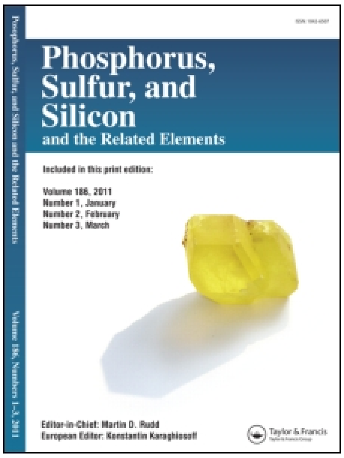

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FORMATION OF A 1,2-DIORGANO-1,2-DICHLORODIPHOSPHINE

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2,6-Dimethoxyphenyldifluorophosphine, **1**, when allowed to stand for several days in solution in $CDCl_3$, was found to undergo a spontaneous transformation to the tetrafluorophosphorane, $ArPF_4$, **2**, and to the unusual 1,2-dichlorodiphosphine, ArP(Cl)P(Cl)Ar, **3**, (Ar = 2,6-dimethoxyphenyl). Compounds **2** and **3** were characterized by n.m.r. spectroscopy and, in part, by elemental analysis. A possible pathway, rationalizing the formation of **2** and **3** is indicated. An X-ray crystal structure determination of **3** has been conducted. The molecule was found to display a staggered conformation, with a PP bond length of 223.6 pm.

Key words: 1,2-Dichloro-1,2-di(2′,6′-dimethoxyphenyl)diphosphine.

Dedicated to Dr. Ludwig Maier on the occasion of his 60th Birthday

The synthesis of the difluorophosphine, **1** $ArPF_2$ ($Ar = 2,6\text{-}(MeO)_2C_6H_3$) has recently been described.[1] When a sample of **1**, dissovled in $CDCl_3$ in an n.m.r. tube, was kept for 2d at 70°C and for 2d at room temperature ^{19}F and ^{31}P n.m.r. spectra revealed that **1** had undergone extensive changes, and formation of both the tetrafluorophosphorane, $ArPF_4$, **2**, and of **3** has been detected.

The interaction of **1** with $CHCl_3$ led to the formation of several products. Only $ArPF_4$, **2**, $ArPCl_2$, **4**, and PF_6^- were identified through their ^{31}P n.m.r. spectra. **4** was known from an independent preparation, but we were unable to isolate this product because of its thermal instability. Via reaction of **4** with NaF in acetonitrile for 3 d **1** was formed and was identified by its ^{31}P-n.m.r. spectrum.

$ArPF_2$, **1**: ^{31}P n.m.r. spectrum (162 MHz): δP 212.8 (t); $^1J(PF)$ 1160 Hz.

$ArPF_4$, **2**: ^{31}P n.m.r. spectrum (162 MHz): $\delta P - 39.3$ (quintet); $^1J(PF)$ 975 ± 2 Hz; ^{19}F n.m.r. spectrum (56.4 MHz): $\delta F - 42.0$ (d); $^1J(FP)$ 972 Hz.

ArP(Cl)P(Cl)Ar, **3**: ^{31}P n.m.r. spectrum (162 MHz): δP 98.8 (s) [CD_3CN]

$ArPCl_2$, **4**: ^{31}P n.m.r. spectrum (24.3 MHz): δP 157.8(s).

Formation of solid **3** was also observed; it was identified by its mass spectrum and by its ^{31}P n.m.r. spectrum as the unusual P-P bonded species, ArP(Cl)P(Cl)Ar.

A 1,2-dichlorodiphosphine, $(^t\mathrm{Bu})P(Cl)P(Cl)(^t\mathrm{Bu})$, was first reported by Baudler and her co-workers in 1981.[2,3] It was obtained as a mixture of optical isomers [both *d,l* and meso forms (*ca.* 20:80)] in the reaction of the cyclotriphosphine, $(^t\mathrm{BuP})_3$ with PCl_5. Accordingly, two signals at δP 113.8 and δP 106.7 ppm, respectively, were observed in the ^{31}P-n.m.r. spectrum. Another aliphatic dichlorodiphosphine, 1,2-dichloro-1,2-bis-(tris[trimethylsilyl]-methyl)diphosphine, was described by Satge and his co-workers.[4] The observation of only one signal in the ^{31}P-n.m.r. spectrum and the reaction mechanism (addition of chlorine to the appropriate trans-phosphene) suggest that the meso product has been obtained.

Formation of a 1,2-dichlorodiphosphine, similar to **3**, has been mentioned by Lappert and his co-workers:[5] 1,2-Dichloro-1,2-bis(2,4,6-tri-*tert*-butylphenyl)-diphosphine, on the basis of its ^{31}P n.m.r. spectrum, was suggested to be one of the products of the reaction of 1,3,1′,3′-tetraethyl-bis(2,2′-imidazolidine) with 2,4,6-tri(*tert*-butyl)phenyldichlorophosphine. In these cases, as well as in the addition reaction of bromine or iodine to bis-(2,4,6-tri-*tert*-butylphenyl)diphosphene, described by Yoshifuji *et al.*[6], only one signal was observed in the ^{31}P n.m.r. spectrum. Quite the opposite was found for the complexed PhP(Cl)P(Cl)Ph. For the bis-chromiumpentacarbonyl complex $[(CO)_5Cr]PhP(Cl)P(Cl)Ph[Cr(CO)_5]$[7] and for the iron tetracarbonyl complex $[(CO)_4Fe]PPh(Cl)P(Cl)Ph$[8] the presence of both diastereomers was confirmed by single crystal X-ray structure determinations. In the latter case the ^{31}P n.m.r. spectrum showed two signals.

For unknown reasons, only the *d,l* form of **3** has been observed in solution (^{31}P n.m.r.) and in the solid state (X-ray).

The formation of **2** and **3** is suggested to occur via the following pathway,

$$\underset{\mathbf{1}}{ArPF_2} + CDCl_3 \rightarrow ArPFCl + CDCl_2F$$

$$ArPFCl + ArPF_2 \rightarrow ArPCl\text{-}PF_3Ar$$

$$ArPCl\text{-}PF_3Ar + ArPFCl \rightarrow \underset{\mathbf{2}}{ArPF_4} + \underset{\mathbf{3}}{ArPCl\text{-}PClAr}$$

This kind of mechanism has been discussed at some length in lit.[1] An intermediate of type R(F)PP(F)R has been considered in connection with the redox disproportionation of difluorophosphines, RPF_2, and with formation of tetrafluorophosphoranes, RPF_4, and polyphosphines, $(RP)_n$. The exchange of fluorine for chlorine in PF compounds by CH_2Cl_2, with formation of CF bonds, was mentioned by Grasser and Schmidbaur.[9]

In the reduction of complexes of type $NiX_2(PhPF_2)_2$ using $PhPF_2$ as a reagent the formation of $Ni(PhPF_2)_4$ and PhP(I)–P(I)Ph has been observed[10] for X = I. In the case of X = Br $PhPBr_2$ was one of the products. Therefore we believe that in these cases and in the case of **3** an intermediate RPFX (X = Cl, Br, I) is involved.

Mixed chlorofluorophosphines, e.g. ArPFCl, are known to be quite unstable, although some have been characterized by ^{31}P n.m.r. spectroscopy.[11] Their δP values are of the order of 240 ppm with ^1J(PF) values *ca.* 1100 Hz[11] while δP values for Ar_2PF are expected at higher field, with ^1J(PF) values < 1000 Hz.[12] In the reaction of $ArPF_2$ with $CDCl_3$ (or $CHCl_3$) mentioned above we have also observed a signal in the ^{31}P n.m.r. spectrum with δP 207.4 ppm, (d) and ^1J(PF) 1107 Hz. The product which this resonance is due to seemed to be of noteable thermal stability, and was formed only upon raising the temperature to 70°C. The signal was assigned to the compound, Ar_2PF, rationalizing the concurrent formation of PF_3 (identified by ^{31}P n.m.r.-spectroscopy) in related experiments.[1] In view of lit.[11] we no longer consider this assignment as unambiguous. In the absence of systematic studies on compounds of type RPFCl (R = hydrocarbon group) we are unable to establish conclusively the identity of the product as Ar_2PF or ArPFCl. No products of type **3** were ever observed in the course of the work reported in lit.[1]

It may be noted, though, that in the system, $2\text{-MeOC}_6H_4PF_2/CDCl_3$ in one out of four experiments a trace quantity of $2\text{-MeOC}_6H_4PCl_2$ was observed in the ^{31}P n.m.r. spectrum (δP(obs.) 162.8 ppm, δP(lit[13]) 163.3 ppm.

The thermal lability of compounds **1**, **2**, and **4**, none of which could be purified by distillation, is thought to be caused by the interaction between the 2,6-methoxy substituents at the phenyl ring and the phosphorus atom.

In the present work we have isolated and fully characterized a 1,2-dichlorodiphosphine, and we are reporting a single crystal X-ray diffraction study of **3**. The structure of **3** in the crystal is shown in Figure 1.

The compound crystallized in the space group $P2_1/n$, with $z = 4$. The symmetry of **3** is close to C2, with a staggered conformation at the PP bond. Unusual bond geometry is observed at the phosphorus atoms in the crystal. Thus, very short distances have been observed between the two phosphorus atoms and three of the oxygen atoms (P(1)—O(2) 285, P(1)—O(8) 302, P(1)—O(12) 273, P(2)—O(8) 271, P(2)—O(12) 303, P(2)—O(18) 285 pm). Such short distances are compatible only with the assumption of an attractive interaction between the P(III) atom and the oxygen atoms (c.f. sum of the van der Waals radii, 328 pm).[14] Such acceptor properties of P(III) have been observed in other cases. It may be assumed, therefore, that the observed stability of **3** is, in part, due to the increase of the co-ordination number of phosphorus.

The PP (223.6) and the PC (181.2 and 182.0 pm, respectively) bond lengths are of the usual order of magnitude.[15] The PCl bonds (211.4 and 212.1 pm,

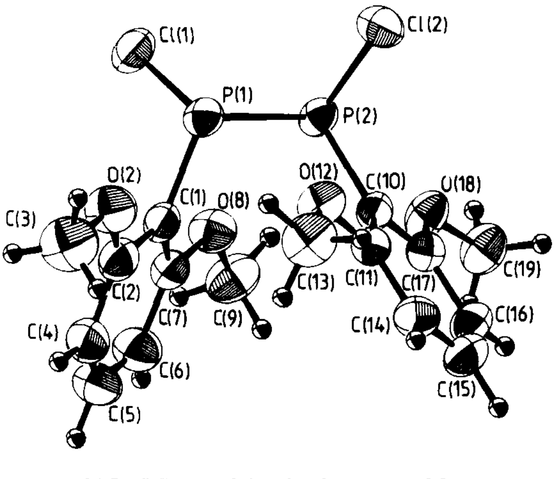

FIGURE 1. Molecular Structure of **3**.

respectively), on the other hand, are relatively long; c.f., e.g. r(PCl) in $C_6H_5N(PCl_2)_2$ (201–205 pm). This is believed to be due to the increase of the co-ordination number at phosphorus. The bond angles at phosphorus (93–104°) are normal for P(III).

EXPERIMENTAL

Experiments were conducted with careful exclusion of air and moisture. N.m.r. spectra were obtained on a Bruker WM 400 (H_3PO_4 as an external reference) or a Jeol JNMR-60HL (^{19}F n.m.r. at 56.4 MHz, $CFCl_3$ as an external reference) instrument in $CDCl_3$. High-frequency chemical shifts, relative to the reference, are listed with positive signs. The EI-mass spectrum of **3** was recorded on a Finnigan MAT 8430 instrument (70 eV), and was found to exhibit the correct isotopic distribution (^{12}C, ^{35}Cl). The melting point was recorded on a Büchi 530 apparatus, using 0.1 mm melting point capillaries, and is uncorrected.

Formation of 1,2-dichloro-1,2-di(2′,6′-dimethoxyphenyl)diphosphine, **3**. In an n.m.r. tube *ca*. 100 mg of **1** was dissolved in *ca*. 1 ml of $CDCl_3$ and the solution was kept for 2 d at 70 °C and for 2 d at room temperature. After this colorless crystals were formed and were separated by filtration. Yield ca. 40 mg. M.p. 154–157°C

$C_{16}H_{18}Cl_2O_4P_2$ (407.17) Found: C 47.29 H 4.54 P 15.02
Calc.: C 47.19 H 4.45 P 15.21

^{31}P-n.m.r. spectrum (in $CDCl_3$) δP 99.0 ppm.

Mass spectrum (at 100°C): $M-H]^+$ 405 (16%), $M-Cl]^+$ 371 (2%), $M-CH_3-HCl]^+$ 355 (12%), $M-CH_3-Cl_2]^+$ 321 (10%), $M-2CH_3Cl]^+$ 305 (8%), $(M/2)+CH_3]^+$ 218 (56%), $(M/2)]^+$ 203 (58%), $(M/2)+CH_3-Cl]^+$ 183 (52%), $(CH_3O)_2C_6H_2P]^+$ 167 (base peak), $(CH_3O)_2C_6H_4]^+$ 138 (60%), $CH_3Cl]^+$ 50 (28%).

The reaction of **1** (*ca*. 10 g; 0.05 mol) with $CHCl_3$ (*ca*. 60 ml; *ca*. 0.7 mol) was carried out at 75°C. ^{31}P-n.m.r. spectra of samples drawn from this reaction mixture were measured in $CDCl_3$ after one

TABLE I

Atomic Positions in 3

	X/A	Y/B	Z/C	UEQ
P(1)	0.1870(1)	0.1462(1)	0.3879(1)	0.043(0)
P(2)	0.1411(1)	0.0913(1)	0.2396(1)	0.040(0)
Cl(1)	0.4040(1)	0.2076(1)	0.3641(1)	0.058(0)
Cl(2)	0.2176(1)	−0.0242(1)	0.2924(1)	0.056(0)
C(1)	0.0380(4)	0.2281(2)	0.3751(2)	0.043(1)
C(2)	−0.0297(4)	0.2500(2)	0.4564(3)	0.051(1)
O(2)	0.0313(3)	0.2078(2)	0.5390(2)	0.065(1)
C(3)	−0.0340(8)	0.2254(4)	0.6246(3)	0.080(2)
C(4)	−0.1480(5)	0.3101(3)	0.4510(3)	0.062(1)
C(5)	−0.1955(5)	0.3504(3)	0.3646(4)	0.071(1)
C(6)	−0.1301(5)	0.3320(2)	0.2842(3)	0.063(1)
C(7)	−0.0160(4)	0.2708(2)	0.2887(2)	0.047(1)
O(8)	0.0529(3)	0.2470(1)	0.2118(2)	0.054(1)
C(9)	−0.0103(6)	0.2807(3)	0.1181(3)	0.066(1)
C(10)	−0.0853(4)	0.0755(2)	0.2128(2)	0.039(1)
C(11)	−0.1846(4)	0.0607(2)	0.2827(2)	0.042(1)
C(12)	−0.1000(3)	0.0588(1)	0.3764(2)	0.050(1)
C(13)	−0.1958(6)	0.0506(4)	0.4518(3)	0.068(1)
C(14)	−0.3552(4)	0.0486(2)	0.2565(3)	0.053(1)
C(15)	−0.4286(5)	0.0514(3)	0.1591(3)	0.061(1)
C(16)	−0.3356(4)	0.0654(2)	0.0888(3)	0.053(1)
C(17)	−0.1648(4)	0.0776(2)	0.1148(2)	0.042(1)
O(18)	−0.0622(3)	0.0920(1)	0.0503(1)	0.052(1)
C(19)	−0.1344(6)	0.0875(3)	−0.0514(3)	0.061(1)

day, two days, four days, one week, and two weeks. In no case the signal δP 99 ppm of **3** was observed. Only **2**, **4**, and PF_6^- were identified from their ^{31}P-n.m.r. spectrum.

Single crystal X-ray-structure determination of **3**. Experimental. Compound **3** crystallized from $CDCl_3$ in the monoclinic space group $P2_1/n$. The lattice constants were obtained by diffraction from 15 reflections ($\pm hkl$): a 809.35(9); b 1673.66(14); c 1399.59(9) pm; β 100.734(10)°; $z = 4$; d(calc.) 1.452 g/cm^3. Intensities were measured at 293 K on a Synthex four-circle diffractometer (type $P2_1$), using monochromatic Mo-Kα radiation ($\lambda = 154.18$ pm) in the range $\Theta - 2\Theta$ ($3° \leq 2\Theta < 50°$). The scan rate varied, depending on the intensity of the reflection, between 2.93° and 29.30°/min.

The data were corrected for Lorentz, polarization, and absorption effects ($\mu = 0.476\ \text{mm}^{-1}$). In the refinement 2356 out of 3258 independent reflexions with $F \geq 4.0\ \delta(F)$ were used. The structure was solved by direct methods and difference-Fourier synthesis. Hydrogen atom positions were determined from the difference-Fourier synthesis, and were refined isotropically, the refinement converging at $R = 0.042$ (R_w 0.037). In the final refinement the ratio of a parameter shift, relative to the estimated standard deviation, was <1.0%. A final difference map displayed no electron density higher than 0.29×10^6 e/pm^3. The program SHELX-76[16] and our own programs were used. Complex atom scattering factors were employed.[17]

Atom coordinates are listed in Table I, and bond lengths and bond angles in Table II, using the numbering scheme employed in Figure 1.

Formation of 2,6-dimethoxyphenyldichlorophosphine, **4**. In a 500 ml round bottom flask resorcine dimethylether (30.0 g; 0.22 mol) in 400 ml of ether was treated with a 15% solution of butyllithium in hexane (80.0 g; 0.19 mol). After stirring for 20 h at room temperature bis(N,N-diethylamino)-chlorophosphine (46.0 g; 0.22 mol) was added dropwise while the mixture was kept at reflux temperature. Refluxing was continued for 2 h and after standing overnight the suspension was filtered, the solvent was removed, and the residue was fractionally distilled. At 122–126°C, 25.8 g of a light

TABLE II

Bond lengths (pm) and angles (°) in **3**

Cl(1)	-P(1)	-P(2)	93.0(0)	C(1)	-P(1)	-P(2)	103.1(1)
C(1)	-P(1)	-Cl(1)	100.0(1)	Cl(2)	-P(2)	-P(1)	93.7(0)
C(10)	-P(2)	-P(1)	103.8(1)	C(10)	-P(2)	-Cl(2)	99.0(1)
C(2)	-C(1)	-P(1)	118.1(3)	C(7)	-C(1)	-P(1)	124.4(2)
C(7)	-C(1)	-C(2)	117.5(3)	O(2)	-C(2)	-C(1)	114.8(3)
C(4)	-C(2)	-C(1)	121.2(4)	C(4)	-C(2)	-O(2)	124.1(3)
C(3)	-O(2)	-C(2)	118.2(4)	C(5)	-C(4)	-C(2)	118.9(4)
C(6)	-C(5)	-C(4)	121.8(4)	C(7)	-C(6)	-C(5)	119.4(4)
C(6)	-C(7)	-C(1)	121.2(3)	O(8)	-C(7)	-C(1)	115.1(3)
O(8)	-C(7)	-C(6)	123.7(3)	C(9)	-O(8)	-C(7)	118.6(3)
C(11)	-C(10)	-P(2)	124.6(2)	C(17)	-C(10)	-P(2)	117.4(2)
C(17)	-C(10)	-C(11)	118.0(3)	O(12)	-C(11)	-C(10)	115.3(3)
C(14)	-C(11)	-C(10)	121.2(3)	C(14)	-C(11)	-O(12)	123.5(3)
C(13)	-O(12)	-C(11)	118.0(3)	C(15)	-C(14)	-C(11)	118.9(3)
C(16)	-C(15)	-C(14)	121.5(3)	C(17)	-C(16)	-C(15)	119.7(3)
C(16)	-C(17)	-C(10)	120.7(3)	O(18)	-C(17)	-C(10)	115.4(3)
O(18)	-C(17)	-C(16)	124.0(3)	C(19)	-O(18)	-C(17)	117.6(3)
P(2)	-P(1)	223.6(1)		Cl(1)	-P(1)	211.4(1)	
C(1)	-P(1)	181.2(3)		Cl(2)	-P(2)	212.1(1)	
C(10)	-P(2)	182.0(3)		C(2)	-C(1)	140.1(4)	
C(7)	-C(1)	140.3(4)		O(2)	-C(2)	136.6(4)	
C(4)	-C(2)	138.2(5)		C(3)	-O(2)	142.7(5)	
C(5)	-C(4)	137.5(6)		C(6)	-C(5)	136.6(6)	
C(7)	-C(6)	137.2(5)		O(8)	-C(7)	136.0(4)	
C(9)	-O(8)	143.2(4)		C(11)	-C(10)	139.9(4)	
C(17)	-C(10)	140.2(4)		O(12)	-C(11)	136.3(3)	
C(14)	-C(11)	137.6(4)		C(13)	-O(12)	142.8(4)	
C(15)	-C(14)	138.3(5)		C(16)	-C(15)	136.5(5)	
C(17)	-C(16)	137.7(4)		O(18)	-C(17)	135.8(4)	
C(19)	-O(18)	143.6(4)					

yellow oil was obtained, δP 90.8 ppm. It contained *ca.* 40% of an unknown product, with δP 32.8 ppm.

This mixture (24.0 g) was treated with excess HCl in petroleum ether (b.r. 60–80°C) until absorption ceased. After 30 min reflux dimethylamine hydrochloride was removed by filtration. An attempt at the distillation of the oily residue failed because of its thermal instability. The ^{31}P-n.m.r. spectrum of the mixture before distillation showed two singlets: *δP* 157.8 ppm for 2,6-dimethoxyphenyldichlorophosphine and *δP* 42.8 ppm for an unknown product, ratio 3:1.

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