Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

Structural Characterization of Chlorospirophosphoranes Existing as Nearly Perfect Rectangular Pyramids[1]

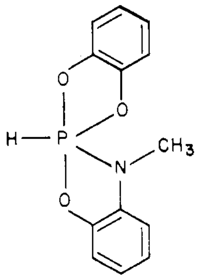
THOMAS E. CLARK,[2] ROBERTA O. DAY, and ROBERT R. HOLMES*

Received September 15, 1978

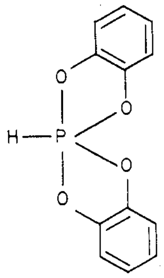
Single-crystal X-ray analysis of 2,3-benzo-7,8-tetrachlorobenzo-1,4,6,9-tetraoxa-5-phenyl-5λ^5-phosphaspiro[4.4]nona-2,7-diene, $(C_6Cl_4O_2)(C_6H_4O_2)P(C_6H_5)$, VI, and 2,3,7,8-bis(tetrachlorobenzo)-5-phenyl-1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]-nona-2,7-diene, $(C_6Cl_4O_2)_2P(C_6H_5)$, VII, showed that they possessed nearly perfect rectangular-pyramidal geometries. The distortion amounts to only 6% for each as measured by the sum of dihedral angles, and the direction of structural displacement is on a coordinate leading to a connecting trigonal-bipyramidal isomer. Data for both compounds were collected on an Enraf-Nonius CAD4 automated diffractometer, by using Mo K$\bar{\alpha}$ radiation, out to a maximum $2\theta_{\mathrm{MoK}\bar{\alpha}}$ of 55°. VI crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.495$ (1) Å, $b = 9.866$ (1) Å, $c = 12.053$ (2) Å, $\alpha = 76.22$ (1)°, $\beta = 71.38$ (1)°, $\gamma = 88.95$ (1)°, and $Z = 2$. Full-matrix least-squares refinement gave $R = 0.029$ and $R_w = 0.039$ for the 2980 reflections having $I \geq 3\sigma_I$. VII crystallizes in the triclinic space group $P\bar{1}$, with two phosphorane molecules and one chlorobenzene molecule, which is disordered about an inversion center, per unit cell. The lattice constants are $a = 8.242$ (4) Å, $b = 12.806$ (2) Å, $c = 12.821$ (3) Å, $\alpha = 72.76$ (2)°, $\beta = 76.78$ (3)°, and $\gamma = 75.58$ (3)°. Full-matrix least-squares refinement gave $R = 0.048$ and $R_w = 0.067$ for the 3331 reflections having $I \geq 3\sigma_I$. The close approach to an ideal rectangular bipyramid for each of these spirocyclics is aided by the electron-withdrawing effect of the chlorine ring substituents and their symmetrical placement.

Introduction

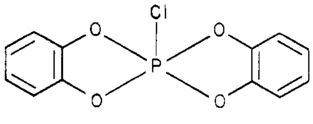
Most structures of cyclic phosphoranes determined thus far by single-crystal X-ray analysis have been found to show distortions which adhere closely to a coordinate connecting an ideal trigonal bipyramid and an ideal square or rectangular pyramid.[3,4] When the various factors that influence the degree of structural displacement from these ideal pentacoordinated configurations are examined for spirocyclic phosphoranes, the steric and electronic requirements of the unique ligand are found to exert large effects. For example, the spiro derivatives I[5] and II[6] have structures that are little displaced from the trigonal bipyramid, 5.5%[4] and about 1.7%, respectively,[4] as measured by the dihedral-angle method based on unit bond lengths.[3] These values are shown in parentheses. In contrast, the derivatives III–V more closely approach an ideal rectangular pyramid.[1b,7,8]



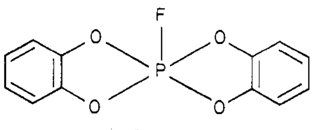
I (5.5%)



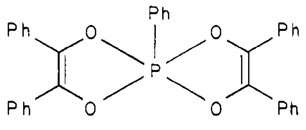
II (~1.7%)



III[7] (72%)

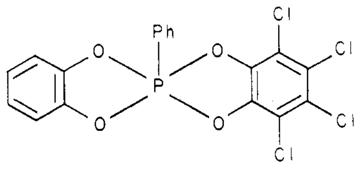


IV[8] (65%)

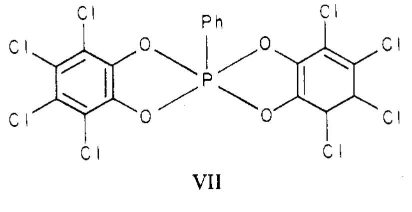


V[1b] (86%)

In the present study, we investigate the influence of ring substitution on structural displacement. Since a number of X-ray analyses have been carried out on spirocyclics in which the phenyl group was present as the unique ligand,[1b,9–14] we continued its use here. Further, a variety of derivatives containing a common spirocyclic ring system of the type II–IV have had their structures determined. Accordingly, the chlorophosphoranes VI and VII were prepared and subjected to X-ray analysis.



VI



VII

Experimental Section

Preparation of VI. Crystals of 2,3-benzo-7,8-tetrachlorobenzo-1,4,6,9-tetraoxa-5-phenyl-5λ^5-phosphaspiro[4.4]nona-2,7-diene, $(C_6Cl_4O_2)(C_6H_4O_2)P(C_6H_5)$, were prepared according to the procedure of Wieber and Hoos[15] by the addition of *o*-phenylene phenylphosphonite[16] to tetrachloro-*o*-quinone in ether. Colorless crystals for the X-ray study were obtained by recrystallization from benzene; mp (uncor) 215.5–217 °C (lit.[15] 136 °C). Anal. Calcd for $C_{18}H_9Cl_4O_4P$: C, 46.79; H, 1.96; P, 6.71. Found: C, 46.96; H, 2.14; P, 6.74.

Preparation of VII. 2,3,7,8-Bis(tetrachlorobenzo)-5-phenyl-1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nona-2,7-diene, $(C_6Cl_4O_2)_2$-

Table I. Atomic Coordinates for $(C_6H_4O_2)(C_6Cl_4O_2)P(C_6H_5)$, VI[a]

atom[b]	10^4x	10^4y	10^4z
P	6650 (1)	11573 (1)	445 (1)
O1	4888 (3)	11677 (2)	1570 (2)
O2	6695 (3)	9857 (2)	1122 (2)
O3	7610 (3)	11048 (2)	−801 (2)
O4	5906 (3)	12909 (2)	−340 (2)
1C1	4649 (4)	10586 (3)	2565 (3)
1C2	3501 (4)	10470 (3)	3690 (3)
1C3	3461 (4)	9260 (3)	4591 (3)
1C4	4539 (4)	8202 (3)	4337 (3)
1C5	5684 (4)	8341 (3)	3174 (3)
1C6	5710 (4)	9535 (3)	2306 (3)
2C1	8265 (4)	12373 (3)	779 (3)
2C2	9817 (5)	11829 (4)	572 (4)
2C3	11064 (6)	12419 (5)	836 (5)
2C4	10785 (6)	13557 (4)	1315 (4)
2C5	9266 (6)	14111 (4)	1529 (4)
2C6	7995 (5)	13536 (4)	1260 (3)
3C1	7771 (4)	12097 (3)	−1835 (3)
3C2	8747 (5)	12114 (4)	−2992 (3)
3C3	8687 (5)	13278 (4)	−3892 (3)
3C4	7676 (5)	14357 (4)	−3623 (3)
3C5	6694 (4)	14324 (4)	−2442 (3)
3C6	6779 (4)	13176 (3)	−1565 (3)
Cl2	2171 (1)	11780 (1)	3954 (1)
Cl3	2042 (1)	9067 (1)	6019 (1)
Cl4	4442 (1)	6703 (1)	5446 (1)
Cl5	7055 (1)	7080 (1)	2821 (1)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled in agreement with Figure 1.

$P(C_6H_5)$, was prepared under a nitrogen atmosphere by first dissolving tetrachlorocatechol[17] (16.5 g, 66.6 mmol) in boiling chlorobenzene (150 mL) in a 500-mL flask. A solution of dichlorophenylphosphine (6.0 g, 33.5 mmol) in chlorobenzene (50 mL) was then added dropwise over a 30-min period. After an initial 20 min during which time no evolution of HCl was noticed, about 95% of the theoretical amount was detected in the next hour. The reaction was allowed to reflux for an additional 15 h. Needle-like crystals formed on cooling the reaction mixture. The crude product was filtered. Recrystallization from chlorobenzene yielded crystals suitable for X-ray analysis; mp (uncor) 319–321 °C (yield 14 g, 64%). The latter assumes a solvent molecule C_6H_5Cl of recrystallization which was detected in the el-

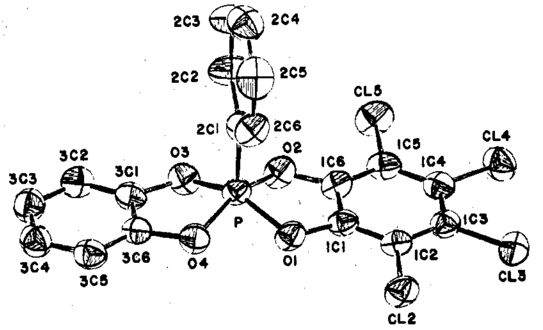


Figure 1. ORTEP plot of the molecular geometry of $(C_6H_4O_2)(C_6Cl_4O_2)P(C_6H_5)$, VI, with thermal ellipsoids at the 50% probability level.

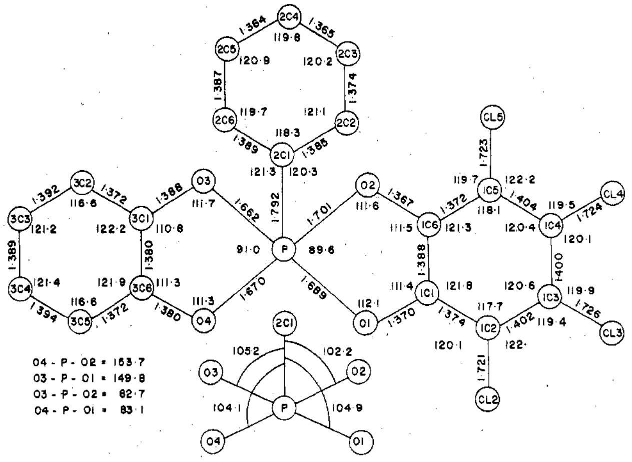


Figure 2. Schematic drawing of $(C_6H_4O_2)(C_6Cl_4O_2)P(C_6H_5)$, VI, showing selected bond distances (Å) and angles (deg).

Table II. Thermal Parameters in $(C_6H_4O_2)(C_6Cl_4O_2)P(C_6H_5)$, VI[a]

atom[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	2.94 (3)	2.70 (3)	3.93 (4)	0.82 (2)	−0.99 (3)	−0.85 (3)
O1	3.3 (1)	3.3 (1)	4.4 (1)	0.9 (1)	−0.7 (1)	−0.5 (1)
O2	3.9 (1)	2.8 (1)	5.0 (1)	0.8 (1)	−0.8 (1)	−0.8 (1)
O3	4.6 (1)	3.4 (1)	4.3 (1)	1.2 (1)	−1.6 (1)	−1.3 (1)
O4	3.8 (1)	3.9 (1)	4.3 (1)	1.5 (1)	−1.1 (1)	−0.7 (1)
1C1	3.0 (1)	2.9 (1)	4.5 (1)	0.3 (1)	−1.3 (1)	−0.7 (1)
1C2	2.8 (1)	3.3 (1)	4.5 (1)	0.3 (1)	−1.3 (1)	−1.0 (1)
1C3	3.3 (1)	3.6 (1)	4.1 (1)	−0.2 (1)	−1.3 (1)	−0.8 (1)
1C4	3.7 (1)	3.0 (1)	4.7 (1)	−0.1 (1)	−1.9 (1)	−0.5 (1)
1C5	3.5 (1)	2.7 (1)	5.6 (2)	0.5 (1)	−1.8 (1)	−0.9 (1)
1C6	3.2 (1)	2.9 (1)	4.4 (1)	0.2 (1)	−1.0 (1)	−1.0 (1)
2C1	3.5 (1)	2.9 (1)	3.3 (1)	0.6 (1)	−0.9 (1)	−0.6 (1)
2C2	4.3 (2)	4.7 (2)	8.3 (2)	1.8 (1)	−2.9 (2)	−3.5 (2)
2C3	4.6 (2)	5.9 (2)	9.2 (3)	1.4 (2)	−3.6 (2)	−3.0 (2)
2C4	6.1 (2)	4.8 (2)	6.0 (2)	−0.7 (2)	−3.0 (2)	−0.9 (1)
2C5	7.3 (3)	4.3 (2)	6.0 (2)	0.1 (2)	−2.0 (2)	−2.3 (2)
2C6	4.4 (2)	3.9 (1)	5.2 (2)	0.9 (1)	−1.0 (1)	−1.8 (1)
3C1	3.6 (1)	3.5 (1)	4.3 (1)	0.3 (1)	−1.8 (1)	−1.3 (1)
3C2	4.3 (2)	4.5 (2)	4.7 (2)	0.7 (1)	−1.6 (1)	−1.9 (1)
3C3	4.6 (2)	5.2 (2)	4.1 (2)	0.0 (1)	−1.1 (1)	−1.2 (1)
3C4	4.8 (2)	4.2 (2)	4.6 (2)	−0.1 (1)	−1.9 (1)	−0.5 (1)
3C5	4.1 (2)	3.9 (1)	5.1 (2)	0.4 (1)	−1.9 (1)	−0.8 (1)
3C6	3.2 (1)	3.6 (1)	4.1 (1)	0.3 (1)	−1.5 (1)	−0.8 (1)
Cl2	3.78 (4)	4.23 (4)	5.28 (4)	1.38 (3)	−0.85 (3)	−1.19 (3)
Cl3	4.55 (4)	5.11 (4)	4.04 (4)	0.14 (3)	−0.94 (3)	−0.65 (3)
Cl4	5.60 (5)	3.79 (4)	5.30 (5)	0.31 (3)	−2.47 (4)	0.18 (3)
Cl5	4.88 (5)	3.33 (4)	7.21 (6)	1.59 (3)	−1.36 (4)	−0.83 (3)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. Anisotropic temperature factors used during refinement are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the B_{ij} in Å^2 given above are related to the dimensionless β_{ij} as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$. [b] Atoms are labeled in agreement with Figure 1.

Table III. Refined Parameters for Hydrogen Atoms in $(C_6H_4O_2)(C_6Cl_4O_2)P(C_6H_5)$, VI[a]

atom[a]	10^3x	10^3y	10^3z	B_{iso}, Å^2
2H2	1003 (5)	1104 (5)	23 (4)	6 (1)
2H3	1203 (6)	1200 (5)	73 (4)	7 (1)
2H4	1164 (6)	1402 (5)	148 (4)	7 (1)
2H5	912 (6)	1493 (5)	180 (4)	7 (1)
2H6	688 (5)	1393 (4)	137 (3)	5 (1)
3H2	940 (5)	1143 (4)	−316 (3)	5 (1)
3H3	939 (5)	1337 (4)	−472 (3)	5 (1)
3H4	776 (5)	1515 (4)	−430 (4)	6 (1)
3H5	598 (5)	1510 (4)	−225 (3)	5 (1)

[a] See footnotes *a* and *b* to Table I.

Table IV. Bond Lengths (Å) and Angles (deg) in $(C_6H_4O_2)(C_6Cl_4O_2)P(C_6H_5)$, VI[a]

	Lengths		
P-O2	1.701 (2)	2C6-2C1	1.389 (5)
P-O4	1.670 (2)	3C1-3C2	1.372 (5)
P-O1	1.689 (2)	3C2-3C3	1.392 (5)
P-O3	1.662 (2)	3C3-3C4	1.389 (5)
P-2C1	1.792 (2)	3C4-3C5	1.394 (5)
O1-1C1	1.370 (4)	3C5-3C6	1.372 (5)
O2-1C6	1.367 (4)	3C6-3C1	1.380 (4)
O3-3C1	1.388 (5)	1C2-Cl2	1.721 (3)
O4-3C6	1.380 (4)	1C3-Cl3	1.726 (3)
1C1-1C2	1.374 (4)	1C4-Cl4	1.724 (3)
1C2-1C3	1.402 (4)	1C5-Cl5	1.723 (3)
1C3-1C4	1.400 (4)	2C2-2H2	0.95 (4)
1C4-1C5	1.404 (5)	2C3-2H3	0.90 (5)
1C5-1C6	1.372 (4)	2C4-2H4	0.96 (5)
1C6-1C1	1.388 (4)	2C5-2H5	0.93 (5)
2C1-2C2	1.385 (5)	2C6-2H6	1.00 (4)
2C2-2C3	1.374 (6)	3C2-3H2	0.88 (4)
2C3-2C4	1.365 (6)	3C3-3H3	0.97 (4)
2C4-2C5	1.364 (7)	3C4-3H4	0.97 (4)
2C5-2C6	1.387 (6)	3C5-3H5	0.99 (4)
	Angles		
O2-P-O4	153.7 (1)	2C6-2C1-P	121.3 (2)
O1-P-O3	149.8 (1)	2C1-2C2-2H2	120 (3)
O2-P-2C1	102.2 (1)	2C1-2C2-2C3	121.1 (4)
O4-P-2C1	104.1 (1)	2H2-2C2-2C3	119 (3)
O1-P-2C1	104.9 (1)	2C2-2C3-2H3	118 (3)
O3-P-2C1	105.2 (1)	2C2-2C3-2C4	120.2 (4)
O1-P-O2	89.6 (1)	2H3-2C3-2C4	122 (3)
O3-P-O4	91.0 (1)	2C3-2C4-2H4	123 (3)
O2-P-O3	82.7 (1)	2C3-2C4-2C5	119.8 (4)
O1-P-O4	83.1 (1)	2H4-2C4-2C5	118 (3)
P-O1-1C1	112.1 (2)	2C4-2C5-2H5	119 (3)
P-O2-1C6	111.6 (2)	2C4-2C5-2C6	120.9 (4)
P-O3-3C1	111.7 (2)	2H5-2C5-2C6	120 (3)
P-O4-3C6	111.3 (2)	2C1-2C6-2H6	117 (2)
O1-1C1-1C2	126.7 (3)	2C1-2C6-2C5	119.7 (3)
O1-1C1-1C6	111.4 (3)	2H6-2C6-2C5	123 (2)
1C2-1C1-1C6	121.8 (3)	O3-3C1-3C2	126.9 (3)
1C1-1C2-1C3	117.7 (3)	O3-3C1-3C6	110.8 (3)
1C1-1C2-Cl2	120.1 (2)	3C2-3C1-3C6	122.2 (3)
1C3-1C2-Cl2	122.2 (2)	3C1-3C2-3H2	122 (3)
1C2-1C3-1C4	120.6 (3)	3C1-3C2-3C3	116.6 (3)
1C2-1C3-Cl3	119.4 (2)	3H2-3C2-3C3	121 (3)
1C4-1C3-Cl3	119.9 (2)	3C2-3C3-3H3	120 (2)
1C3-1C4-1C5	120.4 (3)	3C2-3C3-3C4	121.2 (4)
1C3-1C4-Cl4	120.1 (2)	3H3-3C3-3C4	118 (2)
1C5-1C4-Cl4	119.5 (2)	3C3-3C4-3H4	115 (2)
1C4-1C5-1C6	118.1 (3)	3C3-3C4-3C5	121.4 (3)
1C4-1C5-Cl5	122.2 (2)	3H4-3C4-3C5	123 (2)
1C6-1C5-Cl5	119.7 (2)	3C4-3C5-3H5	121 (2)
O2-1C6-1C5	127.2 (3)	3C4-3C5-3C6	116.6 (3)
O2-1C6-1C1	111.5 (5)	3H5-3C5-3C6	122 (2)
1C5-1C6-1C1	121.3 (3)	O4-3C6-3C5	126.8 (3)
2C2-2C1-2C6	118.3 (3)	O4-3C6-3C1	111.3 (3)
2C2-2C1-P	120.3 (2)	3C5-3C6-3C1	121.9 (3)

[a] See footnotes *a* and *b* to Table I.

emental analysis. Anal. Calcd for $C_{42}H_{15}Cl_{17}O_8P$: C, 38.44; H, 1.15; Cl, 45.93. Found: C, 38.87; H, 1.31; Cl, 46.28.

Table V. Atomic Coordinates for $(C_6Cl_4O_2)_2P(C_6H_5)$, VII[a]

atom[b]	10^4x	10^4y	10^4z
P	1906 (1)	6100 (1)	3725 (1)
O1	1415 (2)	6024 (1)	2546 (1)
O2	2724 (2)	4717 (1)	4032 (1)
O3	1498 (2)	5871 (1)	5119 (1)
O4	293 (2)	7211 (1)	3619 (1)
AC1	3735 (3)	6714 (2)	3297 (2)
AC2	3640 (3)	7831 (2)	2732 (2)
AC3	5071 (4)	8297 (2)	2402 (3)
AC4	6629 (4)	7652 (2)	2627 (2)
AC5	6719 (4)	6560 (3)	3188 (3)
AC6	5308 (3)	6076 (2)	3533 (2)
1C1	583 (3)	6817 (2)	5421 (2)
1C2	368 (4)	7025 (2)	6443 (2)
1C3	−631 (4)	8055 (3)	6575 (2)
1C4	−1363 (3)	8822 (2)	5719 (3)
1C5	−1115 (3)	8616 (2)	4677 (2)
1C6	−129 (3)	7600 (2)	4558 (2)
2C1	2355 (3)	5087 (2)	2234 (2)
2C2	2578 (3)	4872 (2)	1223 (2)
2C3	3606 (4)	3853 (2)	1076 (2)
2C4	4368 (3)	3105 (2)	1941 (2)
2C5	4155 (3)	3333 (2)	2975 (2)
2C6	3107 (3)	4340 (2)	3089 (2)
Cl2	1311 (1)	6059 (1)	7488 (1)
Cl3	−951 (1)	8353 (1)	7853 (1)
Cl4	−2590 (1)	10086 (1)	5903 (1)
Cl5	−1912 (1)	9571 (1)	3570 (1)
Cl2′	1597 (1)	5831 (1)	188 (1)
Cl3′	3914 (1)	3541 (1)	−188 (1)
Cl4′	5667 (1)	1864 (1)	1744 (1)
Cl5′	5079 (1)	2430 (1)	4065 (1)
Cl	2801 (4)	129 (3)	163 (3)
C1	578 (9)	−1059 (4)	281 (3)
C2	1318 (15)	−279 (11)	149 (5)
C3	1476 (24)	962 (13)	−125 (7)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 3.

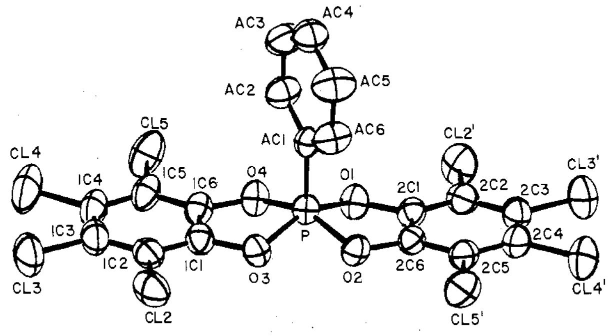


Figure 3. ORTEP plot of the molecular geometry of $(C_6Cl_4O_2)_2P(C_6H_5)$, VII, with thermal ellipsoids at the 50% probability level.

Space Group Determination and Data Collection for VI. A well-formed crystal having dimensions 0.40 mm × 0.30 mm × 0.20 mm was mounted in a thin-walled glass capillary which was sealed as a precautionary measure against hydrolysis. Preliminary investigations using an Enraf-Nonius CAD4 automated diffractor and Zr-filtered molybdenum radiation ($\lambda K\alpha_1$ 0.709 26 Å, $\lambda K\alpha_2$ 0.713 54 Å) indicated triclinic ($\bar{1}$) symmetry. The lattice constants as determined by the least-squares refinement of the diffraction geometry for 21 reflections having $21° < 2\theta_{\mathrm{MoK}\bar{\alpha}} < 30°$ as measured at an ambient laboratory temperature of 22 ± 2 °C are a = 8.495 (1) Å, b = 9.866 (1) Å, c = 12.053 (2) Å, α = 76.22 (1)°, β = 71.38 (1)°, and γ = 88.95 (1)°. A unit cell content of two molecules gives a calculated density of 1.654 g/cm^3 in agreement with the value of 1.69 (4) g/cm^3 as measured by flotation in a methyl iodide–benzene mixture. The space group $P\bar{1}$-C_i^1 [18] was chosen on the assumption that there would be one molecule in the asymmetric unit. This choice was confirmed by all subsequent stages of solution and refinement.

Table VI. Thermal Parameters for $(C_6Cl_4O_2)_2P(C_6H_5)$, VII[a]

atom[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	3.07 (3)	3.29 (2)	3.17 (2)	−0.12 (2)	−1.05 (2)	−0.91 (2)
O1	4.2 (1)	4.2 (1)	3.6 (1)	−0.1 (1)	−1.7 (1)	−1.3 (1)
O2	4.4 (1)	3.2 (1)	3.7 (1)	−0.2 (1)	−1.2 (1)	−0.8 (1)
O3	4.1 (1)	4.3 (1)	3.3 (1)	−0.3 (1)	−0.6 (1)	−1.2 (1)
O4	3.8 (1)	4.1 (1)	4.2 (1)	0.2 (1)	−1.5 (1)	−1.6 (1)
AC1	3.6 (1)	3.3 (1)	3.1 (1)	−0.3 (1)	−1.0 (1)	−1.1 (1)
AC2	4.4 (1)	4.0 (1)	5.4 (1)	−0.6 (1)	−1.2 (1)	−0.6 (1)
AC3	5.2 (1)	3.8 (1)	6.9 (2)	−1.0 (1)	−0.7 (1)	−0.6 (1)
AC4	4.5 (1)	5.7 (1)	5.5 (1)	−1.8 (1)	−0.4 (1)	−1.6 (1)
AC5	4.2 (1)	6.3 (1)	7.0 (2)	−1.7 (1)	−2.1 (1)	−0.4 (1)
AC6	3.7 (1)	4.2 (1)	5.5 (1)	−0.5 (1)	−1.8 (1)	−0.2 (1)
1C1	3.1 (1)	4.3 (1)	4.4 (1)	−0.5 (1)	−0.4 (1)	−1.7 (1)
1C2	4.7 (1)	6.0 (1)	3.9 (1)	−2.3 (1)	0.1 (1)	−1.9 (1)
1C3	4.6 (1)	6.4 (2)	5.7 (1)	−1.8 (1)	0.5 (1)	−3.7 (1)
1C4	3.7 (1)	4.5 (1)	7.1 (2)	0.1 (1)	−0.5 (1)	−3.2 (1)
1C5	3.5 (1)	4.0 (1)	6.6 (1)	0.1 (1)	−1.3 (1)	−2.4 (1)
1C6	3.1 (1)	4.0 (1)	4.8 (1)	−0.2 (1)	−0.9 (1)	−1.8 (1)
2C1	3.5 (1)	4.0 (1)	4.0 (1)	−0.9 (1)	−0.6 (1)	−1.5 (1)
2C2	4.9 (1)	5.3 (1)	3.9 (1)	−2.0 (1)	−0.6 (1)	−1.4 (1)
2C3	5.1 (1)	5.7 (1)	4.6 (1)	−1.9 (1)	0.3 (1)	−2.6 (1)
2C4	4.5 (1)	3.8 (1)	5.6 (1)	−0.4 (1)	0.0 (1)	−1.9 (1)
2C5	3.3 (1)	3.3 (1)	5.1 (1)	−0.1 (1)	−0.3 (1)	−1.0 (1)
2C6	3.0 (1)	3.3 (1)	3.8 (1)	−0.3 (1)	−0.6 (1)	−1.0 (1)
Cl2	6.51 (4)	7.56 (5)	3.55 (3)	−2.03 (3)	−0.65 (3)	−1.38 (3)
Cl3	8.37 (6)	9.27 (6)	6.48 (4)	−2.77 (4)	0.79 (4)	−5.24 (4)
Cl4	7.02 (5)	6.19 (4)	10.81 (6)	0.62 (4)	−0.98 (4)	−5.53 (4)
Cl5	7.47 (5)	4.39 (3)	8.69 (5)	1.16 (3)	−3.80 (3)	−2.34 (3)
Cl2′	8.06 (5)	6.54 (4)	4.31 (3)	−0.97 (3)	−2.62 (4)	−1.53 (3)
Cl3′	8.79 (6)	7.97 (5)	5.40 (4)	−1.88 (4)	0.18 (4)	−4.01 (4)
Cl4′	7.86 (5)	5.39 (4)	8.32 (5)	0.47 (3)	0.42 (4)	−3.62 (4)
Cl5′	5.64 (4)	4.00 (3)	6.27 (4)	0.45 (3)	−1.44 (3)	−0.60 (3)
Cl	9.2 (1)	10.2 (2)	7.3 (1)	−1.2 (1)	0.0 (1)	−2.6 (1)
C1	14.4 (4)	7.7 (2)	5.3 (2)	−1.7 (3)	1.5 (2)	−2.8 (2)
C2	35 (1)	25 (1)	6.1 (3)	−19 (1)	7.3 (6)	−8.1 (5)
C3	50 (2)	40 (2)	8.0 (4)	−35 (2)	12.2 (8)	−13.1 (8)

[a] See footnote *a* to Table II. [b] See footnote *b* to Table V.

Table VII. Refined Parameters for Hydrogen Atoms in $(C_6Cl_4O_2)_2P(C_6H_5)$, VII[a]

atom[a]	10^3x	10^3y	10^3z	B_{iso}, Å^2
H2	267 (3)	819 (2)	246 (2)	4 (1)
H3	492 (5)	899 (3)	202 (3)	9 (1)
H4	767 (3)	804 (2)	230 (2)	4 (1)
H5	769 (4)	614 (3)	337 (3)	7 (1)
H6	548 (4)	527 (3)	392 (3)	8 (1)

[a] See footnotes to Table V.

Data were collected by using the θ–2θ scan mode with a θ scan range of $(0.85 + 0.35 \tan\theta)°$ centered about the calculated Mo K$\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on either side of the aforementioned limits for the measurement of background radiation. The scan rates varied from 0.72 to 4.0 °/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is then given by $I = (FF/S)(P - 2(B1 + B2))$, where P is the number of counts accumulated during the peak scan, $B1$ and $B2$ are the left and right background counts, S is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, σ_I, were computed as $\sigma_I^2 = ((FF)^2/S^2)(P + 4(B1 + B2)) + 0.002I^2$.

A total of 3706 independent reflections having $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$ were measured in the region $\pm h, \pm k, +l$. Four standard reflections, monitored after every 12000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No correction was made for absorption ($\mu_{MoK\bar{\alpha}} = 0.745$ mm^{-1}) and the intensities were reduced to relative amplitudes, F_o, by means of standard Lorentz and polarization corrections.

Solution and Refinement for VI. Initial coordinates for 22 of the 27 independent nonhydrogen atoms were obtained by direct methods (MULTAN). Initial coordinates for the remaining five independent atoms were obtained by using standard Fourier difference techniques. Isotropic unit-weighted full-matrix least-squares refinement[19] of the structural parameters for these 27 atoms and a scale factor gave a conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.108 and a weighted residual $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ of 0.116 for the 1818 reflections having $I \geq 3\sigma_I$ and $(\sin\theta)/\lambda \leq 0.52$. Anisotropic refinement gave $R = 0.039$ and $R_w = 0.042$. Initial coordinates for the nine independent hydrogen atoms were then inferred from the required geometry of the molecule. Subsequent variable-weighted refinement ($w^{1/2} = 2F_oLp/\sigma_I$) including these hydrogen atoms as isotropic contributions led to the final values of $R = 0.029$, $R_w = 0.039$, and GOF[20] = 1.261 for the 2980 reflections having $I \geq 3\sigma_I$ and $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$. During the final cycle of refinement, the largest shift in any parameter was less than 0.01 times its estimated standard deviation. A final Fourier difference synthesis showed a maximum density of 0.26 e/Å^3.

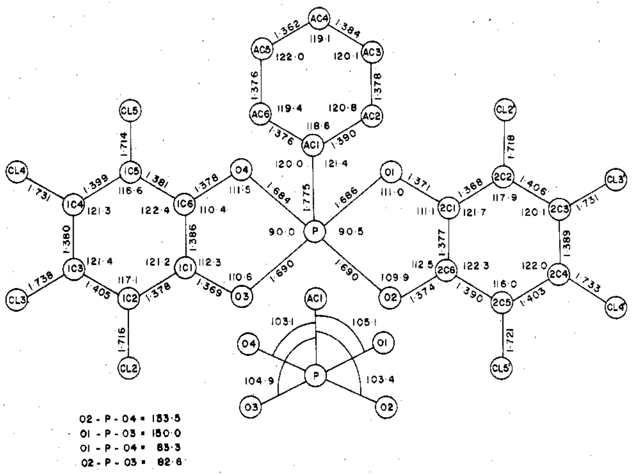


Figure 4. Schematic drawing of $(C_6Cl_4O_2)_2P(C_6H_5)$, VII, showing selected bond distances (Å) and angles (deg).

Table VIII. Bond Lengths (Å) and Angles (deg) in $(C_6Cl_4O_2)_2P(C_6H_5)$, VII[a]

Lengths			
P-O2	1.690 (2)	AC2-AC3	1.378 (4)
P-O4	1.684 (2)	AC3-AC4	1.384 (4)
P-O1	1.686 (2)	AC4-AC5	1.362 (5)
P-O3	1.690 (2)	AC5-AC6	1.376 (4)
P-AC1	1.775 (2)	AC6-AC1	1.376 (3)
O1-2C1	1.371 (3)	1C2-Cl2	1.716 (3)
O2-2C6	1.374 (3)	1C3-Cl3	1.738 (3)
O3-1C1	1.369 (3)	1C4-Cl4	1.731 (3)
O4-1C6	1.378 (3)	1C5-Cl5	1.714 (3)
1C1-1C2	1.378 (3)	2C2-Cl2′	1.718 (3)
1C2-1C3	1.405 (4)	2C3-Cl3′	1.731 (3)
1C3-1C4	1.380 (4)	2C4-Cl4′	1.733 (3)
1C4-1C5	1.399 (4)	2C5-Cl5′	1.721 (3)
1C5-1C6	1.381 (3)	AC2-H2	0.91 (3)
1C6-1C1	1.386 (3)	AC3-H3	0.87 (4)
2C1-2C2	1.368 (3)	AC4-H4	1.04 (2)
2C2-2C3	1.406 (4)	AC5-H5	0.88 (3)
2C3-2C4	1.389 (4)	AC6-H6	0.99 (3)
2C4-2C5	1.403 (4)	C2-C1	1.25 (1)
2C5-2C6	1.390 (3)	C2-Cl	1.45 (1)
2C6-2C1	1.377 (3)	C2-C3	1.55 (2)
AC1-AC2	1.390 (3)	C1-C3′	1.72 (2)
Angles			
O2-P-O4	153.5 (1)	1C3-1C2-Cl2	122.5 (2)
O1-P-O3	150.0 (1)	1C2-1C3-1C4	121.4 (3)
O2-P-AC1	103.4 (1)	1C2-1C3-Cl3	118.8 (2)
O4-P-AC1	103.1 (1)	1C4-1C3-Cl3	119.8 (2)
O1-P-AC1	105.1 (1)	1C3-1C4-1C5	121.3 (3)
O3-P-AC1	104.9 (1)	1C3-1C4-Cl4	120.5 (2)
O1-P-O2	90.5 (1)	1C5-1C4-Cl4	118.1 (2)
O3-P-O4	90.0 (1)	1C4-1C5-1C6	116.6 (2)
O2-P-O3	82.6 (1)	1C4-1C5-Cl5	123.0 (2)
O1-P-O4	83.3 (1)	1C6-1C5-Cl5	120.4 (2)
P-O1-2C1	111.0 (1)	O4-1C6-1C1	110.4 (2)
P-O2-2C6	109.9 (1)	O4-1C6-1C5	127.2 (2)
P-O3-1C1	110.6 (1)	1C1-1C6-1C5	122.4 (2)
P-O4-1C6	111.5 (1)	O1-2C1-2C2	127.1 (2)
P-AC1-AC6	120.0 (2)	O1-2C1-2C6	111.1 (2)
P-AC1-AC2	121.4 (2)	2C2-2C1-2C6	121.7 (2)
AC6-AC1-AC2	118.6 (2)	2C1-2C2-2C3	117.9 (2)
AC1-AC2-H2	117 (2)	2C1-2C2-Cl2′	119.7 (2)
AC1-AC2-AC3	120.8 (3)	2C3-2C2-Cl2′	122.4 (2)
H2-AC2-AC3	121 (2)	2C2-2C3-2C4	120.1 (3)
AC2-AC3-H3	115 (2)	2C2-2C3-Cl3′	119.4 (2)
AC2-AC3-AC4	120.1 (3)	2C4-2C3-Cl3′	120.4 (2)
H3-AC3-AC4	125 (2)	2C3-2C4-2C5	122.0 (2)
AC3-AC4-H4	116 (1)	2C3-2C4-Cl4′	119.7 (2)
AC3-AC4-AC5	119.1 (3)	2C5-2C4-Cl4′	118.3 (2)
H4-AC4-AC5	125 (1)	2C4-2C5-2C6	116.0 (2)
AC4-AC5-H5	121 (2)	2C4-2C5-Cl5′	123.4 (2)
AC4-AC5-AC6	122.0 (3)	2C6-2C5-Cl5′	120.6 (2)
H5-AC5-AC6	117 (2)	O2-2C6-2C1	112.5 (2)
AC1-AC6-H6	123 (2)	O2-2C6-2C5	125.2 (2)
AC1-AC6-AC5	119.4 (3)	2C1-2C6-2C5	122.3 (2)
H6-AC6-AC5	118 (2)	Cl-C2-C1	151 (1)
O3-1C1-1C6	112.3 (2)	C1-C2-C3	155 (1)
O3-1C1-1C2	126.5 (2)	Cl-C2-C3	53 (1)
1C6-1C1-1C2	121.2 (2)	C2-C1-C3′	127 (1)
1C1-1C2-1C3	117.1 (2)	C2-C3-C1′	77 (1)
1C1-1C2-Cl2	120.4 (2)		

[a] See footnotes to Table V.

Space Group Determination and Data Collection for VII. The conditions for data collection and reduction were the same as described for VI, except that the molybdenum radiation was graphite-monochromated and the form of the polarization factor was adjusted accordingly. A well-formed crystal having dimensions of 0.30 mm × 0.31 mm × 0.28 mm was mounted in a sealed thin-walled glass capillary. Preliminary diffractometric investigations indicated triclinic ($\bar{1}$) symmetry. The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $26° < 2\theta_{\mathrm{Mo}K\bar{\alpha}} < 34°$ are $a = 8.242$ (4) Å, $b = 12.806$ (2) Å, $c = 12.821$ (3) Å, $\alpha = 72.76$ (2)°, $\beta = 76.78$ (3)°, and $\gamma = 75.58$ (3)°. The density calculated for two molecules of VII and one chlorobenzene molecule per unit cell is 1.766 g/cm^3. The observed density as measured by flotation in a methyl iodide–benzene mixture was 1.79 (4) g/cm^3. The space group $P\bar{1}$-C_i^1 [18] was adopted on the assumption that there would be one molecule of VII in the asymmetric unit. This choice led to one chlorobenzene molecule per unit cell disordered about an inversion center.

A total of 5639 independent reflections having $2° \leq 2\theta_{\mathrm{Mo}K\bar{\alpha}} \leq 55°$ were measured in the region $+h,\pm k,\pm l$. Nine standard reflections, monitored after every 12000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{\mathrm{Mo}K\bar{\alpha}} = 1.05$ mm^{-1}).

Solution and Refinement for VII. Initial coordinates for the 31 independent nonhydrogen atoms comprising the $(C_6Cl_4O_2)_2P(C_6H_5)$ molecule were obtained by direct methods (MULTAN). The conditions for refinement were the same as stated for VI. Isotropic unit-weighted refinement of the structural parameters for these 31 atoms and a scale factor gave $R = 0.201$ and $R_w = 0.210$ for the 2006 reflections having $I \geq 3\sigma_I$ and $(\sin\theta)/\lambda \leq 0.5$. Anisotropic refinement then gave $R = 0.153$ and $R_w = 0.196$.

At this point a Fourier difference synthesis, phased on the refined parameters, showed four peaks near the origin (a center of inversion). These peaks were interpreted as being due to the presence of a disordered chlorobenzene molecule, with the second half of the molecule being generated by the inversion center. The most intense peak in the difference map (4.2 e/Å^3) was assigned a chlorine atomic scattering factor with a site occupancy of 50%. The other three peaks (average 2.0 e/Å^3) were assigned carbon atomic scattering factors, with 100% occupancy.

Initial coordinates for the five independent hydrogen atoms of the phosphorane moiety were inferred from the required geometry of the molecule. No attempt was made to include the hydrogen atoms of the chlorobenzene molecule. Variable-weighted anisotropic refinement for all nonhydrogen atoms and isotropic refinement for hydrogen atoms led to the final values of $R = 0.048$, $R_w = 0.067$, and GOF[21] = 2.004 for the 3331 reflections having $I > 3\sigma_I$ and $2° \leq 2\theta_{\mathrm{Mo}K\bar{\alpha}} \leq 55°$. During the final cycle of refinement, the largest shift in any parameter was less than 0.05 times its estimated standard deviation. A final Fourier difference synthesis showed a maximum density of 0.56 e/Å^3 in the vicinity of the chlorobenzene molecule.

Computations were done on a CDC 6600 computer (Model Cyber 74-18) by using the direct methods program MULTAN, by Main, Germain, and Woolfson, Zalkin's Fourier program FORDAP, Prewitt's full-matrix least-squares program SFLS, Johnson's thermal ellipsoid plot program ORTEP, and several locally written programs.

Results and Discussion

Figure 1 portrays the molecular geometry of the tetachloro spirocyclic phosphorane VI. The refined positional and thermal parameters for the nonhydrogen atoms are listed in Tables I and II, respectively, while the corresponding parameters for the hydrogen atoms are given in Table III. Refined bond lengths and angles for VI are tabulated in Table IV while Figure 2 schematically summarizes the principal nonhydrogen atom bond parameters.

Analogous data are presented in Tables V–VIII for the octachloro spirocyclic phosphorane VII. Figures 3 and 4 show the respective molecular geometry and pictorial representation of principal bond parameters for VII.

The structural form assumed by each of these chloro derivatives is nearly an ideal rectangular pyramid (RP) with the unique phenyl group located at the apical site and the spirocyclic system occupying the basal positions. Indicative of the high degree of RP character are the average values of the trans-basal angles, 151.8 (1) ± 2.0° for VI and 151.8 (1) ± 1.8° for VII, compared with 150° for an ideal RP (plus or minus values refer to maximum deviations from the average value), the average values of the exocyclic cis-basal angles, 82.9 (1) ± 0.2° for VI and 83.0 (1) ± 0.4° for VII, compared with 82.3° for an ideal RP having 90° endocyclic angles at phosphorus, and the average values of the four apical-basal angles, 104.1 (1) ± 1.9° for VI and 104.1 (1) ± 1.0° for VII, compared with 105° for an ideal RP. In fact the extensive data now available[22] suggest that the appropriate idealized RP

Table IX

Atom Distances from Least-Squares Planes (Å) in $(C_6Cl_4O_2)(C_6H_4O_2)P(C_6H_5)$, VI

	planes						planes continued				
	1	2	3	4^b	5^b		1	2	3	4^b	5^b
P	0.410[a]	−0.006	−0.012	0.000	0.000	O3	−0.029		0.005		0.000
O1	−0.022		0.005	0.000		O4	0.024	0.002			0.000
O2	0.028	0.002		0.000		2C1		0.001	0.002		

plane 6		plane 7		plane 8		plane 9		plane 10		plane 11		plane 12	
1C1	0.008	1C1	0.010	3C1	−0.003	3C1	0.005	2C1	0.002	P	0.353[a]	P	0.362[a]
1C2	−0.007	1C2	−0.013	3C2	−0.001	3C2	0.004	2C2	0.001	O3	0.000	O1	0.003
1C3	0.002	1C3	−0.005	3C3	0.003	3C3	0.001	2C3	−0.002	O4	0.000	O2	−0.003
1C4	0.002	1C4	0.003	3C4	−0.002	3C4	−0.007	2C4	0.000	3C1	0.001	1C1	−0.005
1C5	−0.001	1C5	0.008	3C5	−0.002	3C5	−0.004	2C5	0.003	3C6	−0.001	1C6	0.005
1C6	−0.004	1C6	0.006	3C6	0.005	3C6	0.010	2C6	−0.004				
Cl2	−0.042[a]	O1	0.009			O3	−0.010						
Cl3	−0.015[a]	O2	−0.019			O4	0.001						
Cl4	−0.025[a]												
Cl5	0.020[a]												

Some Dihedral Angles between Least-Squares Planes (deg)

planes	angle	planes	angle	planes	angle	planes	angle
2, 3	86.1	4, 7	16.9	5, 9	17.1	3, 10	36.9
4, 5	40.6						

[a] Indicates atom was *not* included in the definition of a particular least-squares plane. The phosphorus atom is directed upward toward the apical phenyl group in Figure 1. [b] These planes are not least-squares fitted since only these nonlinear points are required to define a plane.

Table X

Atom Distances from Least-Squares Planes (Å) in $(C_6Cl_4O_2)_2P(C_6H_5)$, VII

	planes						planes continued				
	1	2	3	4^b	5^b		1	2	3	4^b	5^b
P	−0.412[a]	0.000	−0.005	0.000	0.000	O3	0.027	0.000			0.000
O1	0.022	0.000		0.000		O4	−0.025		0.002		0.000
O2	−0.025		0.002	0.000		AC1		0.000	0.001		

plane 6		plane 7		plane 8		plane 9		plane 10		plane 11		plane 12		plane 13	
1C1	0.006	2C1	0.002	AC1	−0.005	Cl	0.009	1C1	0.009	2C1	−0.001	O1	−0.001	O3	0.001
1C2	−0.010	2C2	−0.001	AC2	0.000	C1	0.013	1C2	−0.004	2C2	−0.004	O2	0.001	O4	−0.001
1C3	−0.008	2C3	0.004	AC3	0.005	C2	−0.003	1C3	0.004	2C3	0.002	2C1	0.001	1C1	−0.002
1C4	0.011	2C4	0.002	AC4	−0.005	C3	−0.033	1C4	0.009	2C4	0.004	2C6	−0.001	1C6	0.002
1C5	0.002	2C5	−0.012	AC5	0.000	C1′	0.047[c]	1C5	−0.004	2C5	−0.008	P	−0.413[a]	P	−0.412[a]
1C6	−0.001	2C6	0.006	AC6	0.005	C2′	0.032[c]	1C6	−0.005	2C6	0.001				
O3	0.010	O1	−0.007			C3′	−0.002[c]								
O4	−0.012	O2	0.006												
Cl2	−0.047[a]	Cl2′	0.004[a]												
Cl3	−0.017[a]	Cl3′	0.011[a]												
Cl4	0.015[a]	Cl4′	−0.026[a]												
Cl5	−0.056[a]	Cl5′	−0.017[a]												

Some Dihedral Angles between Least-Squares Planes (deg)

planes	angle	planes	angle	planes	angle	planes	angle
2, 3	93.9	4, 7	20.5	5, 6	20.4	3, 8	15.5
4, 5	40.5						

[a] Indicates atom was *not* included in the definition of a particular least-squares plane. The phosphorus atom is directed upward toward the apical phenyl group in Figure 3. [b] These planes are not least-squares fitted since only three nonlinear points are required to define a plane. [c] These atoms are related to the respective unprimed atom by a center of inversion.

applicable to spirocyclic phosphoranes has trans-basal angles of 152° and apical-basal angles of 104°, as observed for average values for VI and VII. A high degree of planarity is apparent for the four basal oxygen atoms in VI and VII (cf. plane 1 in Tables IX and X, respectively), and these atoms form a nearly perfect rectangle in each structure, within the indicated standard deviations (cf. cis O–O nonbonded distances listed in Table XI).

In terms of the sum of dihedral angles (δ_i) from polytopal faces, based on unit bond distances,[3,22] $\sum_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{TP})|$ and $R - \sum_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{RP})|$, where $R = \sum_i|\delta_i(\mathrm{TP}) - \delta_i(\mathrm{RP})| = 217.7°$ and TP stands for trigonal bipyramid, the structures of VI and VII are displaced on the TP–RP coordinate, 93.7 and 94.3%,[23] respectively, toward the RP. The equality of the above two sums for each chloro derivative, 204.0° for VI and 205.2° for VII, shows that the structural distortions lie directly on the TP–RP coordinate.

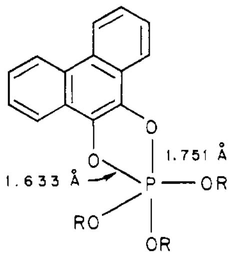
With these structures so closely RP, it is difficult to see evidence for "residual" TP character. Although, the less symmetrical tetrachloro derivative VI has slightly longer P–O bonds accompanying the larger of the two trans-basal angles, O4–P–O2, the more symmetrical octachloro compound has P–O bond lengths that are even closer to each other and do not correlate with the relative magnitude of the trans-basal angles.

If we compare the average P–O bond lengths in VI, 1.680

Table XI. Selected Intramolecular Nonbonded Distances (Å)

$(C_6H_4O_2)(C_6Cl_4O_2)P$-(C_6H_5), VI		$(C_6Cl_4O_2)_2P(C_6H_5)$, VII	
O1–O3	3.236 (3)	O1–O3	3.261 (2)
O2–O4	3.283 (3)	O2–O4	3.285 (2)
O1–O2	2.389 (3)	O1–O2	2.397 (2)
O3–O4	2.377 (3)	O3–O4	2.387 (2)
O1–O4	2.227 (3)	O1–O4	2.239 (2)
O2–O3	2.223 (3)	O2–O3	2.231 (2)
2C1–O1	2.761 (4)	AC1–O1	2.748 (3)
2C1–O2	2.719 (4)	AC1–O2	2.719 (3)
2C1–O3	2.745 (4)	AC1–O3	2.747 (3)
2C1–O4	2.731 (4)	AC1–O4	2.710 (3)
2C1–1C1	3.369 (4)	AC1–2C1	3.326 (3)
2C1–1C6	3.340 (4)	AC1–2C6	3.303 (3)
2C1–3C1	3.381 (4)	AC1–1C1	3.314 (3)
2C1–3C6	3.373 (4)	AC1–1C6	3.313 (3)
2C2–O2	3.116 (4)	AC2–O1	3.378 (3)
2C2–O3	3.080 (5)	AC2–O4	2.942 (3)
2C6–O1	3.113 (4)	AC6–O2	2.921 (3)
2C6–O4	3.170 (4)	AC6–O3	3.352 (3)

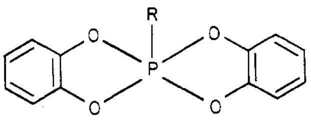
(2) Å, and VII, 1.688 (2) Å, with those in the monoclinic form of the related unsaturated monocyclic phosphorane VIII,[24]



VIII, R = *i*-Pr

which has a structure only 16% displaced from the TP,[3] it is seen that the basal P–O values for VI and VII are intermediate between the axial and equatorial P–O values for the near TP, VIII. This agrees with the trend in bond character obtained from structures which are intermediate between these extremes in geometry,[3] although this trend suggests a convergence in P–O bond length at 1.66 Å for an ideal RP containing unsaturated five-membered rings.

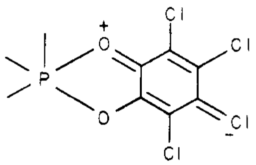
Since the series leading to the value of 1.66 Å involved a number of derivatives IX but contained no ring substituents,



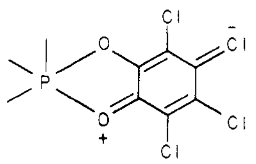
IX

the longer P–O bonds in VI and VIII by 0.02 and 0.03 Å, respectively, may be attributable to electron-withdrawing effects of the attached chlorine atoms. Electron delocalization into the benzo moieties serves to reduce P–O bonding and enhance C–O bonding.[25] This is most in evidence in the tetrachloro derivative VI. Here, the tetrachlorocatechol portion shows, respectively, longer P–O and shorter C–O bond lengths compared to the corresponding bonds in the catechol moiety, and these former bond lengths are comparable to those in the octachloro derivative VII.

From the perspective of resonance theory, representatives X and XI would be stabilized by the electron-withdrawing effect of the chlorine atoms leading to decreased availability of π p–d bonding in the P–O linkages. This kind of bonding is expected to be enhanced in a RP over a TP owing to the



X



XI

equal character of the ring phosphorus bonds compared to that in a TP with the rings spanning axial–equatorial positions.[25] In the absence of chloro ring substituents, i.e., the spirocyclic IX (R = Ph), the structure is displaced 72% along the TP–RP coordinate toward the RP. The greater displacement toward the RP for the chloro derivatives VI and VII is in keeping with the electron delocalization tending to equalize P–O bonding as found in the RP. Further, electron pair repulsion effects[26] among the bonds attached to phosphorus, which favor the TP in the absence of cyclic substituents,[27] are lessened in these spirocyclics.

Acknowledgment. The generous support for this investigation by the National Science Foundation (Grant MPS74-11496) and the National Institutes of Health (Grant GM21466) and the inclusion of funds by NSF for the purchase of an Enraf-Nonius CAD-4 diffractometer are gratefully acknowledged. We are indebted to the University of Massachusetts Computing Center for generous allocation of computing time on the CDC 6600 system.

Registry No. VI, 21229-07-2; VII, 69668-73-1; tetrachlorocatechol, 1198-55-6; dichlorophenylphosphine, 644-97-3.

Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes for VI and VII (40 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Pentacoordinated Molecules. 34. (b) Part 33: T. E. Clark, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, preceding paper in this issue.
(2) This work represents in part a portion of the Ph.D. Thesis of T. E. Clark, University of Massachusetts, Amherst, Mass.
(3) R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977).
(4) R. R. Holmes, *ACS Monogr.*, **No. 175** (1979).
(5) T. E. Clark, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **18**, 1653 (1979).
(6) H. Wunderlich, personal communication.
(7) R. K. Brown and R. R. Holmes, *Inorg. Chem.*, **16**, 2294 (1977).
(8) H. Wunderlich and O. Mootz, *Acta Crystallogr., Sect. B*, **30**, 935 (1974).
(9) R. K. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **99**, 3326 (1977).
(10) J. R. Devillers and R. R. Holmes, *J. Am. Chem. Soc.*, **99**, 3332 (1977).
(11) W. Althoff, R. O. Day, R. K. Brown, and R. R. Holmes, *Inorg. Chem.*, **17**, 3265 (1978).
(12) E. Duff, D. R. Russell, and S. Trippett, *Phosphorus*, **4**, 203 (1974).
(13) R. K. Brown, R. O. Day, S. Husebye, and R. R. Holmes, *Inorg. Chem.*, **17**, 3276 (1978).
(14) R. O. Day, A. C. Sau, and R. R. Holmes, *J. Am. Chem. Soc.*, in press.
(15) M. Wieber and W. R. Hoos, *Tetrahedron Lett.*, **51**, 5333 (1968).
(16) P. C. Crofts, J. H. H. Markes, and H. N. Rydon, *J. Chem. Soc.*, 4250 (1958).
(17) C. L. Jackson and R. D. MacLaurin, *Am. Chem. J.*, **37**, 7 (1907).
(18) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969, p 75.
(19) The function minimized is $\sum w(|F_o| - |F_c|)^2$. Atomic form factors for nonhydrogen atoms were taken from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); scattering factors for hydrogen atoms were taken from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.* **42**, 3175 (1965).
(20) Goodness of fit, GOF = $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$. NO = number of observations = 2980, NV = number of variables = 280.
(21) Reference 20 except NO = 3331 and NV = 336.
(22) Reference 4, Chapter 2.
(23) T. E. Clark, Ph.D. Thesis, University of Massachusetts, Amherst, Mass.
(24) R. D. Spratley, W. C. Hamilton, and J. Ladell, *J. Am. Chem. Soc.*, **89**, 2272 (1967).
(25) R. R. Holmes, *J. Am. Chem. Soc.*, **97**, 5379 (1975).
(26) R. J. Gillespie and R. S. Nyholm, *Q. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); *J. Chem. Educ.*, **40**, 295 (1963); "Molecular Geometry", Van Nostrand Reinhold, New York, N.Y., 1972.
(27) R. R. Holmes, *J. Am. Chem. Soc.*, **96**, 4143 (1974).