The Unusual Oxidation of a 1,5,2,4-Diazadiphosphorinan-6-one with Tetrachloro-*ortho*-benzoquinone[1]

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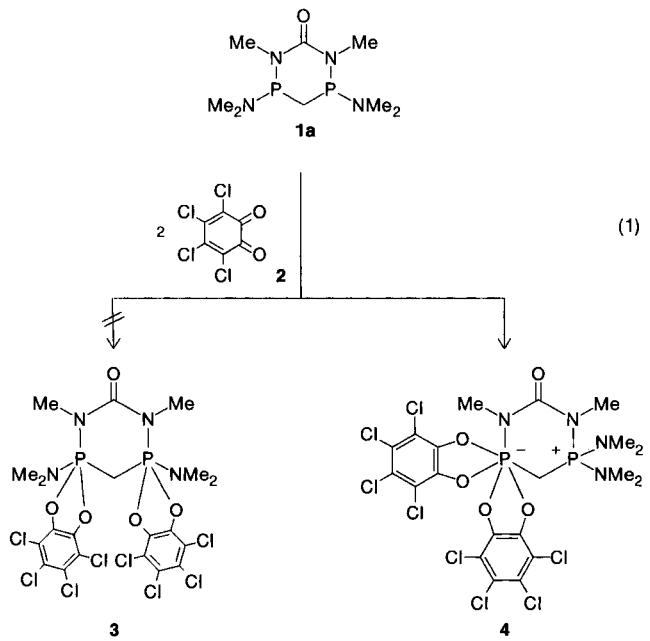
The oxidation of 2,4-bis(diethylamino)-1,5-dimethyl-1,5,2,4-diazadiphosphorinan-6-one (**1b**) with two equivalents of tetrachloro-*ortho*-benzoquinone (TOB) (**2**) leads to the cleavage of the original heterocycle and to the formation of a mixture of compounds, including the 1,3,2-diazaphosphetidine **6** ("λ^6P^-") and the spirophosphorane **7**. Compound **7** exists as two isomers that undergo slow spontaneous transformation in solution to compound **9**, containing a six-coordinate phosphorus atom. When the oxidation of **1b** is carried out in two stages, with the second equivalent of TOB being added after an interval of four days, the cleavage of the original molecule does not occur, and compound **17**, containing a seven-membered ring with two phosphorus atoms of opposite formal charge and different coordination number ("λ^4P^+,λ^6P^-") is formed. The structures of **6**, **7**, **9**, and **17** were established by low-temperature X-ray analysis. Compound **6** displays crystallographic twofold symmetry; the coordination at phosphorus is octahedral, but distorted by the phosphetidine ring. The phosphorus atom in **7** possesses square pyramidal coordination geometry, the pyramid base being defined by the four oxygen atoms. Compound **9** ("λ^6P^-") crystallized with two molecules of $CDCl_3$. Compound **17** crystallized as a dichloromethane solvate. Distorted octahedral and tetrahedral geometries were observed for P1 and P2, respectively. The four-membered ring is planar. The bridging hydroquinone ligand displays much wider O–C–C(–O) and C–O–P angles than the chelating hydroquinone.

In previous work we have found that the oxidation of a mixture of *cis* and *trans* isomers of 2,4-bis(dimethylamino)-1,5-dimethyl-1,5,2,4-diazadiphosphorinan-6-one (**1a**) with tetrachloro-*ortho*-benzoquinone (TOB) (**2**) furnished, instead of the expected spirophosphorane **3**, the heterocyclic compound **4**, which contains two phosphorus atoms of opposite formal charge and different coordination number (λ^4P^+,λ^6P^-)[2] [Eq. (1)].



We have continued the investigation of this reaction, having exchanged the dimethylamino substituents at the phosphorus atoms in compound **1a** for the bulkier diethylamino groups. Earlier, during the study of the *cis*/*trans* isomerism of the diazadiphosphorinanes **1a, b**, we found that this change of substituents markedly affects the methylation of these compounds by methyl iodide[3].

Results and Discussion

In this paper we describe the reaction of TOB with the bis(diethylamino)-substituted diazadiphosphorinane **1b**. The increase of spatial hindrance at the phosphorus atoms does indeed change the course of this reaction dramatically. The addition of two equivalents of TOB to **1b** in ether in the temperature range of -5 to -10°C leads to the cleavage of the original heterocycle [Eq. (2)].

The cleavage of heterocycle **1b** is believed to be preceded by the formation of an intermediate compound **5**, containing λ^3- and λ^5-phosphorus atoms. Further addition of TOB produces a mixture of compounds, including the 1,3,2-diazaphosphetidine **6** ("λ^6P^-") (ca. 10%; $\delta_P = -102.7$) and the spirophosphorane **7** (ca. 20%; $\delta_P = -21.5$) (judging by the ^{31}P-NMR spectrum).

Compound **6** is the first representative of diazaphosphetidines ("λ^6P^-") with the dialkylamino group attached to the carbon atom of the $-N{=}\overset{+}{C}{=}N-$ moiety[4,5], and is obtained as a stable crystalline product which is poorly soluble, even in polar organic solvents. The stability of **6** is certainly determined by the delocalizing influence of the di-

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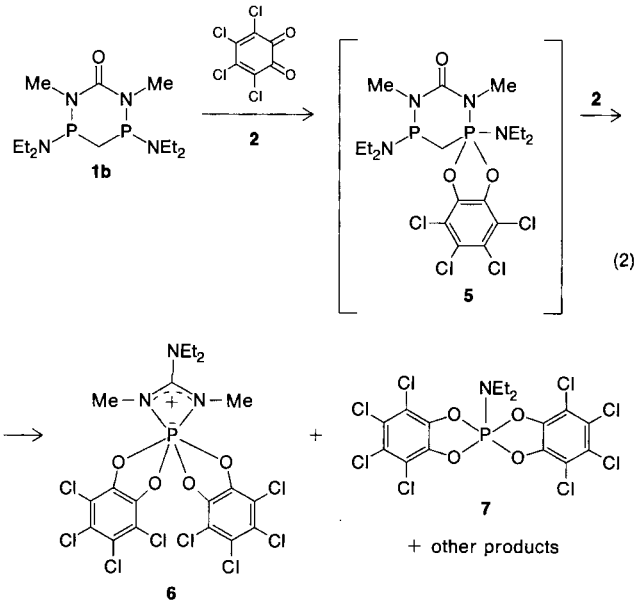
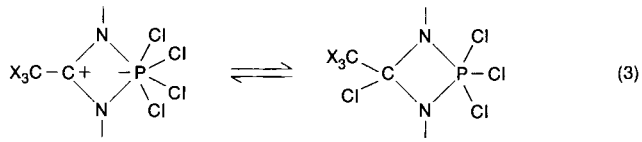


ethylamino group on the positive charge at the carbon atom. The influence of the substituent at the carbon atom of the mesoionic 1,3,2-diazaphosphetidine ("λ^6P^-") ring on its stability has already been noted[6]. For example, the electron-accepting trifluoro- or trichloromethyl groups destabilize the positive charge of the $-N\overset{+}{=}C=N-$ unit[7,8] [Eq. (3)].



The structure of **6**, suggested on the basis of NMR-spectroscopic and analytical data, was ultimately established by X-ray analysis (Figure 1). The molecule possesses crystallographic twofold symmetry, the twofold axis passing through the atoms P, N2, and C8. The four-membered ring is thus exactly planar. The intraannular N1–P–N1^i angle is acute (72.8°), cf. N1–C8–N1^i 103.8°, P–N1–C8 91.7°; the transannular distances are N1···N1^i 212.1, P···C8 227.1 pm. The five-membered chelate ring displays a flat envelope conformation, the phosphorus atom lying 30 pm out of the plane of O1,O2,C1,C6. The coordination at the phosphorus atom is approximately octahedral, the major deviations (e.g. O2–P–N1 168.4°) being imposed by the four-membered ring. The P–O bonds *trans* to the oxygen atom are longer than those *trans* to the nitrogen atom (172.8 versus 170.8 pm), with P–N1 178.8 pm; in compound **4**[2] similar values are observed for P–O *trans* to O (171.1, 171.8 pm), but the P–O bonds *trans* to N (177.5 pm) and C (175.9 pm) are much longer, with P–N 180.4 pm.

The spirophosphorane **7** is a colorless crystalline product, soluble in polar organic solvents. Its δ_P value (−21.5) is characteristic for this type of compounds. The preferred geometry of species with a five-coordinate phosphorus atom is (more or less distorted) trigonal bipyramidal. However,

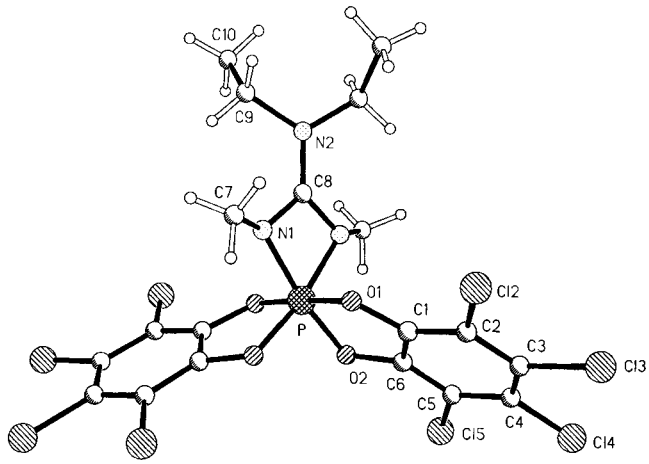


Figure 1. The molecule of compound **6** in the crystal; radii are arbitrary; only the asymmetric unit is numbered; selected bond lengths [pm] and angles [°]: P–O(1) 172.8(2), P–O(2) 170.8(3), P–N(1) 178.8(3), N(1)–C(8) 133.1(7); O(1)–P–O(2) 90.4(1), O(1)–P–N(1) 90.1(1), O(2)–P–N(1) 168.4(1), O(1)–P–O(1^i) 177.0(2), O(2)–P–O(2^i) 95.9(2), N(1)–P–O(1^i) 92.4(1), N(1)–P–O(2^i) 95.6(2), N(1)–P–N(1^i) 72.8(2), O(2)–P–O(1^i) 87.6(1), P–N(1)–C(8) 91.7(2), N(1)–C(8)–N(1^i) 103.8(4); symmetry operator: (i) 1 − *x*, *y*, 1.5 − *z*

the tendency of catechol-like ligands to promote square (better, rectangular) pyramidal geometry at the phosphorus atom has been known for some time[9–13]. The X-ray crystal structure analysis of **7** (Figure 2) shows that it is no exception to this trend; the four oxygen atoms define an almost square pyramidal base (O···O intraligand 238, interligand 221 pm, mean deviation of the four O atoms from the plane 4 pm), to which the apical P–N bond is within 0.3° of perpendicular. The aromatic rings are almost parallel to each other (dihedral angle 5°). The P–O bond lengths are 167.0–168.3 pm, with P–N 162.1 pm, very short for a formal single bond and comparable to the shortest equatorial bonds at a trigonal bipyramidal phosphorus atom (see, e.g., ref.[14]). The chelate rings, as in **6**, adopt an envelope conformation, the phosphorus atom lying 41, 48 pm out of the planes of the other four atoms.

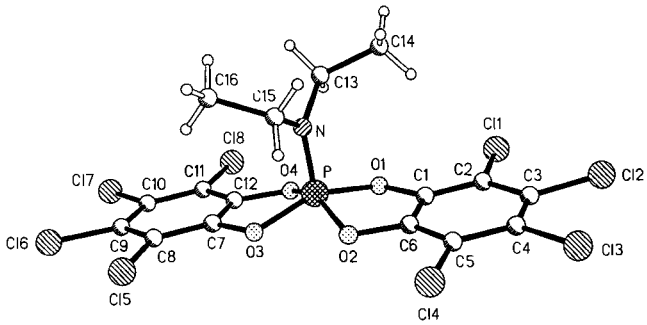
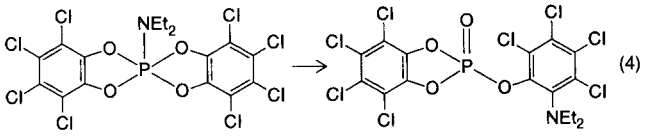


Figure 2. The molecule of compound **7** in the crystal; radii are arbitrary; selected bond lengths [pm] and angles [°]: P–O(1) 168.3(4), P–O(2) 167.0(3), P–O(3) 168.1(4), P–O(4) 167.4(4), P–N 162.1(5); O(1)–P–O(2) 90.5(2), O(1)–P–O(3) 153.9(2), O(2)–P–O(3) 82.5(2), O(1)–P–O(4) 82.3(2), O(2)–P–O(4) 147.8(2), O(3)–P–O(4) 90.3(2), O(1)–P–N 103.2(2), O(2)–P–N 106.3(2), O(3)–P–N 102.9(2), O(4)–P–N 105.9(2)

The spirophosphorane **7** is unstable. On recrystallization or on storage a second signal at $\delta = +11.3$ appears in its ^{31}P-NMR spectrum, and the signals of another NEt_2 group with different δ_H values are observed in the ^{1}H-NMR spectrum. At the same time, the molecular ion signal in the mass spectrum (m/z = 595 [M^+]) and the results of the elemental analysis remain unchanged as the proportion of the second compound increases. These data suggest that the spirophosphorane **7** is transformed into the isomeric phosphate **8** [Eq. (4)]. This is probably the first observation of this process.



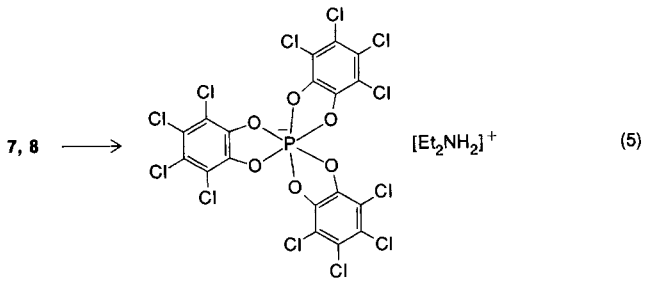
(4)

7 **8**

Earlier, such a rearrangement was either assumed[15] or the two isomers were detected independently[16].

All attempts at the separation of isomers **7** and **8**, and at obtaining a crystal of **8** suitable for an X-ray investigation, failed. It is probable that the isomers are in equilibrium.

The mixture of isomers **7** and **8**, left in $CDCl_3$ solution in an NMR tube, was transformed completely in three weeks into the colorless, crystalline product **9** (m. p. 161–162°C), which was poorly soluble in organic solvents [Eq. (5)].



(5)

9

The X-ray analysis shows that **9** crystallizes with two molecules of $CDCl_3$. The anion (Figures 3, 4) contains a hexacoordinate phosphorus atom; the largest deviation from octahedral angles at the phosphorus atom is 3.3°. The average P–O bond length is 171.3 pm [cf. 171.7 pm in tris(*o*-phenylenedioxy)phosphate[17]]. However, two P–O bond lengths (to O2 and O4) are markedly longer than the others. Closer inspection suggests that this may be due to hydrogen bond formation to the cation, with N···O2 ($-1+x$, y, z) 301 pm and N···O4 ($-1+x$, y, z) 313 pm. The solvent molecules are not involved in short contacts. Figure 4 shows a packing diagram of **9**. The chelate rings, in contrast to those in **6** and **7**, are essentially planar, the phosphorus atom lying only 4–8 pm out of the planes of the other ring atoms.

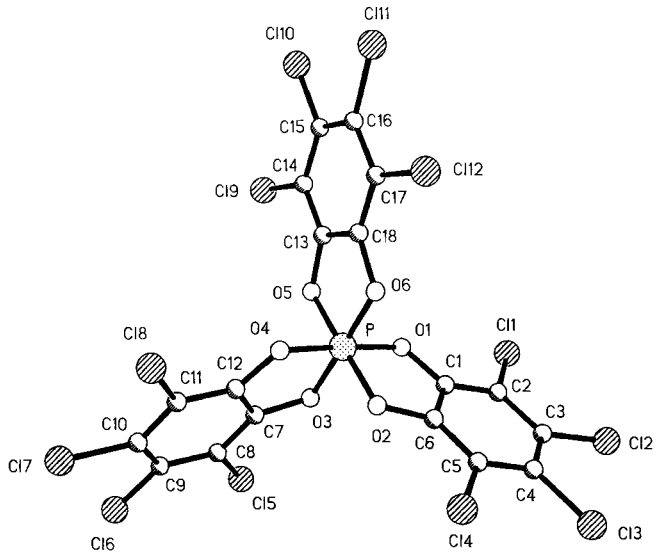


Figure 3. The anion of compound **9** in the crystal; radii are arbitrary; selected bond lengths [pm] and angles [°]: P–O(1) 170.5(4), P–O(2) 173.2(4), P–O(3) 170.4(3), P–O(4) 172.4(4), P–O(5) 170.8(4), P–O(6) 170.6(3); O–P–O 86.7–93.3, 177.0–178.4(2)

The ^{31}P-NMR spectrum of **9** shows a single signal at $\delta = -81.0$, which is characteristic of phosphorates with unsaturated cyclic substituents[18,19]. In the mass spectrum there is a signal from the anion of **9** with m/z = 769 [M^+].

The formation of **9** is probably explained by the slow hydrolysis of the spirophosphorane **7**, in agreement with the results obtained by Munoz et al.[15], and confirms their sug-

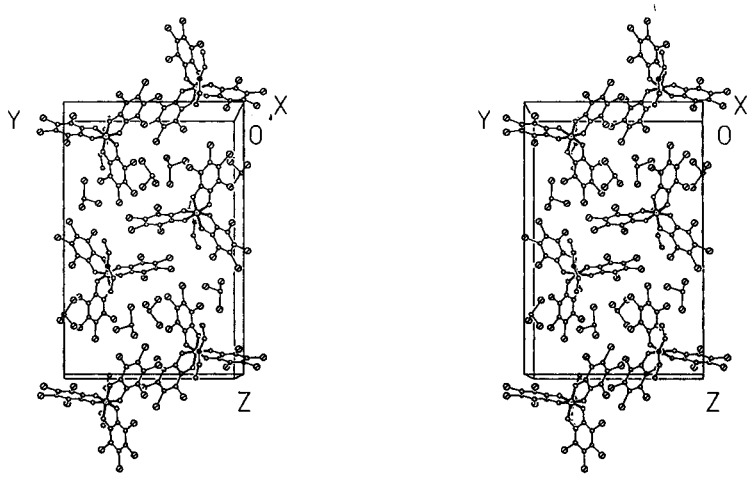
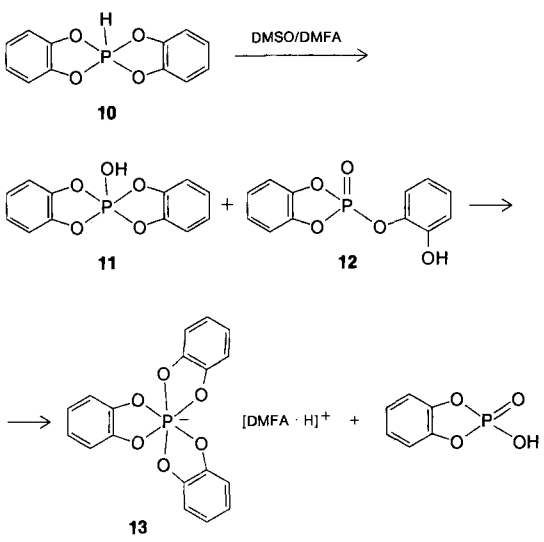


Figure 4. Stereoscopic packing diagram of compound **9** viewed along the x axis; H atoms omitted for clarity

gestion that the oxidation of the phosphorane **10** with dimethyl sulfoxide to the phosphorate **13** in dimethylformamide proceeds via formation of the phosphorane **11** and the isomeric phosphate **12** [Eq. (6)].



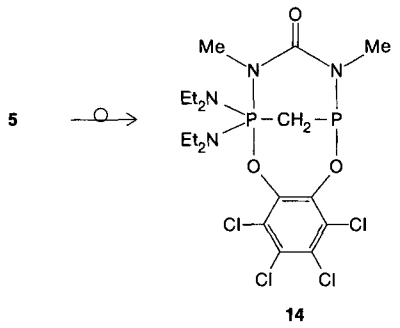
(6)

When the oxidation of the diazadiphosphorinane **1b** by TOB is carried out in toluene at −5 °C in a molar ratio of the reagents **1b**:**2** = 1:1.6, we find that the composition of the reaction mixture is somewhat simplified. The ^{31}P-NMR spectrum, apart from signals of the phosphorate **6** and the spirophosphorane **7** (δ_P = −102.7 and −21.5, respectively), shows an intense signal at δ = +60.1 and a weak signal at δ = +35.

The composition of the reaction mixture is essentially independent of the isomeric composition of the starting compound **1b**. The oxidation of 1:1 and 1:9 mixtures of *cis* and *trans* isomers of **1b** by TOB gives the same results (^{31}P-NMR-spectroscopic control). This can be accounted for by the fact that only one isomer takes part in the reaction. Earlier we showed that the methylation of **1b** by methyl iodide proceeds only through its *cis* isomer, with only one of the two phosphorus atoms being methylated[3]; in the reaction of **1b** with TOB we also believe that only the *cis* isomer takes part. The intermediate **5**, with one oxidized phosphorus atom, is formed first, as is confirmed by the ^{31}P-NMR spectrum of the reaction mixture recorded after the addition of an equimolar amount of TOB. The spectrum contains an intense characteristic double doublet with δ_P = 70.6 and −15.2 [^2J(P,P) = 3.4 Hz].

Compound **5** is unstable. Over four days at 20 °C it is transformed into another compound. This process is accompanied by the appearance and increase in intensity of a new double doublet at δ = 73.4 and −24.0 [^2J(P,P) = 96.3 Hz], and the disappearance of the former double doublet. It is highly probable that **5** is transformed into compound **14**, which contains one three- and one five-coordinate phosphorus atom [Eq. (7)].

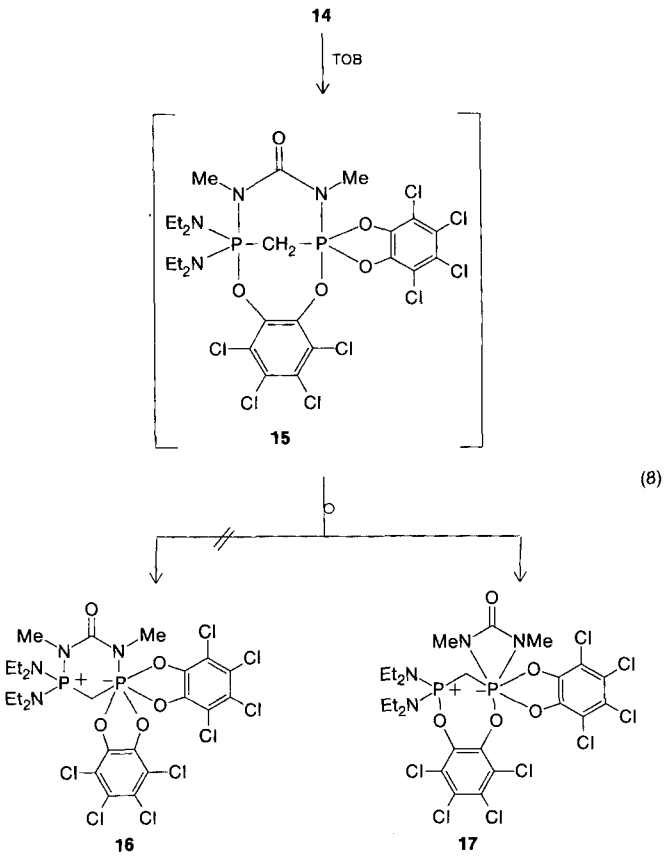
The rearrangement **5** → **14** can probably be explained by the steric overload in **5**. Moreover, the *cis* position of the diethylamino groups in **5** facilitates addition of the tetra-



(7)

chloro-*o*-phenylenedioxy unit to the two phosphorus atoms on one side of the diazadiphosphorinane ring.

One further piece of indirect evidence for the structure of **14** is its reaction with TOB [Eq. (8)]. In contrast to **5**, the oxidation of **14** with TOB which leads, ultimately, to the formation of **17**, proceeds without cleavage of the molecule. The ^{31}P-NMR spectrum of the compound formed shows a double doublet at δ = 59.3 and −137.6 [^2J(P,P) = 21.4 Hz] which indicates, as in the case of **4**[12], the presence of two phosphorus atoms of different coordination number (λ^4P^+,λ^6P^-) in the molecule [Eq. (8)].



(8)

The reaction probably proceeds in two stages. At first, the unstable addition product **15** is formed, containing two five-coordinate phosphorus atoms. The rearrangement of **15** can, in principle, take place in two directions, with the formation of isomers **16** and **17**. Analogously to **4**, the formation of isomer **16** could be expected, but the presence of

two bulky diethylamino groups in the molecule facilitates the formation of **17**, containing 4-, 5-, and 7-membered rings.

Compound **17**, after low-temperature crystallization from a mixture of dichloromethane/ether, is a colorless crystalline product, insoluble in nonpolar organic solvents. Its molecular structure was established by X-ray analysis, the result being shown in Figure 5. Compound **17** crystallizes with one molecule of dichloromethane. The coordination geometry at P1 is distorted octahedral, the major distortions being associated with the four-membered ring (e.g. N3–P1–N4 73.4°). This ring is planar to within 1 pm, with transoid methyl groups and a transannular P···C distance of 230 pm; its geometry is closely similar to that in compound **6**, although the P1–N bonds are slightly shorter in **17**. The P1–O bonds *trans* to the nitrogen atoms are much shorter than the one *trans* to the carbon atom (172.8, 172.9 versus 179.7 pm). The other phosphorus atom, P2, is tetrahedrally coordinated, but the spread of angles is wide (98.4–113.3°). As would be expected, the bonds at P2 are appreciably shorter than those at P1, e.g. P2–O3 159.4 pm, P2–C24 176.5 pm (cf. P1–C24 187.7 pm). The bridging hydroquinone ligand, not constrained by the presence of a five-membered ring, displays wider angles O–C–C(–O) (120, 122° versus 112, 114° in the chelate rings) and C–O–P (129, 127° versus 111, 114° in the chelate rings).

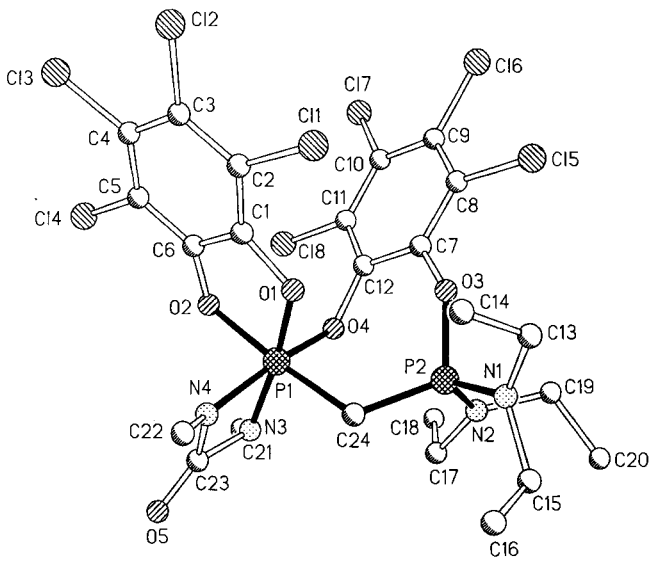


Figure 5. The molecule of compound **17** in the crystal; atom radii are arbitrary; hydrogen atoms and the solvent molecule are omitted; selected bond lengths [pm] and angles [°]: P(1)–N(3) 174.2(6), P(1)–N(4) 176.3(5), P(1)–O(1) 172.8(5), P(1)–O(2) 179.7(4), P(1)–O(4) 172.9(5), P(1)···C(23) 229.9(7), P(1)–C(24) 187.7(6), P(2)–N(1) 162.0(6), P(2)–N(2) 160.2(7), P(2)–O(3) 159.4(4), P(2)–C(24) 176.5(6); N(3)–P(1)–N(4) 73.4(3), N(3)–P(1)–O(1) 172.4(2), N(4)–P(1)–O(1) 99.6(3), N(3)–P(1)–O(2) 89.2(2), N(4)–P(1)–O(2) 89.9(2), O(1)–P(1)–O(2) 87.7(2), N(3)–P(1)–O(4) 90.8(3), N(4)–P(1)–O(4) 164.1(3), O(1)–P(1)–O(4) 96.1(2), O(2)–P(1)–O(4) 88.5(2), N(3)–P(1)–C(24) 97.0(3), N(4)–P(1)–C(24) 92.0(2), O(1)–P(1)–C(24) 86.2(3), O(2)–P(1)–C(24) 173.8(3), O(4)–P(1)–C(24) 91.2(2), N(1)–P(2)–N(2) 110.5(3), N(1)–P(2)–O(3) 98.4(3), N(2)–P(2)–O(3) 111.3(3), N(1)–P(2)–C(24) 113.3(3), N(2)–P(2)–C(24) 112.2(3), O(3)–P(2)–C(24) 110.3(3), P(1)–N(3)–C(23) 93.4(5), P(1)–N(4)–C(23) 94.1(4), N(3)–C(23)–N(4) 99.0(5), P(1)–C(24)–P(2) 118.8(3)

Compound **17** is thermally unstable. Its dissolution in boiling toluene leads to the complete cleavage of the molecule and formation of a mixture of products. The ^{31}P-NMR spectrum of the reaction mixture indicates the presence of phosphorate **6** and spirophosphorane **7** [Eq. (9)].

$$\mathbf{17} \xrightarrow{110\,^{\circ}C,\ \text{toluene}} \mathbf{6} + \mathbf{7} + \text{other products} \qquad (9)$$

Compound **6**, being insoluble in toluene, was isolated in a pure state. The NMR and mass spectral data of **6**, obtained by two methods (see above) are identical.

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Experimental

All experiments were carried out with exclusion of air and moisture; solvents were purified and dried according to the usual methods[20,21]. – NMR: Spectrometer Bruker AC-200 (^{1}H at 200.1 MHz; ^{13}C at 50.3 MHz; ^{31}P at 81.3 MHz); reference substances were $SiMe_4$ (TMS) ext. (^{1}H, ^{13}C), and 85% H_3PO_4 ext. (^{31}P); high-field shifts were given negative, low-field shifts positive signs. – MS: Spectrometer Finnigan MAT 8430; E.I. at 70 eV. – Materials: *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)urea[22] and methylenebis(dichlorophosphane)[23] were synthesized according to procedures described in the literature.

Methylenebis(chlorodiethylaminophosphane): A solution of diethyltrimethylsilylamine (20.6 g, 142 mmol) in 50 ml of ether was added dropwise at 0°C to a solution of methylenebis(dichlorophosphane) (15.0 g, 68.9 mmol) in 150 ml of ether with stirring. After stirring the reaction mixture for 1 h at room temperature, the ether was removed by distillation at 760 mm, and 100 ml of petroleum ether (boiling range 40–60°C) was added. The residue formed was filtered, petroleum ether was removed from the filtrate by distillation at 760 mm, and the oily residue was distilled in vacuo (0.05 mm); colorless liquid, b.p. 115–120°C 0.05 mm, yield 12.3 g (61%). – ^{1}H NMR ($CDCl_3$): δ = 1.13 (t, $^3J_{H,H}$ = 7.16 Hz, CH_3 part of the C_2H_5N group), 2.95–3.15 (m, PCH_2P), 3.08–3.25 (dq, $^3J_{H,H}$ = 7.16 Hz, $^3J_{P,H}$ = 14.01 Hz, CH_2 part of the C_2H_5N group). – ^{31}P NMR ($CDCl_3$): δ = 133.3, 135.2.

$C_9H_{22}Cl_2N_2P_2$ (291.14) Calcd. Cl 24.35 Found Cl 24.25

4-Diethylamino-1,3-dimethyl-2-bis(tetrachloro-o-phenylenedioxy)-1,3,2-diazaphosphetidine (**6**): *N,N'*-Dimethyl-*N,N'*-bis(trimethylsilyl)urea (1.49 g, 6.40 mmol) was added to a solution of methylenebis(chlorodiethylaminophosphane) (1.86 g, 6.40 mmol) in 20 ml of CH_2Cl_2, and the mixture was stirred at room temperature for 40 min. CH_2Cl_2 was removed in vacuo (ca. 0.5 mm), and 15 ml of ether was added. Subsequently, a solution of TOB (3.00 g, 12.2 mmol) in 25 ml of ether was added in portions of 8–10 drops at –5°C while stirring. Each portion of TOB was added at an interval of 2–3 min. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h and decanted from the oily residue precipitated. Ether from the reaction mixture was removed in vacuo (ca. 0.5 mm), and 5 ml of toluene was added. In 5 d, minute amounts of compound **6** were precipitated as colorless crystals; yield 0.17 g (4.0%). Compound **6** was isolated in 10% yield when the experiment was carried out in ether at –30°C (using the same

Table 1. Crystallographic data for compounds **6**, **7**, **9**, and **17**

Compound	**6**	**7**	**9** · 2 $CDCl_3$	**17** · CH_2Cl_2
Formula	$C_{19}H_{16}Cl_8N_3O_4P$	$C_{16}H_{10}Cl_8NO_4P$	$C_{24}H_{12}D_2Cl_{18}NO_6P$	$C_{25}H_{30}Cl_{10}N_4O_5P_2$
M_r	664.9	594.8	1083.4	883.0
Crystal habit	Colorless prism	Colorless prism	Colorless prism	Colorless prism
Crystal size (mm)	0.18 × 0.6 × 0.2	0.4 × 0.2 × 0.2	0.6 × 0.5 × 0.4	0.25 × 0.15 × 0.1
Space group	$C2/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [pm]	2051.3(7)	1500.8(5)	906.2(2)	995.9(4)
b [pm]	1020.0(3)	857.2(3)	1696.6(5)	1183.3(4)
c [pm]	1277.7(4)	1833.6(6)	2551.5(6)	1680.9(6)
α [°]	90	90	90	78.79(3)
β [°]	105.19(3)	113.58(3)	97.56(2)	74.65(3)
γ [°]	90	90	90	76.23(3)
V [nm^3]	2.580	2.162	3.889	1.837
Z	4	4	4	2
D_X [Mg m^{-3}]	1.712	1.828	1.851	1.596
$F(000)$	1336	1184	2144	896
μ [mm^{-1}]	0.97	1.15	1.36	0.89
$2\Theta_{max}$ [°]	50	50	50	50
No. of reflections				
measured	2530	7604	11152	6701
independent	2280	3819	6875	6457
R_{int}	0.030	0.027	0.022	0.022
observed [$> 4\ \sigma(F)$]	1719	2412	5069	3356
R	0.040	0.044	0.057	0.053
wR	0.045	0.046	0.062	0.050
g	0.0003	0.0004	0.0002	0.0003
No. of parameters	166	277	457	433
S	1.5	1.2	2.4	1.4
Max. Δ/σ	0.015	0.001	0.001	0.001
Max. $\Delta\varrho$ [e $pm^{-3} \times 10^6$]	0.4	0.6	1.5	0.5

amounts of starting materials and solvent). The residue formed was dissolved in 2 ml of CH_2Cl_2, and 3 ml of ether was added. In 2 h at 20°C, 0.3 g (10%) of **6** was formed as a colorless amorphous crystalline product; m.p. 267–269°C. – ^{1}H NMR ($CDCl_3$): δ = 1.28 (t, $^3J_{H,H}$ = 7.2 Hz, CH_3 part of the C_2H_5N group), 3.91 (d, $^3J_{P,H}$ = 14.2 Hz, NMe), 3.35 (q, $^3J_{H,H}$ = 7.2 Hz, CH_2 part of the C_2H_5N group). – ^{31}P NMR ($CDCl_3$): δ = –102.7.

$C_{19}H_{16}Cl_8N_3O_4P$ (664.96) Calcd. C 34.32 H 2.43 N 6.32 P 4.66
Found C 32.87 H 2.82 N 5.98 P 4.41
Calcd. 664.96 Found 665 (MS)

Table 2. Atomic coordinates (× 10^5) and equivalent isotropic displacement parameters [pm^2] for compound **6**

	x	y	z	U(eq)
P	50000	48450(13)	75000	210(4)
Cl(2)	29267(5)	50079(10)	47573(7)	303(3)
Cl(3)	18145(5)	35614(10)	55996(7)	318(3)
Cl(4)	22155(5)	20491(10)	78177(8)	376(4)
Cl(5)	37347(5)	20672(10)	92043(7)	323(3)
O(1)	43151(11)	48000(24)	63739(17)	229(8)
O(2)	46199(12)	37242(24)	81393(18)	243(8)
N(1)	53177(14)	62562(29)	69653(22)	216(10)
N(2)	50000	83762(42)	75000	278(15)
C(1)	37831(17)	42150(33)	66187(25)	203(11)
C(2)	31301(17)	42107(34)	59863(25)	209(11)
C(3)	26395(17)	35519(34)	63674(27)	229(11)
C(4)	28177(17)	28921(36)	73578(27)	244(12)
C(5)	34855(18)	29108(34)	79919(26)	230(11)
C(6)	39550(17)	35913(34)	76137(26)	207(11)
C(7)	54071(19)	64487(40)	58756(26)	292(13)
C(8)	50000	70711(51)	75000	218(16)
C(9)	55520(20)	91155(38)	72256(31)	354(14)
C(10)	59152(27)	100020(53)	81284(36)	600(20)

Spirophosphorane **7**: *N,N'*-Dimethyl-*N,N'*-bis(trimethylsilyl)urea (1.49 g, 6.40 mmol) was added to a solution of methylenebis(chlorodiethylaminophosphane) (1.86 g, 6.40 mmol) in 20 ml of CH_2Cl_2, and the mixture was stirred at room temperature for 40 min. The solvent was removed in vacuo (0.5 mm), and 15 ml of ether was added. Subsequently, a solution of TOB (2.68 g, 10.9 mmol) in 20 ml of ether was added in portions of 8–10 drops at –5°C while stirring. Each portion of TOB was added at an interval of 2–3 min. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h and then decanted from the precipitated oily residue. The reaction mixture was concentrated to a volume of 20 ml and then cooled to –20°C. The crystals formed over 24 h were dissolved in 5 ml of CH_2Cl_2, after which 1.5 ml of ether was added. The crystals formed after 24 h at –20°C were filtered and dried in vacuo (0.5 mm); yield 0.41 g (11%), m.p. 226–227°C. – ^{1}H NMR ($CDCl_3$): δ = 1.13 (t, $J_{H,H}$ = 7.3 Hz, CH_3 part of the C_2H_5N group), 3.10 (dq, $^3J_{H,H}$ = 7.3 Hz, $^3J_{P,H}$ = 17.3 Hz, CH_2 part of the C_2H_5N group). – ^{31}P NMR ($CDCl_3$): δ = –21.5.

$C_{16}H_{10}Cl_8NO_4P$ (594.86) Calcd. C 32.31 H 1.69 N 2.35 P 5.21
Found C 32.44 H 1.81 N 2.40 P 5.15
Calcd. 594.86 Found 595 (MS)

On recrystallization or on storage in CH_2Cl_2 solution the spirophosphorane **7** partly isomerizes into *tetrachloro-o-phenylene-*

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters [pm^2] for compound **7**

	x	y	z	U(eq)
P	6842(1)	2348(2)	5312.6(8)	228(5)
O(1)	6319(3)	4121(4)	5104(2)	251(14)
O(2)	5844(2)	1538(4)	4630(2)	258(14)
O(3)	6995(3)	549(4)	5709(2)	268(15)
O(4)	7386(3)	3123(4)	6223(2)	265(15)
N	7638(3)	2410(5)	4922(2)	236(17)
C(1)	5574(3)	4106(6)	4377(3)	212(20)
C(2)	5117(4)	5403(5)	3935(3)	227(22)
C(3)	4357(4)	5147(6)	3183(3)	225(21)
C(4)	4084(4)	3637(6)	2915(3)	221(21)
C(5)	4557(3)	2341(6)	3380(3)	215(20)
C(6)	5299(3)	2624(6)	4101(3)	236(21)
C(7)	7711(4)	563(6)	6455(3)	247(22)
C(8)	8162(3)	-736(6)	6890(3)	224(22)
C(9)	8867(4)	-483(6)	7663(3)	242(21)
C(10)	9091(4)	1038(6)	7955(3)	231(21)
C(11)	8633(4)	2313(6)	7496(3)	234(21)
C(12)	7939(4)	2031(6)	6759(3)	239(22)
C(13)	8174(4)	3836(6)	4934(3)	327(24)
C(14)	7768(5)	4784(8)	4170(4)	487(31)
C(15)	7817(4)	1068(7)	4519(3)	335(24)
C(16)	8748(5)	208(8)	4998(4)	515(33)
Cl(1)	5482(1)	7245(2)	4306.3(8)	307(6)
Cl(2)	3812(1)	6708(2)	2595.0(8)	302(6)
Cl(3)	3169(1)	3310(2)	1997.7(8)	343(6)
Cl(4)	4258(1)	455(2)	3061.3(8)	314(6)
Cl(5)	7846(1)	-2568(2)	6497.0(8)	338(6)
Cl(6)	9477(1)	-2042(2)	8235.5(8)	351(6)
Cl(7)	9969(1)	1346(2)	8904.2(8)	355(6)
Cl(8)	8897(1)	4202(2)	7831.9(8)	343(6)

dioxy-(3,4,5,6-tetrachloro-2-diethylaminophenoxy)phosphate (**8**): ^{1}H NMR ($CDCl_3$): δ = 1.40 (t, $^3J_{H,H}$ = 7.3 Hz CH_3 part of the C_2H_5N group), 3.10 (m, CH_2 part of the C_2H_5N group). – ^{31}P NMR ($CDCl_3$): δ = 11.3.

Formation of the Zwitterionic Product **17**: *N,N'*-Dimethyl-*N,N'*-bis(trimethylsilyl)urea (0.90 g, 3.90 mmol) was added to a solution of methylenebis(chlorodiethylaminophosphane) (1.13 g, 3.90 mmol) in 12 ml of CH_2Cl_2, and the mixture was stirred at room temperature for 40 min. The solvent was removed in vacuo (0.5 mm), and 9 ml of toluene was added. Subsequently, a solution of TOB (0.95 g, 3.90 mmol) in 12 ml of toluene was added in portions of 8–10 drops at –5°C while stirring. Each portion of TOB was added at an interval of 2–3 min. After the addition was completed, the reaction mixture was stirred at room temperature for 30 min. – ^{31}P NMR ($CDCl_3$) of **5** which was formed: δ = 70.6, –15.2 (dd, $^2J_{P,P}$ = 3.4 Hz). – The reaction mixture containing **5** was allowed to stand at 20°C for 48 h. It was decanted from the small residue formed, and a solution of TOB (0.55 g, 2.24 mmol) was slowly added dropwise with stirring at –5°C. The solid residue formed after 3 h at 20°C (0.35 g) was dissolved in 3 ml of CH_2Cl_2. 2 ml of ether was added, and the solution was cooled to –20°C. The crystals of **17** formed after 24 h were separated from the mother liquid and dried in vacuo (0.5 mm); yield 0.28 g (9%). – ^{1}H NMR ($CDCl_3$): δ = 0.95–1.40 (m, CH_3 part of the C_2H_5N group), 2.6–3.5 (m, CH_2 part of the C_2H_5N group, PCH_2P, CH_3N), 5.28 (s, CH_2Cl_2). – ^{31}P NMR ($CDCl_3$): δ = 59.3, –137.6 (dd, $^2J_{P,P}$ = 21.4 Hz).

$C_{24}H_{28}Cl_8N_4O_5P_2 \cdot CH_2Cl_2$ (883.04)
Calcd. C 34.00 H 3.42 N 6.34 P 7.02
Found C 34.54 H 3.72 N 6.61 P 6.81

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters [pm^2] for compound **9**

	x	y	z	U(eq)
P	5348(1)	7577.7(8)	945.7(5)	225(4)
O(1)	4137(3)	8346(2)	951(1)	233(11)
O(2)	6665(4)	8196(2)	731(1)	249(11)
O(3)	4539(4)	7371(2)	320(1)	250(11)
O(4)	6615(3)	6827(2)	915(1)	251(11)
O(5)	4065(4)	6972(2)	1171(1)	244(11)
O(6)	6165(4)	7758(2)	1576(1)	259(11)
C(1)	4751(6)	9033(3)	826(2)	236(16)
C(2)	4085(5)	9764(3)	820(2)	243(16)
C(3)	4872(6)	10429(3)	691(2)	264(16)
C(4)	6329(6)	10341(3)	568(2)	247(16)
C(5)	6988(5)	9595(3)	577(2)	268(17)
C(6)	6194(5)	8957(3)	703(2)	237(16)
C(7)	5169(5)	6742(3)	115(2)	243(16)
C(8)	4762(5)	6403(3)	-372(2)	256(16)
C(9)	5543(6)	5750(3)	-516(2)	304(18)
C(10)	6737(6)	5448(3)	-181(2)	297(17)
C(11)	7146(5)	5798(3)	314(2)	258(16)
C(12)	6355(5)	6431(3)	454(2)	251(16)
C(13)	4313(6)	6904(3)	1704(2)	252(16)
C(14)	3490(6)	6459(3)	2007(2)	278(17)
C(15)	3880(6)	6451(3)	2553(2)	347(19)
C(16)	5103(7)	6870(3)	2784(2)	345(19)
C(17)	5927(6)	7342(3)	2473(2)	288(17)
C(18)	5511(6)	7347(3)	1936(2)	246(16)
Cl(1)	2294(2)	9835.2(8)	971.2(5)	332(4)
Cl(2)	4078(2)	11344.8(8)	696.8(6)	386(5)
Cl(3)	7300(2)	11156.0(8)	404.0(5)	369(5)
Cl(4)	8775(1)	9473.2(9)	432.4(6)	375(5)
Cl(5)	3268(2)	6790.9(9)	-783.7(5)	380(5)
Cl(6)	4994(2)	5304.6(9)	-1120.0(5)	415(5)
Cl(7)	7702(2)	4642.6(9)	-364.3(6)	444(5)
Cl(8)	8656(2)	5463.3(9)	738.4(6)	379(5)
Cl(9)	2004(2)	5910.6(8)	1705.2(6)	387(5)
Cl(10)	2875(2)	5893(1)	2940.4(6)	567(6)
Cl(11)	5646(2)	6824(1)	3454.5(5)	550(6)
Cl(12)	7425(2)	7886(1)	2746.5(5)	452(5)
Cl(90)	1837(2)	3808(1)	2526.6(9)	731(8)
Cl(91)	3143(3)	2965(1)	1723.8(9)	790(8)
Cl(92)	584(3)	3962(1)	1439(1)	916(9)
Cl(93)	7345(3)	555(2)	2980.6(8)	1013(11)
Cl(94)	8865(4)	-250(2)	2242(2)	1810(23)
Cl(95)	6086(4)	535(4)	1947(1)	2397(34)
N	-235(5)	7526(3)	819(2)	426(18)
C(80)	623(6)	7838(4)	1316(3)	469(22)
C(81)	-170(7)	7696(5)	1781(3)	609(28)
C(82)	-405(8)	7326(5)	-144(3)	677(31)
C(83)	561(7)	7567(4)	350(3)	523(25)
C(84)	2233(8)	3832(4)	1866(3)	622(28)
C(85)	7128(10)	-15(5)	2422(4)	965(43)

X-ray Crystal Structure Determination of Compounds **6**, **7**, **9**, *and* **17**: Intensity measurements were carried out at –95°C with a Siemens R3 diffractometer fitted with an LT-2 cooling device. Monochromated Mo-K_α radiation (λ = 71.069 pm) was used. Cell constants were refined from setting angles of 50 reflections in the 2Θ range 20–23°. Structures were solved by direct methods and refined anisotropically on *F*. Hydrogen atoms were included by using a riding model. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed. Detailed crystal data are given in Table 1, with atom coordinates in Tables 2–5. The program system was Siemens SHELXTL PLUS. Further details of the structure determinations

Table 5. Atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters [pm^2] for compound **17**

	x	y	z	U(eq)
P(1)	695(2)	3357(2)	1767(1)	238(7)
P(2)	-2045(2)	5069(2)	2564(1)	243(7)
N(1)	-2457(6)	6377(5)	2824(3)	282(22)
N(2)	-3369(6)	4748(5)	2345(3)	286(22)
N(3)	511(6)	3071(4)	827(3)	250(22)
N(4)	2052(5)	3894(4)	982(3)	241(21)
O(1)	1112(4)	3640(3)	2634(3)	233(17)
O(2)	1855(4)	1947(3)	1879(3)	250(18)
O(3)	-1755(5)	4346(3)	3427(3)	264(18)
O(4)	-716(4)	2695(3)	2308(3)	232(17)
O(5)	2186(5)	3623(4)	-380(3)	340(20)
C(1)	2150(6)	2805(5)	2907(4)	200(25)
C(2)	2726(7)	2833(6)	3560(4)	238(26)
C(3)	3864(7)	1940(6)	3718(4)	266(26)
C(4)	4367(7)	1048(6)	3226(4)	259(26)
C(5)	3729(7)	997(5)	2600(4)	252(26)
C(6)	2597(7)	1874(5)	2446(4)	223(25)
C(7)	-1631(7)	3158(6)	3689(4)	249(27)
C(8)	-2086(7)	2816(6)	4536(4)	274(28)
C(9)	-1980(7)	1624(6)	4841(4)	290(28)
C(10)	-1438(7)	785(6)	4298(5)	315(29)
C(11)	-987(7)	1141(6)	3451(4)	256(27)
C(12)	-1062(7)	2333(6)	3127(4)	236(27)
C(13)	-2109(8)	6685(6)	3546(4)	407(33)
C(14)	-526(8)	6612(7)	3459(6)	528(40)
C(15)	-2942(7)	7357(6)	2204(4)	311(28)
C(16)	-1849(8)	8114(7)	1775(5)	454(35)
C(17)	-3295(7)	4217(6)	1601(4)	294(28)
C(18)	-3819(8)	3067(6)	1814(5)	405(33)
C(19)	-4769(7)	4991(7)	2926(5)	403(32)
C(20)	-5851(8)	5934(7)	2555(5)	453(34)
C(21)	132(8)	2083(6)	609(5)	378(32)
C(22)	2891(8)	4790(7)	862(5)	452(34)
C(23)	1688(7)	3547(6)	360(5)	264(27)
C(24)	-491(6)	4850(5)	1762(4)	229(25)
Cl(1)	1995(2)	3944(2)	4158(1)	351(7)
Cl(2)	4641(2)	1997(2)	4503(1)	417(8)
Cl(3)	5826(2)	-7(2)	3400(1)	416(8)
Cl(4)	4285(2)	-141(2)	2006(1)	406(8)
Cl(5)	-2786(2)	3860(2)	5180(1)	457(8)
Cl(6)	-2547(2)	1193(2)	5892(1)	474(9)
Cl(7)	-1381(2)	-677(2)	4671(1)	433(8)
Cl(8)	-308(2)	135(2)	2766(1)	367(8)
C(90)	6727(10)	850(9)	9706(6)	841(53)
Cl(90)	5102(3)	1818(2)	9692(2)	805(12)
Cl(91)	8144(3)	1467(3)	9102(3)	1305(21)

(complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, F.R.G. Any request for this material should quote the full literature citation and the reference number CSD-55868.

[1] Dedicated to Professor *Viktor Gutmann* on the occasion of his 70th birthday.
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CAS Registry Numbers

2: 2435-53-2 / **5**: 140176-11-0 / **6**: 140176-14-3 / **7**: 140176-12-1 / **8**: 140176-13-2 / **9**: 140176-15-4 / **9** · 2 $CDCl_3$: 140176-17-6 / **17**: 140176-16-5 / **17** · CH_2Cl_2: 140384-79-8 / $Me(Me_3Si)NCON(SiMe_3)Me$: 10218-17-4 / $Cl(Et_2N)PCH_2P(NEt_2)Cl$: 70589-69-4 / Me_3SiNEt_2: 996-50-9 / $Cl_2PCH_2PCl_2$: 28240-68-8