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Structure and Dissociation of Ylidyl Chlorophosphanes

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ABSTRACT

The ylidyl substituent of the chlorophosphane $Ph_3P=CAr-PRCl$ *exerts a strong influence on the P-Cl bond. An X-ray structure investigation of the representative with Ar = Ph, R = Me reveals the longest P-Cl bond ever observed for an acyclic chlorophosphine (226.2(1) pm). It is connected to a conformation that allows an effective negative hyperconjugation. The ylidyl chlorophosphanes with an amino group R are covalent in benzene but become more or less ionic in dichloromethane solution. The solvent-dependent dissociation equilibrium can be followed by* ^{31}P *NMR spectra. In case of an enamine-derived ylidyl chlorophosphane, the equilibrium shifts almost completely from the covalent to the ionic side within a rather narrow range of solvent composition (20 to 70 vol % dichloromethane).* *© 1996 John Wiley & Sons, Inc.*

INTRODUCTION

Chlorophosphanes are covalent compounds. Their dissociation can be achieved, however, when the chloride ion is incorporated in or exchanged for an anion of low basicity (such as $AlCl_4^-$ or $CF_3SO_3^-$) and when, at the same time, the phosphorus substituents participate effectively in the positive charge induced by the dissociation at the phosphenium center [1,2]. Amino groups prove suitable for the latter part and have so far been used in almost all the known cases. Recently, we could demonstrate that triphenylphosphonium ylide substituents are definitely more effective in this part, as bis(ylidyl)chlorophosphanes dissociate spontaneously and bis(ylidyl)phosphenium cations are stable not only with counter ions of low basicity but also as simple halides [3–5]. In this article, we present the synthesis of chlorophosphanes with one ylide substituent and a variety of second substituents, and we report about their ^{31}P NMR data in solvents of different polarity. Three of these compounds were mentioned in previous articles [3,4,6].

X-ray structure investigations of ylidyl dihalophosphanes [6] furthermore demonstrate that an ylide substituent exerts a strong influence on their

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†X-Ray structure analysis.

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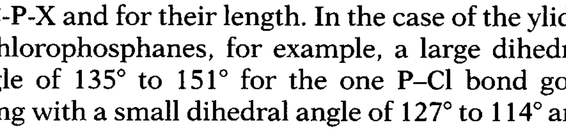
phosphorus-halogen bonds, although in this case it is insufficient to cause dissociation: the two phosphorus-halogen bonds of a compound become structurally nonequivalent both for their dihedral angle P-C-P-X and for their length. In the case of the ylidyl dichlorophosphanes, for example, a large dihedral angle of 135° to 151° for the one P–Cl bond goes along with a small dihedral angle of 127° to 114° and a strongly elongated bond for the other. It seemed of interest to compare with these results the structure of an ylidyl monochlorophosphane that offers an already asymmetric topology at the phosphorus atom to start with.

RESULTS AND DISCUSSION

Synthesis

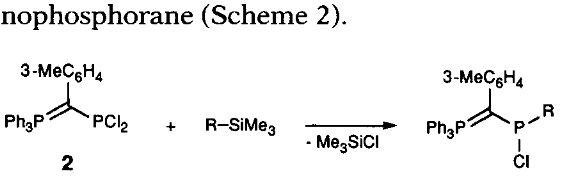
For the preparation of triphenylphosphoniumylidyl monochlorophosphanes, the ylidyl substituent may be introduced in the second or first step. In the former case, the synthesis starts from the trimethylsilyl ylide 1 [6] and involves its reaction with a variety of dichlorophosphanes (Scheme 1).



	R
3	Me
4	CH$_2$Cl
5	Et
6	^{t}Bu
7	Ph
8	C$_{12}$H$_{14}$N
9	NPh$_2$

SCHEME 1

In some other cases, the ylidyl dichlorophosphane 2 (dichlorophosphanyl 2-methylbenzylidene phosphorane) [6] serves as the starting material and is reacted with a trimethylsilyl amine, phosphane, or iminophosphorane (Scheme 2).



	R
10	NEt$_2$
11	PPh$_2$
12	NPPh$_3$

SCHEME 2

In the synthesis of the amino- and imino-substituted derivatives 9, 10, and 12, the ^{31}P NMR spectra of the reaction mixtures always showed, besides the derived products, small amounts of the bis(ylidyl)phosphenium chloride. This obviously results from a dismutation reaction and contaminates the product.

Compounds 3–8 and 11 were isolated as colorless to yellow substances, sensitive to air and moisture. They are easily soluble in dichloromethane and fairly soluble in benzene or THF. In some cases, the color of their solutions deepen with increasing solvent polarity; e.g., the solution of 8 in benzene is yellow, while its solution in dichloromethane is red.

^{31}P NMR Spectra

The chemical shift of the tervalent phosphorus, in general, allows one to distinguish readily between the three-coordinate environment in a chlorophosphane and the two-coordinate environment in a phosphenium ion. Those of acyclic monochlorophosphanes are, in general, found at δ^{31}P < 200 [7] and those of phosphenium ions at δ^{31}P > 260 [2,7]. In a study loosely related to the present one, chemical shifts, δ^{31}P around 200, were observed for the tervalent phosphorus atom of $[(Me_2N)_3P{=}N]Me_2NPCl$ and $[(Et_2N)_3P{=}N]_2PCl$ and were supposed to represent "averaged values of the chemical shifts of tautomers with covalent and ionic chlorine atoms" [8]. No clear evidence for "a certain saltlike character" of these compounds was given, however.

Table 1 contains the chemical shifts of the ylidyl chlorophosphanes 3–11, both in benzene and dichloromethane solution. In every case, they are found to be different in the two solvents, but the differences may be as small as $\Delta\delta^{31}$P = 7 or as large as $\Delta\delta^{31}$P = 194. In an earlier study, the chemical shift of triflate-substituted phosphanes $R_2P–OSO_2CF_3$ [9] was observed to depend upon the solvent in a range of $\Delta\delta^{31}$P < 20 and was believed to "suggest an equilibrium mixture of a phosphenium ion and a tricovalent compound, probably with the latter prevailing."

As evidenced by the chemical shift of the tervalent phosphorus atom, all compounds 3–11 in benzene solution are present as covalent chlorophosphanes. On proceeding to dichloromethane solutions, all signals move downfield, those of the alkyl and aryl phosphanes 3–7 and the diphosphane 11 only up to 17, however, for $\Delta\delta^{31}$P. At the same time, the coupling constant $^2J_{PP}$ decreases by some 3–9 Hz. These changes are rather small as compared with those observed on addition of one equivalent of $AlCl_3$ in CH_2Cl_2 solution, i.e., on converting the chlorophosphines 3–6 to the phosphenium tetrachlo-

TABLE 1 ^{31}P NMR data of ylidyl chlorophosphanes $Ph_3P^B=CAr-P^ARCl$ **3–12** in benzene and dichloromethane and of ylidyl phosphenium tetrachloroaluminates $[Ph_3P^B=CAr-P^AR]AlCl_4$ **13–18** in dichloromethane, coupling constants *J* in Hz. (The specified meaning of R and Ar applies to both the chlorophosphanes **3–12** and the phosphenium ions **13–18**.)

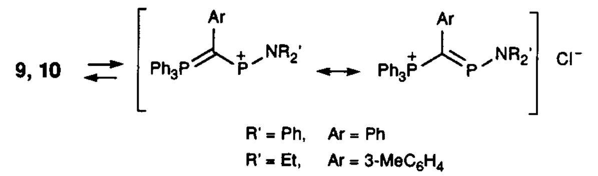
			C_6H_6			*CH_2Cl_2*				*CH_2Cl_2*		
R	*Ar*		δ_A	δ_B	J_{AB}	δ_A	δ_B	J_{AB}		δ_A	δ_B	J_{AB}
Me	Ph	**3**	130.0	23.8	172.4	146.8	24.7	166.3	**13**	389.4	25.4	114.0
CH_2Cl	Ph	**4**	108.4	25.7	178.5	118.3	25.6	175.5	**14**	341.2	24.8	108.8
Et	Ph	**5**	141.7	23.4	166.8	155.8	24.0	162.6	**15**	403.9	24.0	105.8
^tBu	Ph	**6**	152.0	24.5	180.0	162.2	24.3	177.0	**16**	421.8	25.9	107.9
Ph	Ph	**7**	124.1	24.1	196.9	131.0	23.3	188.6				
$C_{12}H_{14}N$	Ph	*E*-**8**	121.6	22.4	192.2	315.4	25.4	136.3	*E*-18	315.6	25.4	136.4
$C_{12}H_{14}N$	Ph	*Z*-**8**	136.1	22.8	186.2	317.7	25.2	136.3	*E*-**18**	317.8	25.2	136.8
NPh_2	Ph	**9**	143.1	24.0	262.7	175.4	25.2	234.1				
NEt_2	$3\text{-}MeC_6H_4$	**10**	178.0	22.2	232.0	281.0	25.8	167.9	**17**	287.8	25.8	162.8
P^CPh_2[a]	$3\text{-}MeC_6H_4$	**11**	139.5	23.5	183.1	152.7	24.7	174.0				
NP^CPh_3[b]	$3\text{-}MeC_6H_4$	*E*-**12**				346.1	23.2	131.3				
NP^CPh_3[c]	$3\text{-}MeC_6H_4$	*Z*-**12**				361.0	16.2	17.3				

[a] In C_6H_6: $\delta_C = -9.8$, $J_{AC} = 169.4$, $J_{BC} = 18.3$Hz; in CH_2Cl_2: $\delta_C = -10.4$, $J_{AC} = 166.3$, $J_{BC} = 18.3$ Hz.
[b] $\delta_C = 22.0$, $J_{AC} = 54.9$, $J_{BC} = 11.2$ Hz.
[c] $\delta_C = 26.6$, $J_{AC} = 64.1$, $J_{BC} = <3$ Hz.

roaluminates **13–16** (Scheme 3, Table 1). Utilizing mean values, $\delta^{31}P$ moves from 133 to 389 and $^2J_{PP}$ decreases from 174 to 109 Hz.

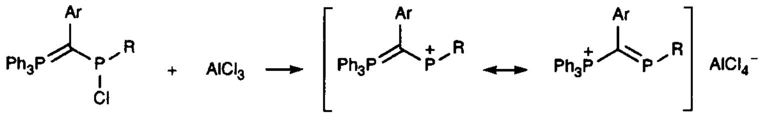
Compounds **3–7** and **11**, thus, seem to remain covalent also in dichloromethane. The observed solvent-induced differences of $\delta^{31}P$ and $^2J_{PP}$ may result from changes in the conformer population (see discussion of the molecular structure of **3**).

A stronger solvent dependence is observed for the tervalent phosphorus atom of the aminophosphines **9** and **10**. In going from dichloromethane to benzene solution, we found moderate differences ($\Delta\delta^{31}P = 32$ and $\Delta^2J_{PP} = -29$ Hz) for the diphenylphosphino derivative **9**, but larger ones ($\Delta\delta^{31}P = 103$ and $\Delta^2J_{PP} = -64$ Hz) for the diethylamino derivative **10**. These differences indicate a mobile dissociation equilibrium for **9** and **10** in CH_2Cl_2 which, in the case of **10**, is almost completely on the side of the dissociated form (Scheme 4). In accord with that concept, its data accordingly approach those of the respective phosphenium tetrachloroaluminate **17**.



SCHEME 4

The ^{31}P NMR signals of **10** in different mixtures of the two solvents (Figure 1) clearly represent the average of the covalent and ionic forms. The observed slope demonstrates the almost complete shift of the equilibrium from the one to the other side, effected just by the change of solvent. While the ^{31}P NMR signal of the tervalent phosphorus atom of **10** is a well-resolved doublet, both in benzene and dichloromethane solution, it broadens and loses its fine structure in the solvent mixtures. This can be understood as an exchange broadening that reaches its maximum when about equal amounts of the covalent and the ionic forms participate in the equilib-



	R	Ar
13	Me	Ph
14	CH_2Cl	Ph
15	Et	Ph
16	^tBu	Ph
17	NEt_2	$3\text{-}MeC_6H_4$
18	$C_{12}H_{14}N$	Ph

SCHEME 3

rium. The signals are sharp, however, when most of the compound is present in the covalent or in the ionic form.

The most pronounced solvent dependence of the ^{31}P NMR data is observed for the chlorophosphane 8, having an ylide and an enamine substituent. This compound is obtained as a 5:1 mixture of two isomers. Their ^{31}P NMR data, especially their coupling constants $^{2}J_{PP}$, are very similar to each other and are also similar to those of the other ylidyl chlorophosphanes 3–7 (Table 1). This suggests an alike conformation for the ylidyl phosphane moiety and leaves the enamine part as the origin of the two isomers *E*- and *Z*-8, as shown in their formulas (Scheme 5). The major isomer is tentatively assigned to *E*-8 [10].

Both isomers of 8 dissociate completely when dissolved in dichloromethane. This becomes evident by comparing the respective data with those of the tetrachloroaluminate 18 (Table 1). The *E*,*Z*-isomers keep their identity during the dissociation. As is demonstrated by Figure 1, the dissociation equilibrium is, in fact, shifted all the way from the covalent to the ionic side within an astonishingly small range of solvent mixture composition.

While the ^{31}P NMR signals of the tervalent phosphorus atoms (signal A) of *E*- and *Z*-8 are sharp doublets in benzene and dichloromethane, they are broad in intermediate solvent mixtures when comparable amounts of the dissociated and undissociated forms are present. This can be explained as previously done for compound 10.

Chemical shift δ, line width, and coupling constant $^{2}J_{PP}$ also depend on the temperature (Table 2) and indicate an increased dissociation at lower temperatures. This may be rationalized by a negative entropy of dissociation due to an increased order of the

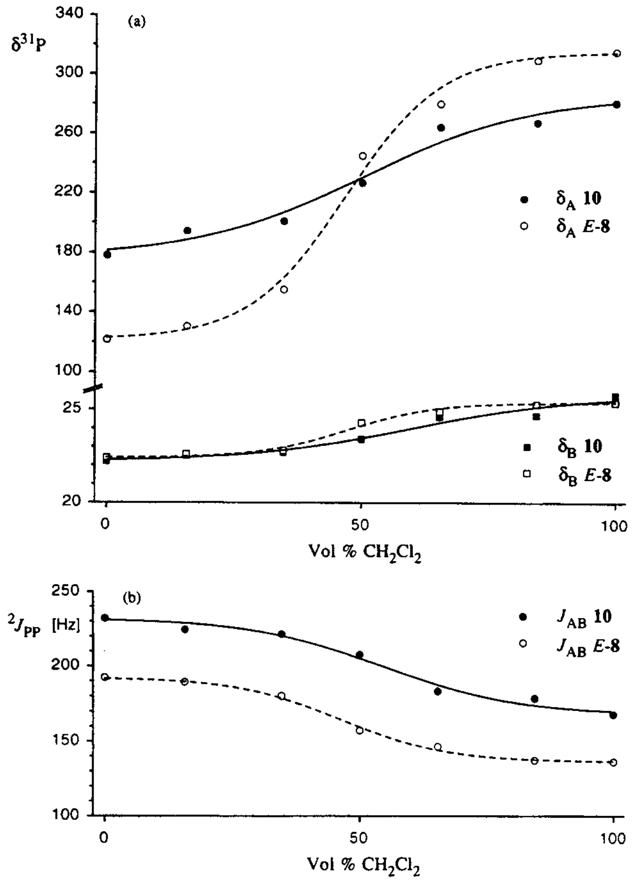
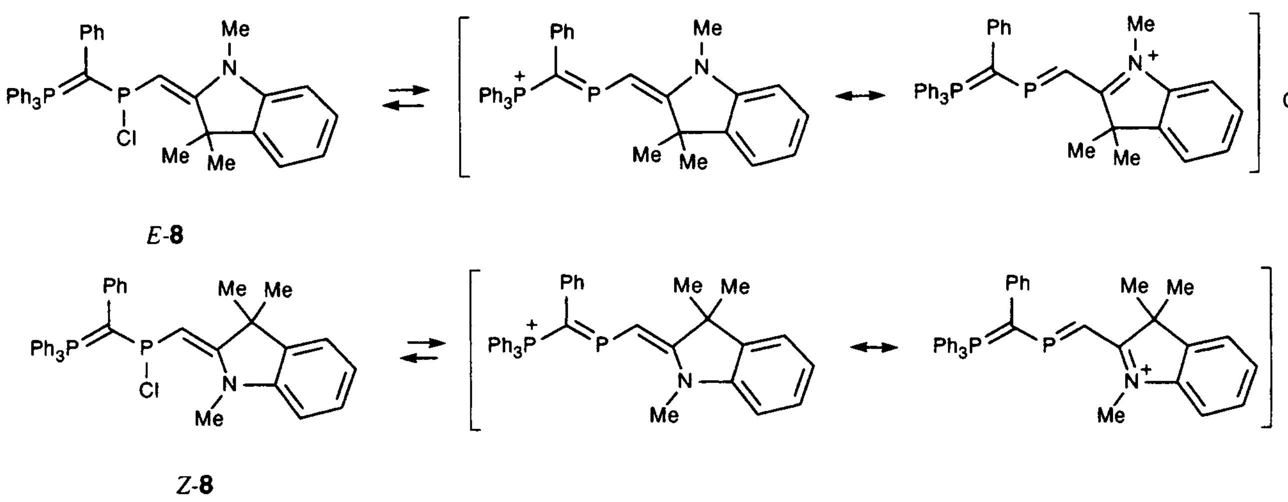
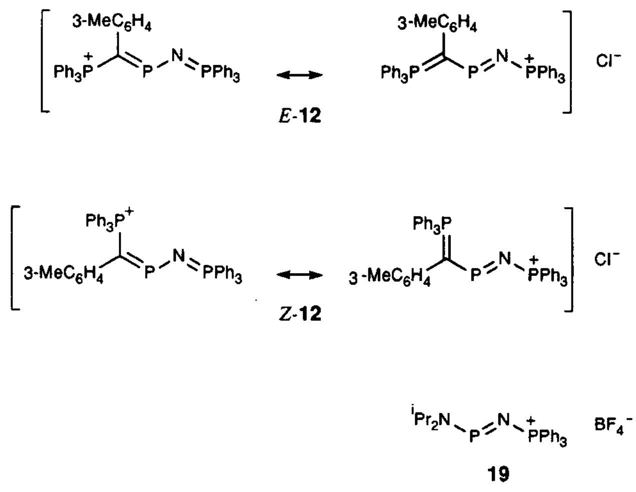


FIGURE 1 (a) Chemical shifts δ_A of the tervalent phosphorus atom and δ_B of the phosphonio groups as well as (b) coupling constants J_{AB} of *E*-**8** (open circles and squares, dashed lines) and of **10** (filled circles and squares, solid lines) in mixtures of benzene and dichloromethane. The curves result from a nonlinear regression.



SCHEME 5



SCHEME 6

solvent molecules [11]. At lower temperatures, the A signal also becomes broader due to the decreasing exchange rate.

The triphenylphosphoranediylamino-substituted compound 12 is obtained in dichloromethane solution. Its ^{31}P NMR spectrum indicates that approximately equal amounts of two isomers are formed, both of which display an ABC spin system. They can be structurally assigned by means of their different coupling constants $^2J_{PP}$ and $^4J_{PP}$ (Scheme 6). The signals of their tervalent phosphorus atoms are found at very low field and indicate an ionic structure for both of them (Table 1, signal A). The shifts, moreover, do not change significantly when a mixture of equal volumes of benzene and dichloromethane is used as a solvent.

TABLE 2 ^{31}P NMR data of compound *E*-**8** dissolved in a mixture of equal volumes dichloromethane and benzene-d$_6$ at different temperatures *T*, coupling constant *J* in Hz.

T	δ_A	δ_B	δ_{AB}
25°C	239.0	24.2	157.2
0°C	272.5	24.9	148.0
−40°C	305.0	25.4	137.3

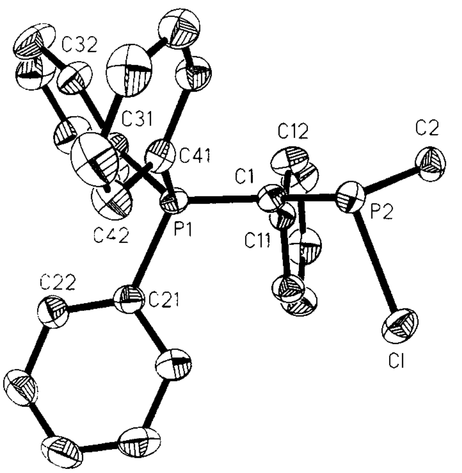


FIGURE 2 Molecular structure of **3** (thermal ellipsoids with 50% probability).

A coplanar P–C–P–N–P backbone must be assumed for the cations of 12, with the coupling constants J_{PNP} and J_{PCP} depending on the conformation in the respective part of the molecule. The coupling constants J_{AC} of the two isomers are alike and similar to $^2J_{PP}$ = 71.1 Hz of the triphenylphosphonio iminophosphane 19 [12]. J_{AC} is therefore assigned to J_{PNP}, and its value is in accord with a synperiplanar orientation of the lone pair at the central phosphorus atom to the *N*-triphenylphosphonio group [6,12] in both isomers. The remaining two-bond coupling constants J_{AB}, which are rather different for the two isomers, must consequently be assigned to J_{PCP}. The large one indicates a synperiplanar orientation of the electron lone pair and the *C*-triphenylphosphonio group, as in *E*-12, and the small one an antiperiplanar orientation, as in *Z*-12 [6]. The fact that J_{BC} is observed for *E*-12, but not for *Z*-12, confirms this assignment [5,13,14].

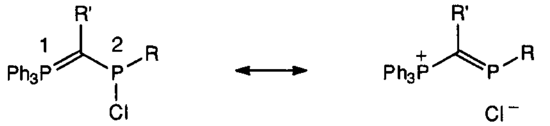
Molecular Structure of 3

A single crystal of compound 3 was used for an X-ray structure determination. It shows the undissociated molecule as assumed from the ^{31}P NMR spectra in solution also to be present in the crystal.

The most prominent features of the molecular structure (Figure 2) are the $(Ph_3)P–C–P–C(H_3)$ backbone approaching planarity, with the methyl and phosphonio groups in the *trans* position and the strongly elongated P–Cl bond, which stands roughly perpendicular to the said plane (see dihedral angles in Table 3). The structure of 3 thus comes close to the geometry that would be expected for the ionic isomer. As compared with the bonds in PCl_3 (204.0(1) pm [6,15]), the P–Cl bond in 3 has become 22 pm longer, and, if the sum of the van der Waals radii (370 pm) is taken as a measure for complete dissociation, the elongation observed for 3 would indicate a 13% stage on this pathway.

The long P–Cl bond in 3 is caused by an electron transfer from the ylidic carbon atom C_1 to the antibonding orbital of the P–Cl bond, which becomes effective by the almost parallel orientation of this bond to the p_z-orbital at C_1 [6] (negative hypercon-

TABLE 3 Selected Bond Lengths [pm], Bond and Dihedral Angles [°] of Compound **3**, and the Respective Structural Data of Two Ylidyl Dichlorophosphanes (The labeling of the atoms refers to Figure 2.)



	3	*[6]*	*[6]*
R	*Me*	*Cl*	*Cl*
R'	*Ph*	*2,6-$Cl_2C_6H_3$*	*Me*
P_1–C_1	173.0(2)	174.1(4)	171.7(3)
C_1–C_{11}	149.8(2)	149.0(5)	152.1(5)
P_2–C_1	172.5(2)	172.1(4)	170.0(3)
P_2–C_2	183.6(2)	210.3(2)^a	209.9(1)^a
P_2–Cl	226.2(1)	212.5(2)	218.8(1)
P_1–C_1–C_{11}	116.8(1)	120.5(3)	117.1(2)
P_2–C_1–C_{11}	122.7(1)	124.8(3)	125.5(3)
P_1–C_1–P_2	118.7(1)	114.5(2)	116.7(2)
C_1–P_2–C_2	101.3(1)	104.6(2)^a	103.0(1)^a
C_1–P_2–Cl	107.2(1)	107.0(2)	104.2(1)
C_2–P_2–Cl	92.2(1)	93.3(1)	92.2(1)
P_1–C_1–P_2–C_2	163.3	135.5^a	150.8^a
P_1–C_1–P_2–Cl	100.8	126.6	113.5

^{a}C1$_2$ in place of C_2.

jugation [16], anomeric effect [17]). As a consequence, the bond P_2–C_1 between the tervalent phosphorus and the ylidic carbon atom is rather short, especially when compared to the normal single bond P_2–C_2. The formal single bond P_2–C_1 is thus shorter than the ylidic bond P_1–C_1.

The P–Cl distance of **3** exceeds considerably the longest distances so far observed for acyclic chlorophosphanes such as $(Me_2N)_2PCl$ (218.0(4) pm [18]) and $Ph_3P = CMePCl_2$ (see Table 3). The only other P–Cl bonds of comparable length have recently been found for cyclic ylidyl chlorophosphanes [19,20]. In these examples, the dihedral angle is given, however, by the ring structure.

As has been mentioned in the Introduction, the structure of **3** may be compared with the structures of some triphenylphosphonium ylidyl dichlorophosphanes (Table 3) that were discussed in detail in a previous article [6]. They can, in fact, be meaningfully extrapolated to the structure of **3**. Of the two nonequivalent chlorine atoms, the methyl group replaces the one at the larger dihedral angle, and a further rotation around P_2–C_1 brings it even closer to the plane around C_1. At the same time, the P–Cl bond approaches a perpendicular orientation and becomes considerably longer.

EXPERIMENTAL

All manipulations were carried out in flame-dried glassware under argon using the Schlenk technique. Dry dichloromethane and benzene were used as obtained (Fluka). Pentane was dried over molecular sieves (4 Å). Tetrahydrofuran was dried by refluxing with sodium/benzophenone and subsequent distillation. Melting points were determined in sealed capillaries.

NMR. JEOL GSX 270 (^{31}P), JEOL EX 400 (^1H, ^{13}C) with Me_4Si (int.) and 85% H_3PO_4 (ext.) as standards. ^{31}P NMR data are given in Tables 1 and 2. The atoms of the *P*-phenyl groups are identified as *o,m,p*-H and *i,o,m,p*-C; the atoms of the *C*-phenyl groups, as 2,3,4-H and C-1,2,3,4.

Dichlorophosphanes $RPCl_2$ (R = Me, CH_2Cl, Et, ^{t}Bu, Ph) were distilled prior to use. Trimethylsilyl benzylidenetriphenylphosphorane **1** [6], dichlorophosphanyl3-methylbenzylidenetriphenylphosphorane **2** [6], 1,3,3-trimethylindolin-2-ylidenemethylene dichlorophosphane [10], diphenylaminodichlorophosphane [21], trimethylsilyl diphenylphosphane [22], and *N*-trimethylsilyl triphenyliminophosphorane [23] were prepared as described in the literature.

3. 6.06 g (51.9 mmol) of methyldichlorophosphane was added slowly through a syringe to a stirred solution of 23.99 g (51.8 mmol) of **1** in 300 mL of benzene at room temperature. After the resulting pale yellow solution had been stirred for 10 hours, it was concentrated in vacuo to half of its original volume, and 50 mL of pentane was added. The formed colorless precipitate was filtered off, washed three times with a 1:1 mixture of benzene and pentane, and dried in vacuo. Concentration of the filtrate to one-third of its former volume afforded a second crop. Yield: 19.83 g (88%), mp 172–174°C; anal calcd for $C_{26}H_{23}ClP_2$ (432.9): C, 72.14; H, 5.36; found: C, 71.87; H, 5.14; ^1H NMR (C_6D_6): δ = 1.90 (d, $^2J_{PH}$ = 11.7 Hz, 3H), 6.92–7.09 (m, 12H, arom. H), 7.46–7.49 (m, 2H, 2-H), 7.55–7.61 (m, 6H, *o*-H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.0 (dd, $^1J_{PC}$ = 29.0 Hz, $^3J_{PC}$ = 15.3 Hz, CH_3), 52.9 (dd, $^1J_{PC}$ = 105.3, 58.8 Hz, $CPPh_3$), 125.1 (d, $^5J_{PC}$ = 2.3 Hz, C-4), 127.9 (superimposed, C-3), 128.6 (superimposed, *i*-C), 128.7 (d, $^3J_{PC}$ = 11.5 Hz, *m*-C), 132.1, (d, $^4J_{PC}$ = 3.1 Hz, *p*-C), 133.6 (t, $^3J_{PC}$ = 5.3 Hz, C-2), 134.5 (dd, $^2J_{PC}$ = 9.2 Hz, $^4J_{PC}$ = 2.3 Hz, *o*-C), 139.6 (dd, $^2J_{PC}$ = 8.4, 3.8 Hz, C-1).

4. Prepared as described earlier, from 0.48 g

TABLE 4 Crystallographic Data and Details of Data Collection and Structure Refinement of Compound **3**

Crystal data	
Formula	$C_{26}H_{23}ClP_2$
M_r	432.87
Crystal system	triclinic
Space group	P(−1) [No. 2]
Crystal dimensions (mm)	0.2 · 0.35 · 0.45
a (Å)	9.709(1)
b (Å)	10.270(1)
c (Å)	12.168(1)
α (°)	108.00(1)
β (°)	98.02(1)
γ (°)	92.29(1)
V (Å^3)	1138.1(2)
D_{calc} (g cm^{-3})	1.268
Z	2
F(000) (e)	452
μ(Mo K_α) (cm^{-1})	3.18
Data collection	
Diffractometer	Enraf Nonius CAD4
Radiation	Mo K_α, 0.71069 Å, graphite monochromator
T (°C)	−68
Scan mode	ω
hkl range	±11/±12/+14
$\sin(\theta/\lambda)_{max}$ (Å^{-1})	0.59
Measured refl.	3992
Unique refl.	3990
Observed refl.	3970
$F_0 \geq$	$2\ \sigma F_0$
Refinement	
Refined parameters	262
H atoms (found/calcd)	0/23
$R1$[a]	0.0290
$wR2$[b]	0.0766
(shift/error)$_{max}$	0.001
$\Delta\rho_{fin}$ (max/min) (eÅ^{-3})	+0.364/−0.216

[a] $R1 = \Sigma(\lVert F_0\rvert - \lvert F_c\rVert)/\Sigma\lvert F_0\rvert$.
[b] $wR^2 = [\Sigma w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$; $w = q/2\sigma^2(F_0^2) + (ap)^2 + bp$; $p = (F_0^2 + 2F_c^2)/3$; a = 0.0431, b = 0.44.

(7.5 mmol) of chloromethyldichlorophosphane and 3.14 g (6.8 mmol) of 1 in 30 mL of benzene. Yield: 3.11 g (98%), decomp. > 145°C; anal calcd for $C_{26}H_{22}Cl_2P_2$ (467.3): C, 66.83; H, 4.75; found: C, 66.84; H, 4.95; ^{1}H NMR (C_6D_6): δ = 3.86–4.11 (m, 2H, CH_2), 6.94–7.07 (m, 12H, arom. H), 7.52–7.54 (m, 2H, 2-H), 7.56–7.62 (m, 6H, *o*-H); ^{13}C{^{1}H} NMR (C_6D_6): δ = 43.9 (dd, $^1J_{PC}$ = 34.9 Hz, $^3J_{PC}$ = 16.2 Hz, CH_2), 49.3 (dd, $^1J_{PC}$ = 107.6, 57.8 Hz, $CPPh_3$), 125.9 (m, C-4), 127.5 (dd, $^3J_{PC}$ = 6.7 Hz, superimposed, *i*-C), 128.3 (s, C-3), 128.8 (d, $^3J_{PC}$ = 12.1 Hz, *m*-C), 132.4 (d, $^4J_{PC}$ = 2.7 Hz, *p*-C), 134.1 (t, $^3J_{PC}$ = 4.7 Hz, C-2), 134.5 (d, $^2J_{PC}$ = 9.4 Hz, *o*-C), 137.5 (dd, $^2J_{PC}$ = 4.0 Hz, C-1).

5. Prepared as described earlier, from 5.40 g (41.3 mmol) of ethyldichlorophosphane and 19.08 g (41.2 mmol) of 1 in 200 mL of benzene. Yield: 16.58 g (90%), mp 162–165°C; anal calcd for $C_{27}H_{25}ClP_2$ (446.9): C, 72.57; H, 5.64; found: C, 72.04; H, 5.32; ^{1}H NMR (C_6D_6): δ = 1.13 (dt, $^3J_{PH}$ = 17.8 Hz, $^3J_{HH}$ = 7.8 Hz, 3H, CH_3), 2.32 (m, 2H, -CH_2), 6.91–7.09 (m, 12H, arom. H), 7.49–7.55 (m, 2H, 2-H), 7.59–7.64 (m, 6H, *o*-H); ^{13}C{^{1}H} NMR (C_6D_6): δ = 10.8 (d, $^2J_{PC}$ = 21.4 Hz, CH_3), 29.7 (dd, $^1J_{PC}$ = 24.4 Hz; $^3J_{PC}$ = 14.5 Hz, CH_2), 50.7 (dd, $^1J_{PC}$ = 106.1, 59.5 Hz, $CPPh_3$), 124.9 (d, $^5J_{PC}$ = 2.3 Hz, C-4), 128.7 (d, $^3J_{PC}$ = 12.2 Hz, *m*-C), 128.7 (superimposed, C-1), 128.7 (superimposed, C-3), 132.1 (d, $^4J_{PC}$ = 2.3 Hz, *p*-C), 133.2 (t, $^3J_{PC}$ = 5.3 Hz, C-2), 134.5 (dd, $^2J_{PC}$ = 9.2 Hz, $^4J_{PC}$ = 2.3 Hz, *o*-C), 140.0 (dd, $^2J_{PC}$ = 8.4, 3.8 Hz, C-1).

6. Prepared as described earlier, from 4.66 g (29.3 mmol) of *t*-butyldichlorophosphane and 13.58 g (29.3 mmol) of 1 in 150 mL of benzene. Yield: 10.56 g (76%), mp 167–169°C; anal calcd for $C_{29}H_{29}ClP_2$ (474.9): C, 73.34; H, 6.15; found: C, 73.67; H, 6.10; ^{1}H NMR ($CDCl_3$): δ = 0.88 (d, $^3J_{PH}$ = 13.4 Hz, 9H, CH_3), 6.89–7.45 (m, 20H, arom. H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 28.1 (d, $^2J_{PC}$ = 17.0 Hz, CH_3), 40.0 (dd, $^1J_{PC}$ = 30.3 Hz, $^3J_{PC}$ = 17.0 Hz, C-$(CH_3)_3$), 49.1 (dd, $^1J_{PC}$ = 100.9, 66.6 Hz, $CPPh_3$), 125.1 (d, $^5J_{PC}$ = 3.1 Hz, C-4), 127.4 (d, $^4J_{PC}$ = 2.7 Hz, C-3), 128.0 (dd, $^1J_{PC}$ = 87.4 Hz, $^3J_{PC}$ = 6.7 Hz, *i*-C), 128.2 (d, $^3J_{PC}$ = 11.6 Hz, *m*-C), 131.8 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C), 134.3 (dd, $^2J_{PC}$ = 9.2 Hz, $^4J_{PC}$ = 2.1 Hz, *o*-C), 134.8 (t, $^3J_{PC}$ = 4.6 Hz, C-2), 139.2 (dd, $^2J_{PC}$ = 7.2, 2.7 Hz, C-1).

7. Prepared as described earlier, from 0.37 g (2.1 mmol) of phenyldichlorophosphane and 1.05 g (2.1 mmol) of 1 in 30 mL of benzene. Yield: 0.72 g (69%), mp 189–191°C; anal calcd for $C_{31}H_{25}ClP_2$ (494.94): C, 75.23; H, 5.09; found: C, 74.03; H, 5.34. ^{1}H NMR (CD_2Cl_2): δ = 6.78–6.87 (m, 4H, arom. H), 7.01 (m, 2H, arom. H), 7.13–7.20 (m, 4H, arom. H), 7.50–7.55 (m, 6H, *m*-H), 7.64 (m, 3H, *p*-H), 7.68–7.80 (m, 6H, *o*-H); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 51.1 (dd, $^1J_{PC}$ = 103.2, 58.3 Hz, $CPPh_3$), 123.2 (d, $^5J_{PC}$ = 1.3 Hz, C-4), 127.3 (s, C-8), 127.4 (dd, $^1J_{PC}$ = 88.5, $^3J_{PC}$ = 8.3 Hz, *i*-C), 127.5 (d, $^4J_{PC}$ = 1.3 Hz, C-3), 127.6 (d, $^3J_{PC}$ = 3.9 Hz, C-7), 128.8 (d, $^3J_{PC}$ = 12.2 Hz, *m*-C), 131.3 (dd, $^3J_{PC}$ = 6.7, 4.8 Hz, C-2), 131.3 (d, $^2J_{PC}$ = 19.9 Hz, C-6), 132.5 (d, $^4J_{PC}$ = 3.2 Hz, *p*-C), 134.5 (dd, $^2J_{PC}$ = 9.6, $^4J_{PC}$ = 2.6 Hz, *o*-C), 139.8 (dd, $^2J_{PC}$ = 8.3, 3.2 Hz, C-1), 144.1 (dd, $^1J_{PC}$ = 34.0, $^3J_{PC}$ = 18.6 Hz, C-5).

8. A solution of 0.63 g (2.3 mmol) of 1,3,3-trimethylindolin-2-ylidenemethylene dichlorophosphane and 1.07 g (2.3 mmol) of 1 in 10 mL of dichloromethane was stirred for 15 hours at room temperature. All volatiles were removed in vacuo, and the residue was dissolved in 20 mL of benzene. After 15 hours, the yellow precipitate was filtered off, washed twice with a 1:1 mixture of benzene and pentane, and dried in vacuo. Yield: 0.72 g (50%), mp 160–163°C; anal calcd for $C_{37}H_{29}ClNP_2$ (585.05): C, 75.96; H, 5.00; N, 2.39; found: C, 75.54; H, 4.88; N, 2.18. ^{1}H and ^{13}C NMR data are given for the major isomer *E*-**8** only. ^{1}H NMR (CD_2Cl_2): δ = 1.56 (s, 6H, C–CH_3), 2.95 (s, 3H, N–CH_3), 6.04 (d, $^{2}J_{PH}$ = 10.8 Hz, PCH), 6.86–6.88 (m, 2H), 6.99 (m, 1H), 7.06 (m, 1H), 7.24 (m, 1H), 7.33–7.35 (m, 3H), 7.47–7.52 (m, 6H, *o*-H), 7.60 (m, 6H, *m*-H), 7.79 (m, 3H, *p*-H); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ = 29.6 (s, N–CH_3), 30.0 (d, $^{4}J_{PC}$ = 14.2 Hz, C–$\underline{C}H_3$), 48.7, (s, $\underline{C}$–CH_3), 103.6 (dd, $^{1}J_{PC}$ = 45.5, $^{3}J_{PC}$ = 19.0 Hz, C = $\underline{C}$P), 109.3 (s), 118.5 (dd, $^{1}J_{PC}$ = 118.5, 85.9 Hz, $CPPh_3$), 120.8 (d, $^{1}J_{PC}$ = 89.1 Hz, *i*-C), 121.7 (s), 123.3 (s), 128.0 (s), 129.3 (s), 129.4 (d, $^{3}J_{PC}$ = 12.3 Hz, *m*-C), 130.7 (m), 134.3 (s, *p*-C), 134.4 (d, $^{2}J_{PC}$ = 8.5 Hz, *o*-C), 135.0 (d, J_{PC} = 1.9 Hz), 135.6 (s), 140.0 (s), 142.9 (s), 176.7 (d, $^{2}J_{PC}$ = 34.1 Hz, $\underline{C}$ = CP).

11. A solution of 2.32 g (8.9 mmol) of diphenyl trimethylsilylphosphane in 15 mL of THF was added dropwise to a stirred solution of 4.18 g (8.9 mmol) of **2** in 20 mL of THF at 0°C within 30 minutes. The resulting yellow solution was stirred for 15 hours at room temperature, then all volatiles were removed in vacuo. The residue was dissolved in 2 mL of dichloromethane and 4 mL of benzene. After addition of 6 mL of pentane, yellow crystals of **11** precipitated. Yield: 4.30 g (78%); ^{1}H NMR (d_8-THF): δ = 2.24 (s, 3H, CH_3), 6.96 (m, 2H, arom. H), 7.09 (m, 1H, arom. H), 7.17 (m, 1H, arom. H), 7.30–7.61 (m, 25H, arom. H); $^{13}C\{^{1}H\}$ NMR (d_8-THF): δ = 21.5 (s, CH_3), 49.0 (ddd, $^{1}J_{PC}$ = 101.6, 65.4 Hz, $^{2}J_{PC}$ = 15.2 Hz, $CPPh_3$), 125.3 (s), 127.0 (dd, $^{1}J_{PC}$ = 87.4, $^{3}J_{PC}$ = 8.0 Hz, *i*-C), 127.3 (s), 128.1 (d, J_{PC} = 6.7 Hz), 128.7 (d, $^{3}J_{PC}$ = 12.1 Hz, *m*-C), 129.1 (m), 132.4 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-C), 133.0 (m), 134.4 (d, $^{2}J_{PC}$ = 8.1 Hz, *o*-C), 135.0 (s), 136.7 (s), 138.0 (dd, J_{PC} = 24.2, J_{PC} = 13.4 Hz), 140.6 (m).

CRYSTAL STRUCTURE DETERMINATION

A suitable single crystal of **3** was sealed in a glass capillary and used for measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Diffraction intensities were corrected for Lp effects. The structure was solved by direct methods and refined by full matrix least-squares calculations against F^2. The thermal motion of all nonhydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)}$ = $1.5 \cdot U_{eq}$ of the corresponding C atom). Further information on crystal data, data collection, and structure refinement is summarized in Table 4. Final atomic positional and isotropic equivalent displacement parameters, anisotropic thermal parameters, tables of interatomic distances and angles, and tables of observed and calculated structure factors have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 59279.

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