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Chlorophosphaethenyl Phosphonium Ions by Chloride Abstraction from Dichlorophosphanyl Ylides

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ABSTRACT

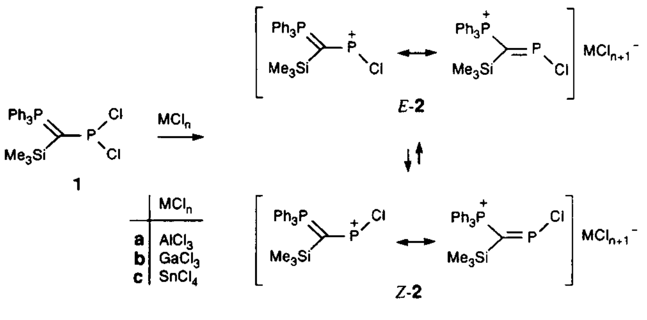
Dichlorophosphanyl ylides readily lose a chloride ion to Lewis acidic metal chlorides. In the cations so generated, a considerable part of the phosphenium charge is transferred to the phosphonium center leading to a chlorophosphaalkene structure. This is demonstrated by NMR data as well as by an X-ray structure analysis. The residual phosphenium charge becomes visible in weak but definite contacts with the $GaCl_4^-$ *anions that expand the coordination sphere of the P(III) atom from ψ-trigonal two-coordination to ψ-trigonal bipyramidal (ψ-TBP) tetra-coordination. © 1996 John Wiley & Sons, Inc.*

INTRODUCTION

Aminosubstituted chlorophosphanes $(R_2N)_nPCl_{3-n}$ allow the abstraction of a chloride ion. This results in phosphenium salts, which are well documented in the case of $n = 2$. Chloride abstraction from amino-dichlorophosphanes ($n = 1$) leads to amino-chlorophosphenium ions [1]. These have been characterized by NMR spectroscopy, but no crystal structure is yet available. As ylide substituents are of stronger influence on a PCl bond than amino substituents [2,3], we hoped that the chloride abstraction from a dichlorophosphanyl ylide would yield more stable chlorophosphenium salts that might be suitable for an X-ray structure investigation.

RESULTS AND DISCUSSION

Dichlorophosphanyl trimethylsilyl methylenephosphorane 1 reacts with an equimolar amount of $AlCl_3$, $GaCl_3$, or $SnCl_4$ in dichloromethane with complete abstraction of one chloride ion to give a 93:7 mixture of two isomeric cations that are identified by ^{31}P NMR spectroscopy (see next page) as *E*- and *Z*-**2**. From a reaction in benzene, the tetrachlorogallate **2b** was obtained in pure form and in good crystal quality.



	MCl_n
a	$AlCl_3$
b	$GaCl_3$
c	$SnCl_4$

In contrast to the related phosphoranediylamino-substituted chlorophosphenium salts $[(Me_2N)_3P{=}NPCl]TfO$ [4] and also to the phospho-

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Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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†X-ray structure analysis.

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ranediylmethyl-substituted alkylphosphenium salts [$Ph_3P=CHPtBu]BF_4$ [5], which dimerize in solution, the salts **2** stay monomeric for days in solution but decompose slowly.

NMR Spectra

The ^{31}P NMR spectra of **2b,c** are identical to the spectrum of **2a** (Table 1); i.e., the spectra are independent of the counter ion. Table 1 also includes the data of related compounds with alkyl or aryl groups in place of Me_3Si. In every case, δ(PCl) is characteristic of a two-coordinate phosphorus atom of the phosphenium type [6]. Where two isomers can be distinguished, their data show some differences. Most pronounced are the differences of $^2J_{PP}$. As the geminal coupling constant $^2J_{PP}$ of a tervalent phosphorus atom is generally large for a synperiplanar orientation of its lone pair and the second phosphorus atom, and small for an antiperiplanar orientation, the observed coupling constants are readily assigned to the *E*- and *Z*-isomer. For the trimethylsilyl derivatives **2**, the two coupling constants differ more strongly than the alkyl and aryl derivatives. The *E*-isomer is always prevailing and often the only one observed.

The ^{31}P chemical shifts of the *Z*-isomer are always found at higher field than those of the *E*-isomer, and the difference is more marked for δ(PCl) than for $\delta(PPh_3)$. As compared to δ(PCl) of compounds with alkyl and aryl substituents, R, the P(III) signal is found at significantly lower field and shows a more pronounced shift difference for the *E*- and *Z*-isomers in the case of the trimethylsilyl derivative **2**.

As *E*- and *Z*-isomers are observed separately in the ^{31}P NMR spectra at room temperature, the rotation barrier between the two must be high, and the second resonance formula (preceding page) must be important. The cations should thus be addressed as phosphaethenyl phosphonium rather than as phosphoniumylidyl phosphenium ions.

TABLE 1 ^{31}P NMR Data of *E*- and *Z*-Isomers of Chlorophosphaethenyl Triphenyl-phosphonium Tetrachloroaluminates $[Ph_3P{-}CR=PCl]AlCl_4$ in CH_2Cl_2; Coupling Constant *J* in Hz

	$\delta(PCl)$		$\delta(PPh_3)$		$^2J_{PP}$		
R	*E*	*Z*	*E*	*Z*	*E*	*Z*	*Ref.*
Me	340.7		25.9		122.8		[2]
Et	341.0		24.3		125.1		[2]
Ph	339.1	323.9	24.5	22.7	123.6	23.3	[2,14]
$3\text{-}CH_3C_6H_4$	338.6	322.9	23.3	21.7	126.2	24.4	[2,14]
$4\text{-}NO_2C_6H_4$[a]	340.0		23.5		117.5		[2]
Me_3Si (**2a**)	408.1	375.8	24.0	19.5	142.4	8.1	

[a] At −40°C, unstable at room temperature.

The increased withdrawal of electrons from the ylidic carbon atom in **2** as compared with **1**, and the consequent changes in the bond order of the two PC bonds, is consistently reflected also in the ^{13}C NMR data: $\delta^{13}C$ moves downfield from 43.5 (**1**) to 172.1 (*E*-**2**) and enters the range $\delta^{13}C$ = 170–210 characteristic of phosphaalkenes [7]. While $^1J_{P(V)C}$ decreases from 92.6 Hz (**1**) to 33.9 Hz (*E*-**2**), $^1J_{P(III)C}$ increases from 66.5 Hz (**1**) to 99.0 Hz (*E*-**2**).

Molecular Structure

Figure 1 shows the molecular structure of the cation and anion of **2b** as well as their contacts in the crystal; Table 2 gives the relevant structural data. The ylidic carbon atom C1 has a planar environment (sum of bond angles 359.6°), and the chlorine atom Cl1 is found almost in the same plane *trans* to P2 of the phosphonio group, i.e., with the dihedral angle P2–C1–P1–Cl1 close to 180°.

The bond P1–C1 (166.8 pm) is as short, as expected for the double bond of a phosphaalkene. Its average length is 167 pm [7]. The bond P2–C1 (179.2 pm), on the other hand, is considerably longer than it was before the chloride abstraction, i.e., as it is in a dichlorophosphanyl ylide of type **1** with an average length of 173 pm [2]. Both results are again in full accord with the bonding situation shown in the second resonance formula for *E*-**2**. So far, the structure

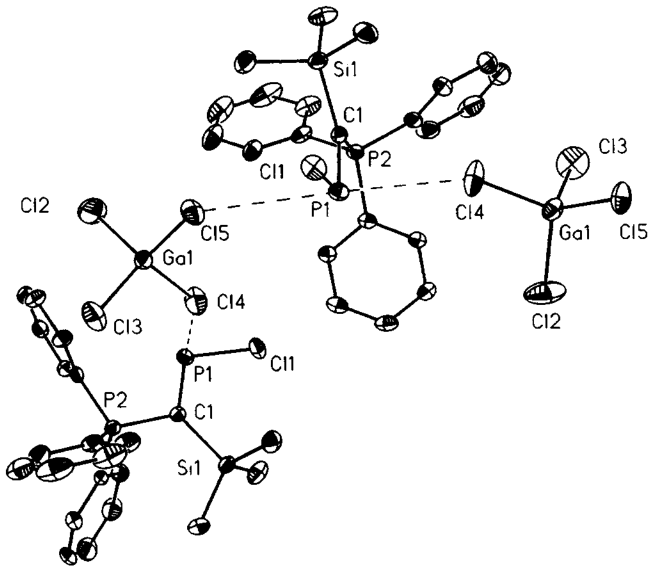

FIGURE 1 Molecular structure of two cations and two anions of *E*-**2b**, as part of the chainlike orientation in the crystal, hydrogen atoms omitted, thermal ellipsoids with 25% probability.

TABLE 2 Relevant Lengths (pm) and Angles (deg) of Bonds and of Cation/Anion Contacts in *E*–**2b**

P2–C1	179.2(5)	P1–C1–P2	109.2(3)
P1–C1	166.8(5)	P1–C1–Si1	128.9(3)
Si1–C1	192.8(5)	P2–C1–Si1	121.5(3)
P1–Cl1	204.6(2)	C1–P1–Cl1	105.4(2)
P1–Cl4	338.4	C1–P1–Cl4	95.0
P1–Cl5	362.6	C1–P1–Cl5	95.8
		Cl1–P1–Cl4	87.7
Ga1–Cl2	214.6(2)	Cl1–P1–Cl5	77.9
Ga1–Cl3	215.8(2)	Cl4–P1–Cl5	163.9
Ga1–Cl4	216.1(2)		
Ga1–Cl5	217.2(2)	Cl2–Ga1–Cl3	108.4(1)
		Cl2–Ga1–Cl4	111.3(1)
		Cl2–Ga1–Cl5	110.7(1)
		Cl3–Ga1–Cl4	109.2(1)
		Cl3–Ga1–Cl5	109.6(1)
		Cl4–Ga1–Cl5	107.7
		P2–C1–P1–Cl1	177.1

of **2b** compares well with that of the *P*-aminosubstituted phosphoniophosphaethene $[Ph_3P^2{-}CH{=}P^1{-}NiPr_2]BF_4$ with the bond lengths P1–C1 168 pm and P2–C1 179 pm [5].

As was to be expected, the PCl bond (P1–Cl1 204.6 pm) in the cation is shorter than the PCl bonds in the dichlorophosphanyl ylides (208.5–218.8 pm [2]) and as short as in PCl_3 (204.0 pm [8]). The CPCl angle is quite small (105.4°), half way between the angles 90° and 120°, as expected for a *p* orbital and for an sp^3 hybrid orbital of phosphorus, respectively, being employed for bonding the chlorine substituent. No molecular structure of a *P*-chlorophosphaalkene that would be suitable for comparison seems to be known so far. For a *P*-chloroiminophosphine, the PCl bond [214.2(4) pm] has been found to be much longer and the bond angle at phosphorus [112.4(2)°] considerably larger [9].

That a remainder of phosphenium character is left at the two-coordinate phosphorus atom of **2** is demonstrated by its weak but definite interaction with a chlorine atom of each (Cl4 and Cl5) of two tetrachlorogallate anions. The distances (338.4 and 362.6 pm) are only a little less than the sum of the van der Waals radii (370 pm [10]), but the Cl atoms are in positions to be expected for axial substituents of a ψ-trigonal bipyramidal (ψ-TBP) coordination of P1. This coordination geometry is well known for P(III) in the tetrahalophosphites (tetrahalophosphoranides) PX_4^-, where X = F [11], Cl [12], and Br [13]. As expected for a ψ-TBP coordination, the axis Cl4–P1–Cl5 is somewhat bent (163.9°), and it bends predominantly toward the equatorial chlorine substituent Cl1 (averaged angles Cl_{axial}–P–$Cl_{equatorial}$ = 82.8°). With the π-bonded carbon atom C1, on the other hand, the axial chlorine atoms Cl4 and Cl5 form angles >90° (averaged angles 95.4°). These details also seem plausible in terms of the VSEPR model and seem not to be accidental.

As both the cation and the anion have two interionic contacts, they form chains of alternating cations and anions extending through the crystal structure (Figure 1). The GaCl bonds involved in the interionic contacts are marginally longer (average 216.7 pm) than those not involved (average 215.2 pm).

EXPERIMENTAL

All glassware was flame-dried. Dry dichloromethane and benzene were used as obtained (Fluka). NMR: JEOL GSX 270 (^{31}P), JEOL EX 400 (^1H, ^{13}C) with Me_4Si (int.) and 85% H_3PO_4 (ext.) as standards.

Preparation of 2

2b: To a suspension of **1** [2] (1.06 g, 2.36 mmol) in 7 ml of benzene at room temperature, gallium trichloride (0.42 g, 2.36 mmol) in 4 mL of benzene was added with stirring. The precipitate was separated and recrystallized from a 1:1 mixture of benzene and dichloromethane. Colorless crystals, mp 133°C (decomp), yield 0.74 g (47%); anal. calcd for $C_{22}H_{24}Cl_5GaP_2Si \cdot 0.5\ CH_2Cl_2$ (667.9): C, 40.46; H, 3.77. Found: C, 40.04; H, 3.77. ^1H-NMR (CD_2Cl_2): δ = 0.27 (s, 9H, Me), 7.76 (m, 12H, *o,m*-H), 7.92 (m, 3H, *p*-H). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ = 1.4 (s, Me), 118.8 (dd, $^1J_{PC}$ = 89.1 Hz, $^3J_{PC}$ = 6.9 Hz, *i*-C), 130.9 (d, $^3J_{PC}$ = 13.0 Hz, *m*-C), 134.3 (dd, $^2J_{PC}$ = 10.5 Hz, $^4J_{PC}$ = 2.1 Hz, *o*-C), 135.9 (d, $^4J_{PC}$ = 3.1 Hz, *p*-C), 172.1 (dd, $^1J_{P(V)C}$ = 33.9 Hz, $^1J_{P(III)C}$ = 99.0 Hz, ylidic C). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): AB, δ_A = 408.3, δ_B = 24.3, $^2J_{AB}$ = 142.5 Hz (93%, *E*-isomer); AB, δ_A = 376.0, δ_B = 19.8, $^2J_{AB}$ = 6.1 Hz (7%, *Z*-isomer).

2a,c: Solutions of equimolar amounts of **1** and $AlCl_3$ or $SnCl_4$ in dichloromethane were combined at 0°C, and their $^{31}P\{^1H\}$ NMR spectra after 1 hour were recorded at room temperature (Table 1).

*X-ray Structure Analysis of E-*2b

The crystal selected for X-ray diffraction did not contain solvent molecules. $C_{22}H_{24}Cl_5GaP_2Si$, M = 625.41, crystal size: 0.6 × 0.55 × 0.25 mm^3, colorless prism, monoclinic, space group $P2_1/n$, a = 10.082(2) Å, b = 16.278(3) Å, c = 17.765(4) Å, β = 104.00(1)°, V = 2829(1) $Å^3$, Z = 4, d_{calcd} = 1.468 Mg m^{-3}, μ = 1.610 mm^{-1}, $F(000)$ = 1264. Siemens P4 diffractometer, Mo-Kα, $\lambda = 0.71073$ Å, ω scans, $T = 193$ K, 2Θ range = 3.44 to 50.02° in index ranges $-1 \le h \le 11, 0 \le k \le 19, -21 \le l- \le 20$, reflections collected: 5833, independent reflections: 4928 ($R_{int} = 0.0891$), observed reflections: 3433 ($F > 4\sigma(F)$), semi-empirical absorption correction, max. and min. transmission: 1.000 and 0.433, scan speed: 4.0 to 60.0° min^{-1} in ω, scan range (ω): 1.2°.

Structure solution program: XS (Siemens), direct methods; data-to-parameter ratio: 17.4:1 (12.1:[$F > 4\sigma(F)$]); final R indices [$F > 4\sigma(F)$]: $R1 = 0.0591$, $wR2 = 0.1459$, GoF on $F^2 = 1.034$; largest and mean Δ/σ: -0.003, 0.000; largest difference peak/hole: 0.872, -0.692 eÅ^{-3}; program used: SHELXL (Sheldrick 1993). Further details are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depositing number CSD 405529.

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