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Specific Interactions and the Nature of the Chemical Nonequivalence of Chlorine Atoms in the ECl_3 Group (E = C, P) of Trichlorophosphonium Ylides and Isomeric Dichloro(trichloromethyl)phosphine

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Abstract — The nature of the asymmetry of the ECl_3 group (E = C, P) in dichloro(trichloromethyl)phosphine and trichlorophosphonium methylide and dichloromethylide was studied by nonempirical and MNDO–PM3 calculations and ^{35}Cl NQR spectroscopy. The chemical nonequivalence of chlorine atoms in the CCl_3 group of dichloro(trichloromethyl)phosphine is caused by steric interaction with the PCl_2 fragment. In the PCl_3 group of trichlorophosphonium methylide and dichloromethylide, this nonequivalence arises from specific interactions with the lone electron pair of the ylide carbon atom, whose *p*-character is about 94% on the RHF/6-311^{++}G(3df,3pd) level. The alteration of the type of interaction predicts inversion of the ^{35}Cl NQR signals of the PCl_3 group in trichlorophosphonium ylide and dichloromethylide in relation to those of the CCl_3 group in the experimental spectrum of dichloro(trichloromethyl)phosphine. The MNDO–PM3 method characterizes dichloro- and diphenylmethylides as unstabilized structurally stable ylides.

Recently [1] we considered the conformational structure of dichloro(chloromethyl)phosphines, that proved to be quite sensitive to the degree of chlorination of the methyl group. The transition from the monochloromethyl to trichloromethyl derivative is accompanied by the transformation of the *gauche* to staggered conformation, noticeable distortion of the C_{3v} local symmetry of the CCl_3 group, and increase in the activation energy of hindered rotation of this group about the phosphorus–carbom bond [2].

Trichlorophosphonium ylides isomeric to dichloro(chloromethyl)phosphines, unlike related phosphorus oxides and imines, have not yet been isolated pure, even though some of their representatives exhibit thermodynamic and kinetic stability [1, 2]. Trichlorophosponium ylides present interest in terms of the investigation of peculiar details of interaction of their phosphonium and carbanionic fragments by following alterations in the local symmetry of the trichlorophosphonium group PCl_3 (analogous to those of the CCl_3 group of trichloromethylphosphines) as a specific probe.

In the present work we made use of quantum-chemical calculations and ^{35}Cl NQR spectroscopy to compare the effect of specific and steric interactions on the structure of the ECl_3 group (E = C,P) and chemical nonequivalence and lability of chlorine atoms of this group in dichloro(trichloromethyl)phosphine (**I**), trichlorophosphonium methylide (**II**), and isomeric trichlorophosphonium dichloromethylide (**III**), and to discuss the specific structural features of dichloromethylides R_2ClPCl_2 [R = Cl (**III**), *t*-Bu (**IV**), and NEt_2 (**V**] and diphenylmethylylide *t*-$BuClPCPh_2$ (**VI**). Nonempirical calculations of compounds **I**–**III** were carried out at the Hartree–Fock level using the 6-31^{++}G(d,p) basis set [3]. With ylide **II**, these calculations were compared with calculations including electron correlation (MP2) [3] and those with the 6-311^{++}G(3df, 3pd) (5D, 7F basis) extended triple split valence set [4] including diffusive and polarization functions on light and heavy atoms. Analysis of specific donor–acceptor interactions, hybridization characteristics, and redistribution of electron density was carried out in terms of natural bond orbitals [5] using the NBO 3.1 program [6]. The structure of chlorophosphonium ylides **II**–**VI** was examined in terms of MNDO–PM3 semiempirical calculations [7] and experimentally.

The calculated structures of compounds **I**–**III** are shown in Fig. 1. According to the calculations, both phosphine **I** and ylides **II** and **III** have C_s symmetry. The PCl_2 and CR_2 fragments are located in the transoid position to each other and have equivalent chlorine or hydrogen atoms related by the σ_h sym-

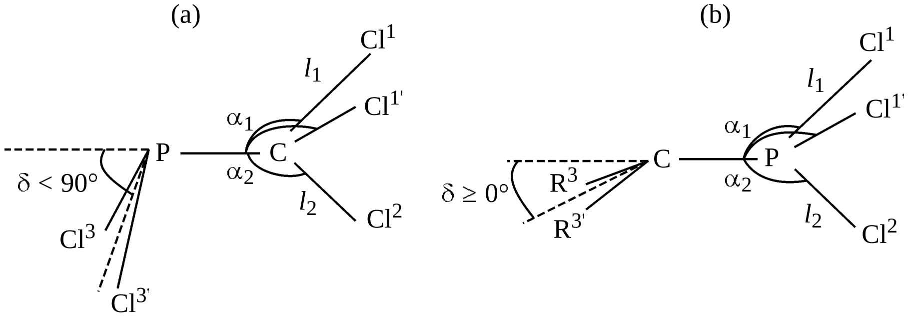

Fig. 1. C_s symmetry, transoid conformation, and denotation system for (a) phosphine **I** and (b) ylides **II** ($R^3 = R^{3'} = H$) and **III** ($C^3 = R^{3'} = Cl$).

metry axis that passes through the bisectors of the angles of the fragments and the phosphorus–carbon bond. Evidently, the peculiarity of the structure of both types of compounds is connected with the boundary values of the δ angle that measures deviation of the planes of the PCl_2 and CR_2 planes from the direction of the P–C bond (90° in phosphine **I** and 0° in ylides **II** and **III**). It was found that the boundary values of δ qualitatively characterize different mechanisms of interaction of the ECl_3 group with the rest molecule, leading to different tendencies in variation of the chemical nonequivalence of the same chlorine atoms $Cl^{1(1')}$ and Cl^2 in the ECl_3 group of phosphine **I** and ylides **II** and **III**.

Dichloro(trichloromethyl)phosphine (I). On the one hand, the closeness of the δ angle close to 90°C in the Cl_3PC fragment of phosphine **I** has three important consequences. Firstly, the steric interactions between the Cl^3 ($Cl^{3'}$) atoms of the PCl_2 group and the nontransoid Cl^2 atom of the trichloromethyl group sharply enhance, because the $Cl^{3(3')}\cdots Cl^2$ distance decreases to 3.457 Å which is smaller than the sum of the van der Waals radii of chlorine (3.6 Å [8]). Secondly, the symmetry of the lone electron pair of phosphorus is close to spherical (*s* 64%, *p* 36%), which excludes donor–acceptor interaction of this orbital with the antibonding orbital of the C–Cl^2 bond and weakening of the latter bond. Finally, rehybridization of the bonding orbital of the phosphorus atom of the P–C bond decreases the contribution of the *s* component (*s* 16%, *p* 81%), thus weakening this bond and makes the P–C dissociation pathway preferred over the C–Cl dissociation pathway in the chlorotropic transformation of phosphine **I** to ylide **III** [2].

On the other hand, the steric interactions with the PCl_2 group decrease the symmetry of the trichloromethyl group of phosphine **I** and result in chemical nonequivalence of the C–$Cl^{1(1')}$ and C–Cl^2 bonds (Table 1). In this case, the $PCCl^2$ bond angle (α_2) increases considerably, and the C–Cl^2 bond length (l_2) decreases with the increasing *s* character of the bonding orbital of the carbon atom. As a result, the ionicity of this bond and its related mobility of Cl^2 decrease, thereby increasing the ^{35}Cl NQR frequency related to the C–Cl^2 bond compared to the equivalent bonds C–Cl^1 and C–$Cl^{1'}$. The structural (Δl, $\Delta\alpha$), spectral ($\Delta\nu$), and charge ($\Delta q \sim \Delta i$, where *i* is the bond ionicity) parameters that relate to the chemical nonequivalence of the C–$Cl^{1(1')}$ and C–Cl^2 bonds of the trichloromethyl group of phosphine **I** are presented in the lower part of Table 1. The pattern of the trichloromethyl part of the ^{35}Cl NQR spectrum (77 K) of phosphine **I** is quite characteristic [2] and is determined by the C_s symmetry of the CCl_3 group and the stronger ionicity of the transoid C–Cl^1($C^{1'}$) bonds: The distance between the low-frequency (Cl^1, $Cl^{1'}$) and high frequency (Cl^2) components of the spectrum ($\Delta\nu$) is 0.6 MHz, and their intensity ratio is 2 : 1 (Fig. 2).

Trichlorophosphonium ylides II and III. Bernardi *et al.* [9] had been the first to suggest a model of bonding in phosphonium ylides, that later became commonly accepted. According to this model, the lone electron pair of phosphorus forms a σ bond with carbon that completes its octet of electrons, and the excess negative charge is located on a *p* orbital of carbon, that forms the back bond with the lowest unoccupied σ* orbital of *e* symmetry of the phosphonium fragment. The carbon *p* orbital is eclipsing one of the bonds of the phosphonium fragment, which minimizes the total energy of the molecule and renders this bond longer compared to the other bonds of the phosphonium group. This bonding model is supported by high-level nonempirical calculations of methylenephospohorane H_3PCH_2, that reveal elongation of one of the P–H bonds {1.414 and 1.389 Å in the DZ approximation including polarization and

Table 1. Structural (l, α), spectral (ν), and charge characteristics of the ECl_3 group of dichloro(trichloromethyl)phosphine (**I**), trichlorophosphonium methylide (**II**), and trichlorophosphonium dichloromethylide (**III**) as given by RHF/6-31^{++}G(d,p) calculations

Parameter[a]	I	II			III
		A	B	C	
$-E^{ZPC}$, au	2675.982	1758.150	1758.807	1758.310	2675.933
l_1, Å	1.776	2.008	2.014	1.994	1.992
α_1, deg	105.8	112.0	110.9	112.2	110.9
q_1, e	–0.020	0.005	0.033	–0.223	0.072
ν_1, MHz	38.851(2)[b]	–	–	–	–
l_2, Å	1.753	2.070	2.090	2.054	2.057
α_2, deg	116.2	124.9	118.6	123.8	123.9
q_2, e	0.059	–0.020	–0.020	–0.298	0.015
ν_2, MHz	39.471(1)[b]	–	–	–	–
Δl, Å	–0.030	0.06	0.08	0.06	0.07
$\Delta\alpha$, deg	10.4	12.9	9.7	11.6	13.0
Δq, e	0.08	–0.03	–0.050	–0.080	–0.09
$\Delta\nu$, MHz	0.6	~–0.6	~–0.6	~–0.6	~–0.6

[a] (E^{ZPC}) Total energy corrected for zero-point vibrations. The B and C variants relate to the MP2/6-31^{++}G(d,p) and RHF/6-311^{++}G(3df, 3pd) levels, respectively. (Δ) Difference in the parameters labeled 1 and 2 according to Fig. 1. Mulliken atomic charges are given, except for those for the IIC variant for which natural atomic charges are given for comparison.

[b] Parenthesized are relative intensities.

diffuse functions [10] and 1.440 and 1.404Å in the MP-2/6-31G* approximation [11]}, as well as a unique X-ray diffraction study of the P-chloroylide t-$Bu_2 \cdot ClPCPh_2$ (**VI**) [12], that reveal a noticeable elongation of the eclipsed P–Cl bond (to 2.235 Å).

Our calculations, too, give evidence for this model. Contrary to the shortening of the C–Cl^2 bond of the trichloromethyl group in phosphine **I**, the respective P–Cl^2 bond of the trichlorophosphonium group in ylides **II** and **III** is much elongated compared with the other bonds of the PCl_3 group at comparable bond angles α_2 of 116.2° in **I** and 118°–124° in **II** and **III** (Table 1). As ylides **II** and **III** lack steric hindrances associated with substituents R^3 (δ ~0) (Fig. 1b), electrostatic interactions of the excess negative charge of 1.898 e on the 2p orbital of the ylide carbon atom ($sp^{19.9}d^{0.1}f^{0.1}$ hybride with a 94% p-character) with the charge of the coplanar P–Cl^2 bond gain primary significance (Table 2). Actually, assuming that the van der Waals radius of the carbon 2p orbital are approximately equal to half the effective thickness of the p-orbital cloud in aromatic hydrocarbons (1.7 Å [8]) we obtain a C···Cl^2 distance of 3.5 Å, which is noticeably larger than the calculated C···Cl^2 distance of 3.28 Å roughly the same in ylides **II** and **III**.

Repulsion of the negative charges enlarges the $CPCl^2$ angle and shifts the electron density to the Cl^2 atom. This mechanism is evidently responsible for the rehybridization of the bond orbital of the phosphorus atom of the P–Cl^2 bond, but it does not explain the weakening of this bond. The final elongation of the P–Cl^2 bond in ylides **II** and **III** is evidently mainly

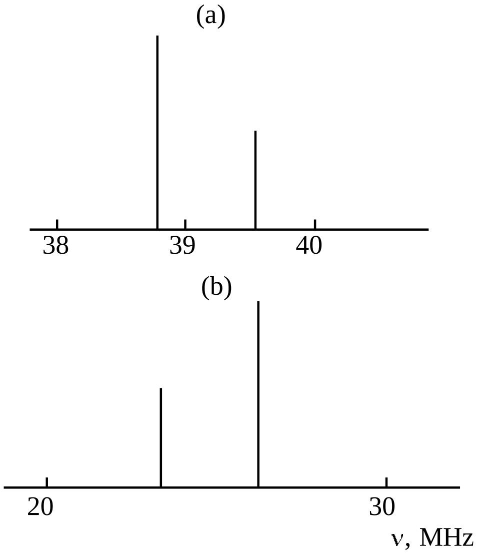

Fig. 2. (a) Experimental ^{35}Cl NQR spectrum of phosphine **I** (77 K) and (b) proposed spectrum of ylides **II** and **III** in the absorption range of the trichloromethyl and trichlorophosphonium groups of C_s symmetry.

Table 2. Parameters of hybrid orbitals and specific interactions (MP2) of bonds of the PCl_3 group with the $P^+–C^-$ bond in the ylide Cl_3PCH_2 (**II**) in the NBO approximation of the RHF/6-311^{++}G(3df,3pf) method

Bond (donor)	Energy, au	Population, e	Hybrid orbital[a]		Acceptor	
			P	C (Cl)	bond[b]	$E(2)$, kJ mol^{-1}
π(PC)	–0.360	1.898	$sp^{50.7}d^{32.4}f^{0.07}$ (19.5)	$sp^{19.9}d^{0.1}f^{0.01}$ (80.5)	$\sigma^*(PCl^2)$	194.6
$\sigma(PCl^2)$	–0.733	1.835	$sp^{2.3}d^{1.9}f^{0.02}$ (26.4)	$sp^{5.5}d^{0.07}$ (73.6)	π^*(PC)	475.7
$\sigma(PCl^{1(1')})$	–0.889	1.946	$sp^{3.4}d^{0.5}f^{0.01}$ (33.6)	$sp^{4.8}d^{0.07}$ (66.4)	π^*(PC)	107.9
σ(PC)	–0.934	1.980	$sp^{1.5}d^{0.05}$ (41.4)	$sp^{2.2}d^{0.03}$ (58.6)	$\sigma^*(PCl^2)$	35.6

[a] Relative contribution of atomic orbital in % is given in brackets. [b] The bond whose donor–acceptor interactions contribute most into the correlation correction. The energy of specific interactions of the chlorine lone electron pair with the ylide bond $E(2)$ does not exceed 60 kJ mol^{-1} and compares with the energy of σ(PC)–*(PCl^2) interactions.

Table 3. Effect of specific interactions on the form of natural localized molecular orbitals of ylide Cl_3PCH_2 **II** as given by RHF/6-311^{++}G(3df,3pf) calculations

Molecular orbital	Hybridized atomic orbitals, %				β[a]
	P	C	$Cl^{1(1')}$	Cl^2	
1	$sp^{100}d^{8.1}f^{0.05}$ (22.2)	$sp^{20.7}d^{0.1}f^{0.01}$ (76.8)	$sp^{5.8}d^{1.4}f^{0.03}$ (0.30)	$sp^{5.2}d^{0.4}f^{0.01}$ (0.67)	94.8
2	$sp^{2.1}d^{0.13}$ (30.0)	$sp^{100}d^{9.6}f^{0.18}$ (1.32)	$sp^{5.7}d^{0.1}f^{0.01}$ (0.44)	$sp^{5.5}d^{0.07}$ (67.8)	91.5
3	$sp^{2.0}d^{0.08}$ (35.0)	$sp^{2.5}d^{0.4}f^{0.01}$ (0.23)	$sp^{4.8}d^{0.07}$ (64.5)	$sp^{6.1}d^{0.2}f^{0.01}$ (0.17)	97.2
4	$sp^{1.1}d^{0.02}$ (41.5)	$sp^{2.3}d^{0.03}$ (58.1)	$sp^{5.4}d^{0.4}f^{0.02}$ (0.09)	$sp^{5.3}d^{0.5}f^{0.01}$ (0.18)	99.0

[a] β is the contribution of the related natural bond orbitals, %

determined by the electron density transfer from the 2*p* orbital of the ylide carbon atom to the antibonding σ^* orbital of the P–Cl^2 bond by the mechanism of negative hyperconjugation [2]. The energy of the π(PC)–$\sigma^*(PCl^2)$-interaction is 194.6 kJ mol^{-1}, which, in terms of the second-order pertrubation theory (MP2), is one of the highest in ylide **II** (Table 2) and comprises more than three times the interaction energy with transoid bonds (63.4 kJ mol^{-1}). The degree of $\pi\sigma^*$ and $\sigma\pi^*$ mixing of the ylide bond and the phosphonium fragment is clearly followed by the degree of deviation of the natural localized molecular orbital from the related natural bond orbital of ylide **II** (Table 3).

On the whole, the degree of deviation of the natural localized molecular orbital from the related natural bond orbital is proportional to the energies of specific $\pi\sigma^*$ and $\sigma\pi^*$ interactions of the phosphonium and carbanionic fragments in ylides **II** and **III**: The largest deviations are characteristic of the strongest interactions. Together the above-considered mechanisms operate to elongate the PCl^2 bond, increase its ionicity (proportional to the charge on the terminal chlorine atom) (Table 1), and, as a result, to render Cl^2 more mobile compared with the $Cl^{1(1')}$ atom of the trichlorophosphonium fragment. Hence, the P–Cl bond in the P-chloroylide *t*-$Bu_2ClPCPh_2$ (**VI**, weakened by n_C–σ^*(PCl) interactions allows the chloride ion to be eliminated under the action of such a relatively weak Lewis acid as $SnCl_2$ [12].

Chlorophosphonium dichloromethylides III–**V**. Unlike trichlorophosphonium ylides, stable P-chloroylides whose structure could be studied by X-ray diffraction and ^{35}Cl NQR spectroscopy were isolated only recently [12–14]. The results of MNDO–PM3 and RHF/6-31^{++}G(d,p) calculations together with some experimental structural and frequency characteristics of chlorophosphonium dichloromethylides $R_2ClP^+–C^-Cl_2$, [R = Cl (**III**), NEt_2 (**IV**), *t*-Bu (**V**], and diphenylmethylide *t*-$Bu_2ClP^+–C^-Cl_2$ (**VI**) are listed in Table 4.

As judged from the formation energies, bonding attenuates in the series **III**–**VI**, even though the positive definiteness of the Hessian in these compounds suggests their structural stability. Bond weakening enhances as stronger and stronger electron-

Table 4. Parameters of chlorophosphonium ylides **III**–**VI** as given by MNDO–PM3 and RHF/6-31^{++} calculations and X-ray diffraction [12] and ^{35}Cl NQR [13, 14] experiments

Parameter	III		IV		V		VI	
	PM3	6-31++G**	PM3	NQR	PM3	NQR	PM3	PCA[a]
ΔH_f,[b] kJ mol^{-1}	–227.2	–56.9[c]	–198.9	–	–157.7	–	109.6	–
ε(HOMO), eV	–8.88	–5.59	–8.02	–	–7.84	–	–8.19	–
ε(LUMO), eV	–2.77	–1.25	–1.25	–	–0.83	–	–0.67	–
R(PC), Å	1.514	1.650	1.535	–	1.534	–	1.573	1.668
R(PCl), Å	2.041	2.057	2.106	–	2.102	–	2.109	2.235
ω(CPCl), deg	119.7	123.9	112.5	–	114.8	–	113.9	117.5
τ(ClCPCl), deg	90.5	79.3	104.0	–	90.7	–	83.1	86.7
q(C), *e*	–1.167	–0.183	–1.083	36.26[d]	–1.062	36.80[e]	–0.903	–
q(Cl), *e*	–0.401	0.015	–0.550	23.82[f]	–0.522	–	–0.541	–

[a] X-ray diffraction analysis. [b] Formation energies at 298 K. [c] Gibbs formation energy Δ*G*. [d] Mean frequency (MHz) of dichloromethylene chlorine atoms [13]. [e] Mean frequency (MHz) of the dichloromethylene chlorine atoms in the P-fluoro analog *t*-Bu_2FP^+–C^-Cl_2 [14]. [f] Frequency (MHz) of the P–Cl chlorine atom [13].

donor substituents that weaken both the ylide P–C bond and P–Cl bonds are introduced first by phosphorus (**III**–**V**) (this leads to destabilization of the frontier orbitals) and then by carbon (**VI**). The fact that the charges on the ylide carbon and P–Cl carbon atoms in compounds **III**–**VI** vary in opposite directions (now in terms of the semiempirical calculation method) provides further evidence for the mechanism of negative hyperconjugation, that operates to weaken the latter bond. These findings allow the structure of P-chloroylides **III**–**VI** to be presented by canonical structures **A** and **B**.

$$\underset{\mathbf{A}}{R_2ClP^+{-}C^-R'_2} \longleftrightarrow \underset{\mathbf{B}}{Cl^-R_2CP^+{=}CR'_2}.$$

The actual enhancement of electron-donor properties of the lone electron pair of the ylide carbon atom along the series **III**–**VI** decreases the negative charge on this carbon and reveals itself in increased ^{35}Cl NQR frequency of the dichloromethylene group in ylide **V** as compared to ylide **IV**. The close correspondence of parameters [*q*(C) –1.10 e, *q*(Cl) –0.59 e, and *R*(PCl) 2.121 Å] of unstabilized P-chloroylide $(Et_2N)_2ClP^+$–C^-H_2 [13] to respective parameters of chlorophosphonium dichloro- and diphenylmethylides **III**–**VI** (Table 4) together with the positive definiteness of the Hessians allows the latter compounds to be also classed with unstabilized structurally stable ylides. In the case of dichloromethylides, this is connected with the inefficiency of chlorine *d* orbitls as π-acceptors of the electron density of the carbon lone electron pair, whereas in the case of diphenylmethylides, with the almost coplanar arrangement of the carbon lone electron pair and the planes of both phenyl substituents, which prevents delocalization of the lone electron pair onto the carbanionic fragment (the charges on the phenyl rings in ylide **VI** are +0.04 e). Note that at the 6-31^{++}G(d,p) level the charges on the ylide carbon atom in ylides **III**–**VI** are –0.492 and –0.183 e, respectively. These values point to certain stabilization of the carbon lone electron pair in dichloromethylide **III**, which is associated with the effective electronegativity of the latter increased by the inductive effect of chlorine. The P–C and P–Cl bonds in ylide **IV** are longer than in ylides **III, V**, and **VI**, which is connected with the additional π-electron-donor effect of the diethylamino groups, as evidenced by the fact that ylide **IV** has the lowest ^{35}Cl NQR frequency for the P–Cl bond (23.823 MHz) among known chlorine derivatives of fourcoordinate phosphorus.

The MNDO–PM3 method significantly underestimates the ylide P–C bond in ylides **III**–**VI**, as seen from a comparison with the RHF/6-31^{++}G(d,p) value for compound **III** and the X-ray diffraction data for compound **VI** (Table 4). This probably also relates to P–Cl bonds. The antibonding σ* orbital of the P–Cl bond in P-chloroylide **VI** is 0.1 eV lower by energy than the σ* orbital of the P–C bond of the *tert*-butyl group. From the energetic point of view, this fact suggests that the P–Cl bond is eclipsing the C_{2p} orbital. Evidence for this suggestion comes from the X-ray diffraction data in [12], that show that the unit cell of P-chloroylide **VI** comprises three independent conformers **VIa**–**VIc**. They differ sinificantly by two related parameters, viz. rotation angle of the diphenylmethylene group and P–Cl bond length. The longest P–Cl bond, 2.235 Å, is found in conformer **VIa** (Table 4), where the CPh_2 group is almost orthogonal to the P–Cl bond.

Our estimates for the structural stability of ylides **II**–**VI** and the synthetic data for perchloro-1λ^5,3λ^5-diphosphetane [15] that spontaneously decomposes on handling make us to expect that trichlorophosphonium ylides **II** and **III** can be isolated pure. In view of the instability of the dimer $(Cl_3P \cdot CCl_2)_2$, it is highly probable that the ylide Cld3PCCl$_2$ will be successfully isolated by fast low-temperature (77 K) crystallization of the melt of the dimeric form, by analogy with the preparation of a crystalline trichlorophosphazopentafluorobenzene from the dimer $(Cl_3PNPh_F)_2$ [16]. The quantitative nonempirical estimates in this work predict a doublet structure of the ^{35}Cl NQR spectra of the trichlorophosphonium fragment in ylides **II** and **III** with a splitting of about 0.6 MHz and inverse intensity ratio of the low- and high-frequency components compared with that observed in the spectrum of dichloro(trichloromethyl)-phosphine (**I**) (Fig. 2b), which reflects the different nature of the asymmetry of the ECl_3 group in these systems.

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