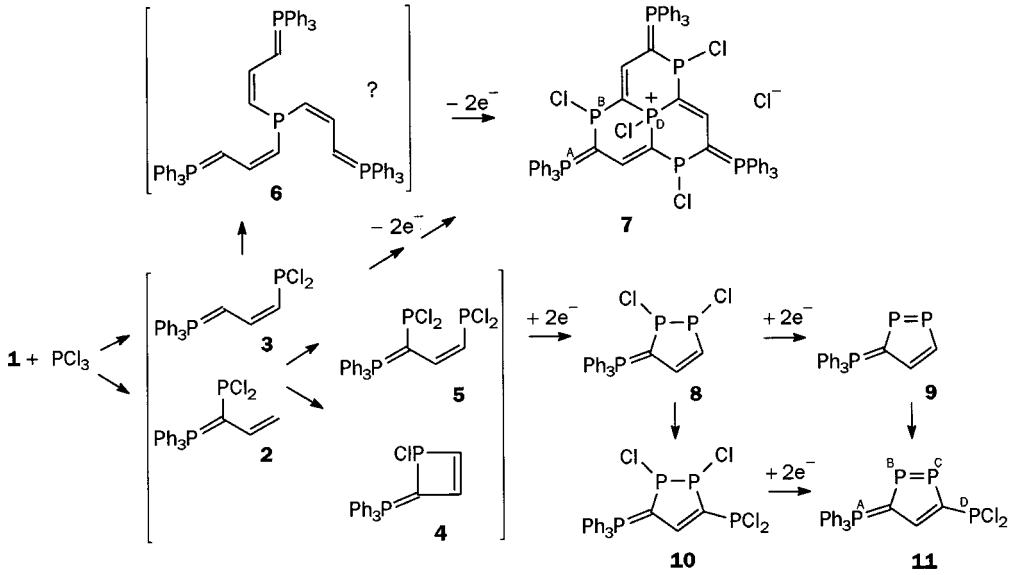
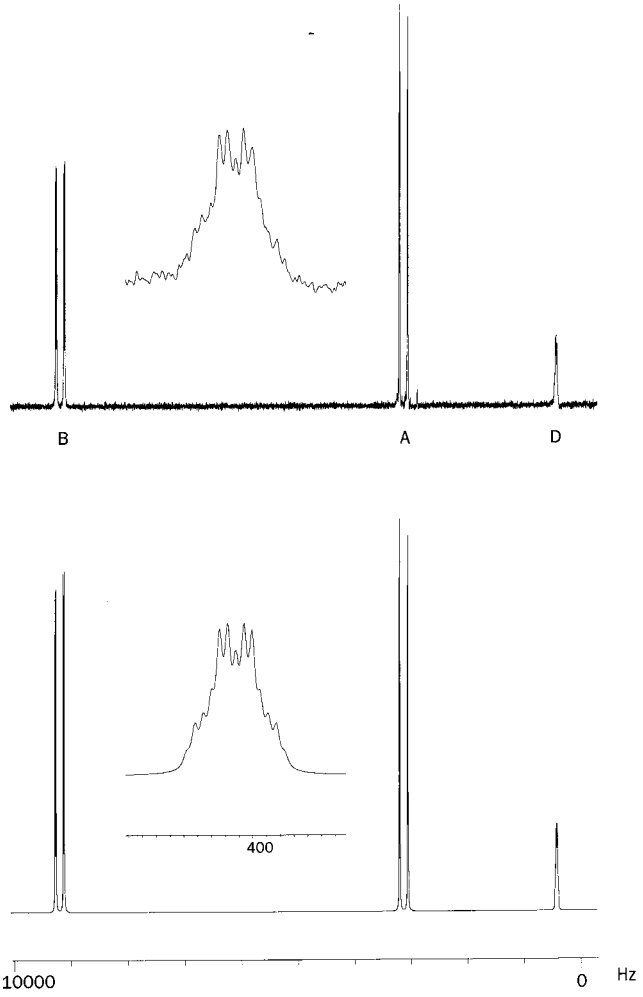


Figure 1. Experimental and calculated $^{31}P\{^1H\}$-NMR spectrum of **7**; ν_o = 109.380 MHz



In fact, the overall formation of **7** as represented by equation (1) in Scheme 1 involves an oxidation.

Table 1. ^{31}P-NMR data of the tetraphosphaphenalenes **7** and **18** (in pyridine); coupling constants *J* in Hz

	7	**18**
δ_A	28.5	27.6
δ_B	83.9	−20.6
δ_C		−23.1
δ_D	3.8	11.2
$^2J_{AB}$	145.0	139.0
$^3J_{AC}$		7.6
$^4J_{AD}$	6.0	3.7
$^1J_{BC}$		−141.0
$^2J_{BD}$	17.8	17.6

Scheme 1. Equations leading to the products **7**−**11** (R = Ph_3PC_3H, RH_3 = **1**, Py = pyridine)

$$3\,RH_3 + 4\,PCl_3 + 9\,Py \xrightarrow{-2e^-} \underset{\mathbf{7}}{R_3P_4Cl_4^+} + 9\,PyH^+ + 8\,Cl^- \quad (1)$$

$$RH_3 + 2\,PCl_3 + 2\,Py \xrightarrow{+2e^-} \underset{\mathbf{8}}{RHP_2Cl_2} + 2\,PyH^+ + 4\,Cl^- \quad (2)$$

$$RH_3 + 2\,PCl_3 + 2\,Py \xrightarrow{+4e^-} \underset{\mathbf{9}}{RHP_2} + 2\,PyH^+ + 6\,Cl^- \quad (3)$$

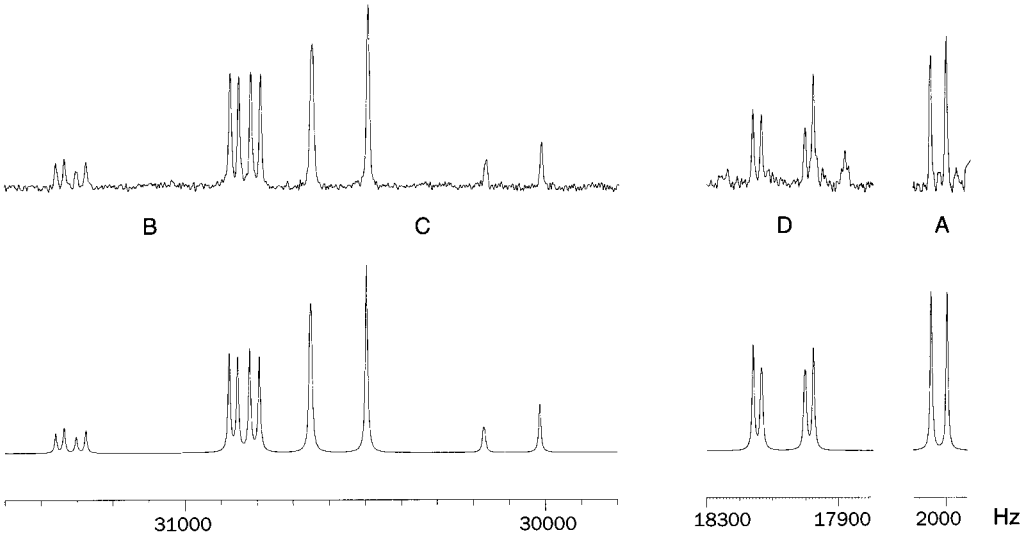
$$RH_3 + 3\,PCl_3 + 3\,Py \xrightarrow{+2e^-} \underset{\mathbf{10}}{RP_3Cl_4} + 3\,PyH^+ + 5\,Cl^- \quad (4)$$

$$RH_3 + 3\,PCl_3 + 3\,Py \xrightarrow{+4e^-} \underset{\mathbf{11}}{RP_3Cl_2} + 3\,PyH^+ + 7\,Cl^- \quad (5)$$

With equimolar amounts of **1** and PCl_3 the reaction is similar to the one described above in that **7** finally becomes the main product. In this case it takes several months, however. As before several intermediates are observed, which already contain the central chlorophosphonium unit as in **7** (with $\delta^{31}P = 0-5$) but which are less symmetric. After 10

months their signals have disappeared in favour of **7**. This suggests that in the synthesis of **7** at first triallylphosphanes such as **6** form and become oxidized before the rings are closed by the peripheral PCl units. As a second final product, compound **11** is observed in this reaction. It is readily recognized by its $^{31}P\{^{1}H\}$-NMR spectrum (Figure 2) representing an ABCD spin system, and in particular by the low-field chemical shifts δ_B and δ_C and by the large coupling constant J_{BC} (see below, Table 2).

Figure 2. Experimental and calculated $^{31}P\{^{1}H\}$-NMR spectrum of **11**; ν_o = 109.380 MHz



If a still smaller molar ratio (3:4) of the reaction partners is used, compound **10** is observed in an early stage of the reaction (after 12 h) followed again by **11**. The formation of **10** and **11** involves a reduction and is described by equations (4) and (5) in Scheme 1. A combination of (1) and (4) or of (1) and (5) allows the formulation of a consistent overall reaction.

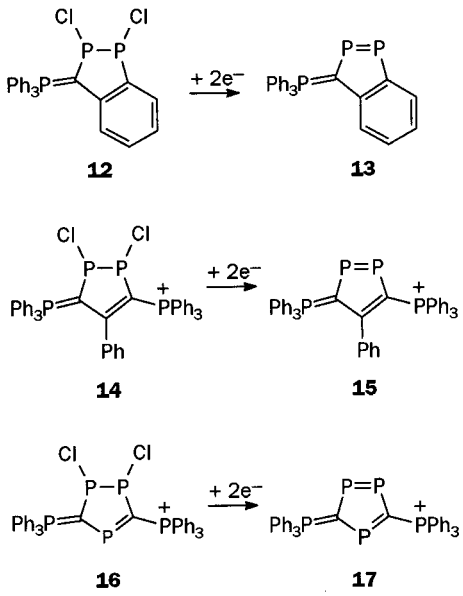
The identified products **7**, **10**, and **11** have in common an exhaustive substitution of **1** in which all three α- and γ-hydrogen atoms are replaced by phosphorus. In the formation of **10** and **11** it cannot be decided at what stage of substitution the PP bond is formed and the five-membered ring is closed.

A little further insight is provided by the reactions with a low molar ratio (1:3) of the partners and with an additional reducing agent (PBu_3). Although an excess of PCl_3 was used and unreacted PCl_3 is still present, compounds **8** and **9** are observed in this case (equations 2 and 3). In these compounds one γ-hydrogen atom of **1** is left unsubstituted. The added tributylphosphane apparently makes the reduction faster than the last step of substitution. Compounds **10** and **11** seem to form from **8** and **9** by a consecutive substitution.

1,2-Diphosphole Derivatives

The formation of **8** from **1** is closely related to that of its benzo derivative **12** in the reaction of benzyl triphenylphosphonium bromide with PCl_3 in presence of a base[7]. The *ortho* position of the ylide here displays a reactivity similar to that of the γ position in **1**. Furthermore, **12** is readily reduced to **13**, which is the benzo derivative of **9**.

The reaction of a γ-phosphonio-substituted allylidene phosphorane with PCl_3 also parallels the formation of **8** and leads to its symmetrically substituted derivative **14**[8]. In this reaction a four-membered dihydrophosphete ring was observed as an intermediate and consequently the analogous compound **4** has to be considered as an intermediate on the way to **8**.



The preferred formation of five-membered rings of type **8** is documented by still another example: The reaction of [bis(trimethylsilyl)methylene]phosphorane with PCl_3 yields as a secondary product the dihydrotriphosphole **16**[9], which is the 4-phospha derivative of **14**. Both **14** and **16** can be

reduced to give the corresponding diphosphole **15** and triphosphole **17**.

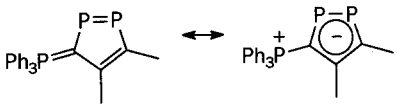
Table 2. ^{31}P-NMR data of the dihydrodiphosphole/diphosphole pairs **8**/**9** (in pyridine), **10**/**11** (in pyridine), **12**/**13** (in CH_2Cl_2)[7], **14**/**15** (in CH_2Cl_2)[8], and of the dihydrotriphosphole/triphosphole pair **16**/**17** (in CH_2Cl_2/C_6D_6)[9]. δ_A refers to 3-PPh_3, $\delta_{B,C}$ refer to P-1,2 as indicated in formula **11**. Coupling constants J in Hz.

	δ_A	δ_B	δ_C	δ_D	$^2J_{AB}$	$^3J_{AC}$	$^1J_{BC}$	$^3J_{BD}$	$^2J_{CD}$
8	25.0	129.6	112.5		87.7		−257.9		
9	[a]	254.2	236.3		70.9		−480.7		
10	20.2	116.8	104.2	176.7	70.2		−262.5		25.9
11	18.5	283.3	278.1	165.2	67.9	−7.0	−481.2	4.3	175.9
12	18.6	132.4	78.7		96.7		−249.7		
13	14.9	317.1	229.4		87.5	−6.1	−480.2		
14	16.9	101.9			85.3	−5.2	−260.9		
15	15.6	285.7			80.0	−6.7	−465.5		
16	22.9	136.1		405.5	76.0	−4.5	−298.1		16.4
17	21.2	365.7		356.5	71.4	−0.7	−487.3		26.7

[a] Superimposed.

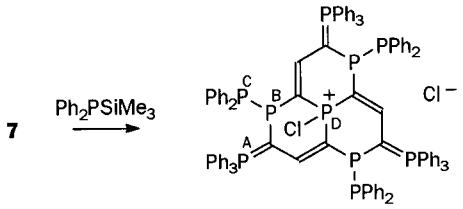
In Table 2 the ^{31}P-NMR data of the new compounds **8**−**11** are compared to the related known compounds **12**−**17**. In case of the unsymmetrically substituted compounds **8**, **10**, **12** and **9**, **11**, **13**, the phosphorus atom P^B which is adjacent to the ylidic ring member and which consequently is more strongly influenced[10], always appears less shielded than P^C. The difference for **8**−**11** is smaller, however, than for **12** and **13**. The reduction is always accompanied by a downfield chemical shift of the now two-coordinate phosphorus atoms ($\delta_{B,C}$ = 229−366) and by a sharp increase in the one-bond coupling constant ($|^1J_{BC}|$ = 465−487 Hz).

The charge of the phosphonio substituents according to δ_A seems to decrease somewhat on reduction. It nevertheless corresponds to the polar resonance formula for the reduced compounds **9**, **11**, **13**, **15**, **17**.



Tetraphosphaphenalene Derivatives

For a further chemical identification of **7** it was treated with diphenyl(trimethylsilyl)phosphane. In a clean reaction only the chlorine atoms at P^{III} are replaced by PPh_2 groups while the central P^VCl unit remains unchanged. This leads to compound **18**. Its ^{31}P{^{1}H}-NMR spectrum (Figure 3) represents a $(ABC)_3D$ spin system (Table 1).



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ture analysis. They contain 2.7 pyridine molecules per formula unit of **7**. Whereas the cation lattice is of good quality, the location of the chloride anions and the solvent molecules is rather uncertain due to strong disorder. Figure 4 shows the structure of a cation. Its skeleton is built from three allylic units C1,2,3 joined by three phosphorus atoms P2 to give a twelve-membered ring and by the central P1 to give a tetraphosphaphenalene system. The allylic carbon atoms C1, C2, and C3 lie in a plane together with the four phosphorus atoms P1, P2, P2B, and P3 bonded to them. The three planes meet at the central atom P1 forming a flat bowl. Under the influence of the three ylide units attached to the chlorophosphonium center the P1−Cl1 bond becomes rather long (Table 3)[11][12]. The bonds P2−Cl2 point to the same direction, i.e. to the convex side of the bowl.

In the crystal two of the described bowl-shaped cations approach each other with their concave sides face to face to encapsulate a chloride ion Cl3 like a shell encapsulates a pearl (Figure 5). The bonds P1−Cl1 of the two cations and Cl3 lie on a three-fold symmetry axis around which the two cations are mutually twisted by 60° against each other. The chloride ion Cl3 thus becomes walled in by six phenyl groups belonging alternately to PPh_3 units of one or the other cations. The *o*- and *m*-hydrogen atoms of these phenyl groups approach Cl3 at 284 and 296 pm, which is less than the sum of the van der Waals radii (320 pm). At the origin

Figure 3. Experimental and calculated $^{31}P\{^{1}H\}$-NMR spectrum of **18**; ν_o = 109.380 MHz

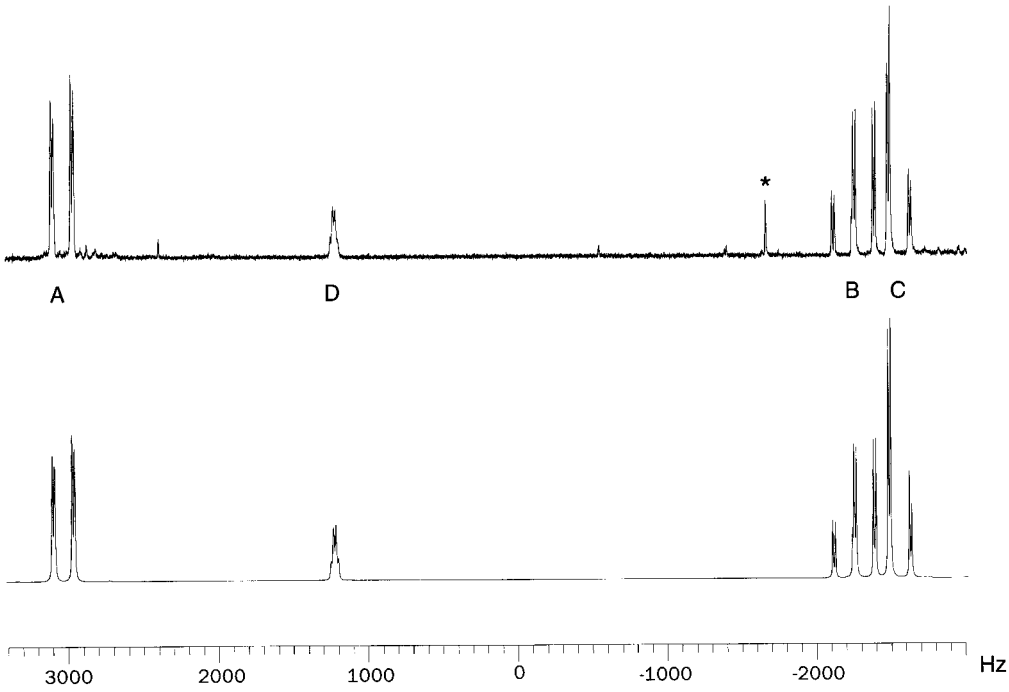


Figure 4. Molecular structure of the cation in **7** (thermal ellipsoids with 30% probability); the three phenyl groups at P3 are omitted for clarity

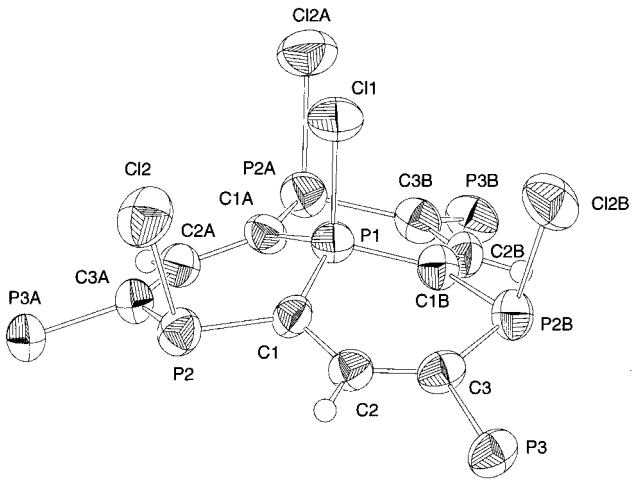
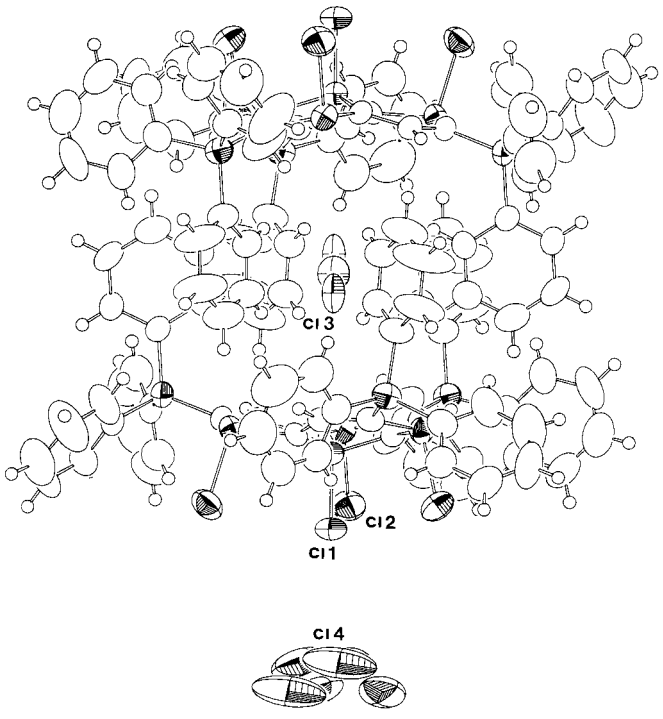


Table 3. Relevant bond lengths [pm] and bond angles [°] of **7**

P1−C1	172.2(8)	C1−P1−C1A	111.6(3)
P1−Cl1	206.6(5)	C1−P1−Cl1	107.3(3)
P2−C1	175.7(8)	C1−P2−C3A	102.5(4)
P2−C3	179.8(9)	C1−P2−Cl2	102.1(3)
P2−Cl2	216.1(4)	C3A−P2−Cl2	100.8(3)
P3−C3	176.7(8)	C2−C1−P1	118.9(7)
		C2−C1−P2	118.8(6)
		P1−C1−P2	122.2(4)
		C1−C2−C3	129.9(8)
		C2−C3−P3	116.7(7)
		C2−C3−P2B	127.5(6)
		P3−C3−P2B	115.0(5)

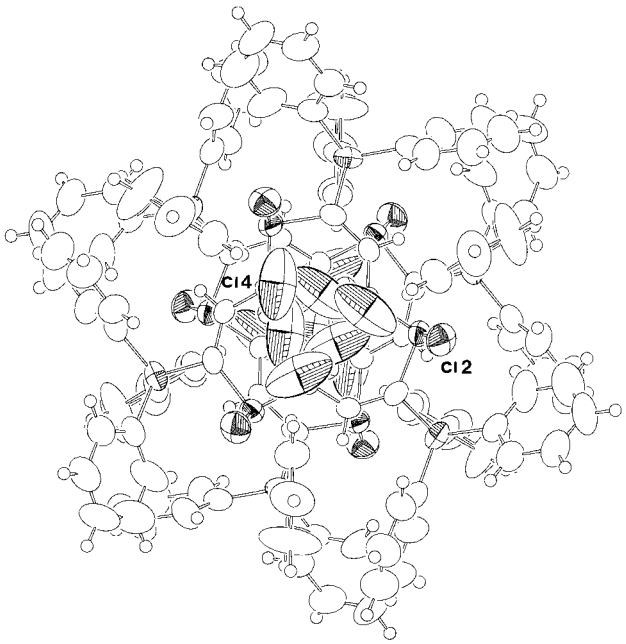
Figure 5. A $(cation)_2Cl^+$ unit and a Cl^- anion of **7** viewed perpendicular to the threefold axis; Cl3 (within the $(cation)_2Cl^+$ unit) is split and disordered along the threefold axis; Cl4 (the isolated Cl^- anion) is split and disordered on two levels around the threefold axis. The pyridine molecules are not shown



within the cage formed thus, the position of Cl3 is split. The other chloride ion Cl4 distributes on 2 × 3 symmetry-equivalent positions close to the threefold axis (Figures 5

and 6). The crystal lattice is eventually composed of an equal number of the $(cation)_2Cl^+$ units and isolated Cl^- anions alternating along the threefold axis and of 5.4 molecules of pyridine on 2×3 positions of 0.5 occupancy and 2×3 positions of 0.4 occupancy around one sequence of these ions.

Figure 6. View along the *c*-axis of **7**; Cl4 is split and disordered on two positions near the threefold axis. The pyridine molecules are not shown



Experimental Section

All manipulations were carried out in flame-dried glassware under argon with Schlenk tube techniques. Dry pyridine was used as obtained (Fluka). Pentane was dried over molecular sieves (4 Å).

NMR: Jeol EX 400 (^{1}H), Jeol GSX 270 (^{31}P) with Me_4Si (int.) and 85% H_3PO_4 (ext.) as standards.

Allylidenetriphenylphosphorane (**1**)[5] was prepared from 3-bromopropene and Ph_3P and subsequent deprotonation of the resulting phosphonium bromide with $NaN(SiMe_3)_2$[13].

Reaction of **1** *with* PCl_3. – *a) In a 3:1 Molar Ratio:* To **1** (0.56 g, 1.9 mmol) in 25 ml of pyridine at 0°C was added PCl_3 (0.054 ml, 0.6 mmol). The dark red solution brightened for a few minutes before becoming dark red again. After 2 d at room temperature the $^{31}P\{^1H\}$-NMR spectrum showed a wide variety of signals among which those of **7** were found with 12% of the total intensity. After 10 months the relative intensity had increased to 27%.

b) In a 3:4 Molar Ratio: **1** (0.97 g, 3.2 mmol) and PCl_3 (0.37 ml, 4.2 mmol) were added as before. In the $^{31}P\{^1H\}$-NMR spectrum after 12 h at room temperature among a large variety of signals only those of **10** were identified with 2% relative intensity. During 10 more months pyridinium chloride separated from the dark red solution and was removed. The spectrum of the filtrate showed **7** (41%), **10** (10%), and **11** (13% relative intensity). In this solution dark yellow crystals of **7** formed which were used for X-ray analysis; they decomposed at 93°C. – ^{1}H NMR (CD_2Cl_2): δ = 7.27–7.59 (m, 3 H, \$-H), 7.58–7.68 (m, 36 H, *o*-, *m*-H), 8.67–8.69 (m, 9 H, *p*-H).

c) In a 1:3 Molar Ratio and Additional PBu_3*:* To **1** (1.69 g, 5.6 mmol) PCl_3 (1.46 ml, 16.7 mmol) was added as before. After 10 min, PBu_3 (0.90 ml, 5.6 mmol) was added to the red solution. In the $^{31}P\{^1H\}$-NMR spectrum after 12 h at room temperature among a variety of signals those of **8** (1%), **9** (5%), **10** (2%), and **11** (0.5%) were identified. After heating under reflux for 2 d the spectrum showed **7** (3%), **8** (8%), **9** (9%), **10** (11%), and **11** (0.5%).

Reaction of **7** *with* Ph_2PSiMe_3*:* To a solution of **7** (42 mg, 0.04 mmol) in 0.5 ml of pyridine was added Ph_2PSiMe_3 (40 mg, 0.15 mmol). After 10 min a $^{31}P\{^1H\}$-NMR spectrum of the orange solution showed the signals of **18**.

Crystal Structure Analysis of **7**: Table 4; the chloride anion Cl3 is disordered on the threefold axis and the chloride anion Cl4 is disordered on the split position Cl4/Cl4A near the threefold axis, thus leading to 2 times 3 positions. Cl4/Cl4A were refined with the same U_{ij} temperature factor components. One of the pyridine solvent molecules is disordered around a center and the other is on a common position. Both pyridine molecules were fitted by restraints during the least squares procedure. Further details are available from the Cambridge Crystallographic Data Center on quoting the depository number CCDC-101626, the names of the authors and the journal citation (E-mail: deposit@ccdc.cam.ac.uk).

Table 4. Crystal data and structure refinement for **7**

Empirical formula	$C_{76.5}H_{61.5}Cl_5N_{2.7}P_7$
Formula weight	1199.1
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	rhombohedral
Space group	$R\bar{3}$
Unit cell dimensions	a = 18.450(4) Å c = 41.97(3) Å
Volume	12371(8) Å^3
Z	6
Density (calculated)	1.138 Mg/m^3
Absorption coefficient	0.351 mm^{-1}
F(000)	4376
Crystal size	0.40 × 0.33 × 0.27 mm
Θ range for data collection	2.32 to 22.00°
Index ranges	$0 \le h \le 19$, $-17 \le k \le 0$, $-45 \le l \le 45$
Reflections collected	3756
Independent reflections	3372 [R_{int} = 0.0307]
Observed reflections ($I > 2\sigma I$)	1919
Absorption correction	Semi-empirical from ψ-scans
Max. and min. transmission	0.9990 and 0.9790
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3372 / 60 / 305
Goodness-of-fit on F^2	1.100
Final R indices (I > 2σI)	$R1$ = 0.1071, $wR2$ = 0.2833
R indices (all data)	$R1$ = 0.1713, $wR2$ = 0.3349
Largest diff. peak and hole	0.624 and −0.431 eÅ^{-3}

[1] For calculated charge distribution see: K. A. Ostoja Starzewski, H. Bock, *J. Am. Chem. Soc.* **1976**, *98*, 8486–8494.
[2] Proton exchange involves both the α- and the γ-position: H. J. Bestmann, O. Kratzer, H. Simon, *Chem. Ber.* **1962**, *95*, 2750–2754.
[3] For an example of an exclusive reaction at the α-position see: B. Bogdanovic, S. Konstantinovic, *Synthesis* **1972**, 481–483.
[4] For examples of reactions at the γ-position see: H. J. Bestmann, R. Zimmermann in *Houben-Weyl: Methoden der organischen Chemie* (Ed. M. Regitz), Thieme, Stuttgart **1982**, 677 f.

[5] K. Issleib, M. Lischewski, *J. Prakt. Chem.* **1969**, *311*, 857−868, M. Lischewski, Thesis, Universität Halle-Wittenberg **1970**.
[6] G. Jochem, M. Schmidt, H. Nöth, A. Schmidpeter, *Z. Naturforsch. B* **1996**, *51*, 1761−1767.
[7] G. Jochem. A. Schmidpeter, M. Thomann, H. Nöth, *Angew. Chem.* **1994**, *106*, 708−711; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 663−665.
[8] G. Jochem, A. Schmidpeter, H. Nöth, *Chem. Eur. J.* **1996**, *2*, 221−227.
[9] H.-P. Schrödel, A.Schmidpeter, H. Nöth, M. Schmidt, *Z. Naturforsch. B.* **1996**, *51*, 1022−1032.
[10] A. Schmidpeter, H. Nöth, J. Jochem, H.-P. Schrödel, K. Karaghiosoff, *Chem. Ber.* **1995**, *128*, 379−393.
[11] In the cation Ph_3PCl^+ for comparison *d*PCl = 198(1) pm has been found: J. H. Enemark, J. A. Ibers, *Inorg. Chem.* **1968**, *7*, 2636−2642.
[12] A similar elongation of the P−Cl bond, although less pronounced, has been found for other ylide-substituted chlorophosphonium units too: $Ph_3P-C[-PCl-(Ph_3P=)C-]_3PCl^{2+}$, *d*PCl = 202.8(2) pm, H.-P. Schrödel, A. Schmidpeter, H. Nöth, *Z. Naturforsch. B*, in press; $(PhP_3=PhC-)_2PCl_2^+$, *d*PCl (average) = 204.4(4) pm: A. Schmidpeter, G. Jochem, C. Klinger, C. Robl, H. Nöth, *J. Organomet. Chem.* **1997**, *529*, 87−102.
[13] H.-J. Bestmann, R. Zimmermann in *Methoden der Organischen Chemie (Houben-Weyl)* (Ed.: M. Regitz), vol. E1, Thieme, Stuttgart, **1982**.

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