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Specific Features of Chlorotropism in the ENC Triad ($E = P^{IV}–P^{VI}$, C) of High-Coordination Phosphorus Chlorides and Trichloromethyl Isocyanate

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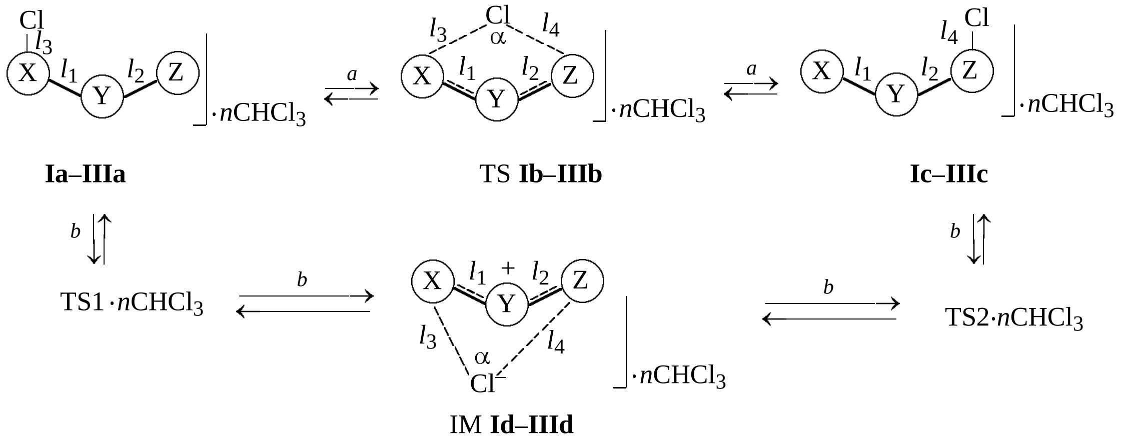
Abstract—The semiempirical MNDO method and its parametrized PM3 version in supermolecular approximation was used for a comparative study of the structure and alternative mechanisms of chlorotropism in the ENC triad ($E = P^{IV–VI}$, C) of amidinium tetrachlorophosphorate $Cl_4P(NCH_3)_2CCCl_3$ (**I**), phosphazopentachloroethane $Cl_5C_2NPO_2C_6H_4$, (**II**), trichloromethyl isocyanate Cl_3CNCO (**III**), and their 1:2 chloroform solvates. The absence of the thermodynamically stable intermediate as a separated ion pair in the chlorotropic transformations of structures **I, III** and the high enthalpy of the substrate–intermediate transformation for structure **II** show that the sigmatropic mechanism of chlorotropism in compounds under study is the only probable one. The activation barrier of chlorotropism in phosphorus systems **I, II** is much reduced. In the case of specific solvation, a weak tendency to further reduction of the activation barrier for structures **I–III** is observed, and the equilibrium for phosphorus systems **I, II**, is appreciably shifted, unlike system **III**, where, according to experimental data, the equilibrium is fully to the side of the carbamoyl isomer $Cl_2C=NC(O)Cl$.

Previously we showed [1, 2] that chlorine migration in the PNC and CNC triads of cyclic amidinium tetrachlorophosphorates and chloromethyl isocyanates proceeds intramolecularly by the sigmatropic mechanism, but paid no attention to the alternative dissociation–recombination mechanism of the transformation and the effect of specific solvation, which play an important role in the chlorotropic transformation of *P*-chloroylides [3]. The studies were initiated in view of scarce kinetic data and lack of theoretical considerations of halotropism in really existing CNC and PNC systems whose characteristics might be compared with experimental results. The reliability of geometric and energetic characteristics estimated by the semiempirical MNDO–PM3 method in the supermolecular approach to specific solvation with account for a limited number of solvent molecules, especially as applied to transition states, we checked recently [4] on an example of halotropism in *P*-haloylides. It was found that the method satisfactorily fits experimental data, especially when its reasonable computing expences compared with higher level approaches are taken into consideration [5–7]. The energy of specific solvation is mostly contributed by two molecules of the solvation shell, which directly interact with the halide ion in the transition state of the chlorotropic transformation of *P*-haloylides (with subsequent saturation as the the solvation coordination number equal to 8 [4] is attained). This finding gives evidence for the assumption that in evaluating tendencies in the effect of specific solvation on the chlorotropic transformation in ENC systems one can take into account a limited number of molecules in the solvation shell.

In the present work by the semiempirical MNDO (CNC system) and MNDO–PM3 (PNC system) methods [8] in supermolecular approximation we performed a comparative study of the effects of heteroatom and specific solvation on the structure and alternative mechanisms of the chlorotropism in the ENC triad ($E = P^{IV–VI}$, C) of chlorotropic isomers of amidinium tetrachlorophosphate $Cl_4P(NCH_3)_2CCCl_3$ (**I**), phosphazopentachloroethane $Cl_5C_2NPO_2C_6H_4$ (**II**), trichloromethyl isocyanate Cl_3CNCO (**III**), and their 1:2 chloroform solvates. Structures $M \cdot nCHCl_3$ (where $n = 0$ and 2, and M relates to the chlorotropic isomers of amidinium tetrachlorophosphorate (**Ia, Ic**), phosphazopentachloroethane (**IIa, IIc**, trichloromethyl isocyanate (**IIIa, IIIc**), intermediate (IM) **IId**, and transition states (TS) **Ib**–**IIIb** of the alternative sigmatropic (*a*) and dissociation–recombination (*b*) mechanisms of the 1,3-chlorine shift according to scheme (1).

The search for transition states $\mathbf{Ib_2}$–$\mathbf{IIIb_2}$ (as earlier in [1–4]) was performed by the difference vector procedure [9], and the subsequent refinment of the geometric and energetic characteristics of the transition state was performed by the eigenvector tracing

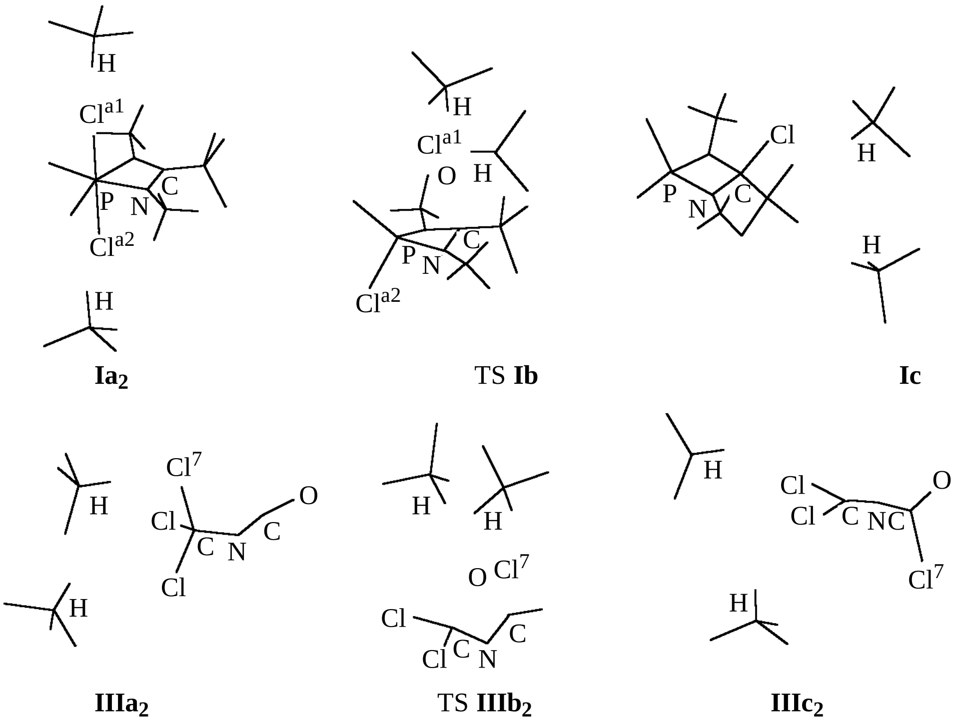


(1)

X = PCl$_3$NCH$_3$, Y = NCH$_3$, Z = CCCl$_3$, n = 0 (**Ia–Id**), 2 (**Ia$_2$–Id$_2$**); X = PClO$_2$C$_6$H$_4$, Y = –N=, Z = CClCCl$_3$, n = 0 (**IIa–IId**), 2 (**IIa$_2$–IId$_2$**); X = C^{1}Cl$_2$, Y = –N=, Z = C^2=O, n = 0 (**IIIa–IIId**), 2 (**IIIa$_2$–IIId$_2$**).

procedure [10]. Stationary points were identified by the type of the Hessian via solving the vibrational problem. Electron correlation was not included, since it is inexplicitly accounted for in parameters of the MNDO method.

The results of the calculations are listed in Tables 1–4 (together with the characteristics of the nonsolvated molecules, obtained in [1, 2]). The mutual location of substrate and chloroform molecules for representatives of phosphorus **I** and carbon **III** solvates is shown scheme 2 as graphical representations of optimized Z matrices, and the corresponding geometric parameters are listed in Table 1.



(2)

Table 1. Calculated principal energetic and geometric characteristics of amidinium tetrachlorophosphorate **Ia** and dichlorophosphorane **IIa** (MNDO–PM3), trichloromethyl isocyanate **IIIa** (MNDO), their chlorotropic isomers **Ic**–**IIIc**, transition states **Ib**–**IIIb**, and intermediate **IId** for the free molecules ($n = 0$) and 1 : 2 chloroform solvates $M \cdot n CHCl_3$ ($n = 2$)

Comp. no.	ΔH_f(298), kJ/mol	M = **I**–**III**						$CHCl_3$, Δl(C–H), Å	$l(E \cdots HCCl_3)^b$, Å
		l_1, Å	l_2, Å	l_3, Å	l_4, Å	α, deg	τ^a, deg		
					$n = 0$				
Ia	–469.8	1.903	1.356	2.111	–	89.9^c	89.9		
Ib^d	–339.6	1.837	1.415	2.569	2.132	58.4	50.8		
Ic	–429.6	1.793	1.468	–	1.811	113.7^c	110.6		
IIa	–557.6	1.746	1.277	2.131	–	92.2^c	22.0		
IIb^d	–442.8	1.669	1.343	2.416	2.199	69.3	22.9		
IIc	–507.8	1.594	1.414	–	1.809	114.3^c	64.2		
IId	–272.8	1.701	1.291	7.420	8.728	17.9	4.9		
IIIa	–130.7	1.408	1.256	1.788	–	107.0^c	0.0		
IIIb^d	35.9	1.357	1.339	2.181	2.070	63.9	23.1		
IIIc	–157.8	1.269	1.412	–	1.771	112.1^c	93.1		
					$n = 2$				
Ia$_2$	–665.1	1.898	1.356	2.124	–	89.6^c	89.8	0.01	2.56 (Cl^{a1})
								0.01	2.43 (Cl^{a2})
Ib$_2^d$	–544.1	1.828	1.411	2.756	2.194	55.3	52.3	0.01	2.40 (Cl^{a1})
								0.01	2.38 (Cl^{a1})
Ic$_2$	–613.1	1.808	1.471	–	1.812	113.2^c	109.3	0.00	2.82 (Cl)
								0.00	2.58 (Cl)
IIa$_2$	–751.2	1.744	1.280	2.140	–	92.9^c	22.0	0.00	2.46 (Cl^4)
								0.00	2.49 (Cl^6)
IIb$_2^d$	–639.6	1.658	1.345	2.530	2.189	67.6	23.7	0.00	2.41 (Cl^4)
								0.00	2.44 (Cl^4)
IIc$_2$	–693.7	1.596	1.410	–	1.811	115.0^c	58.0	0.00	2.57 (Cl)
								0.00	2.78 (Cl)
IId$_2$	–557.3	1.698	1.290	7.575	9.306	15.2	1.5	0.07	1.74 (Cl^4)
								0.07	1.74 (Cl^4)
IIIa$_2$	–371.8	1.408	1.257	1.805	–	107.2^c	1.0	0.00	3.46 (Cl)
								0.00	3.88 (Cl)
IIIb$_2^d$	–212.9	1.350	1.334	2.233	2.057	64.2	14.6	0.00	3.54 (Cl^7)
								0.00	4.92 (Cl^7)
IIIc$_2$	–396.0	1.269	1.416	–	1.770	112.3^c	91.2	0.00	3.42 (Cl)
								0.00	3.89 (Cl)

[a] Dihedral angle ClPNC(ClCNC). [b] Shortest molecular contact, atom E is given in parentheses; indices 4 and 6 relate to the P–Cl bonds (**IIa**$_2$), transit atom (**IIb**$_2$), or chloride ion (**IId**$_2$); for solvates **Ic**$_2$, **IIc**$_2$, **IIIa**$_2$, and **IIIc**$_2$ the contacts relate to chlorine atoms of the trichloromethyl or dichloromethylene groups {see scheme (2) and reference [4]; [c] Bond angle NPC(NCCl)}. [d] The imaginary vibration frequencies ν_{im} are 316, 251, 365, 311, 626, and 599 cm^{-1} for transition states **Ib, Ib**$_2$**, IIb, IIb**$_2$**, IIIb**, and **IIIb**$_2$, respectively.

The thermodynamically most stable isomers of PNC phosphorus systems **I, II** are higher coordination phosphorus ones: P^{VI} isomer **Ia** and P^V isomer **IIa** (Table 1). This make possible experimental isolation of the corresponding compounds as phosphorates [11] and phosphoranes [12]. However, both phosphorus isomers of systems **I, II** would be expected to have labile chlorine atoms on the exchanging P and C centers, because the P–Cl [2.111 (**Ia**) and 2.131 Å (**IIa**)] and C–Cl bond lengths [1.811 (**Ic**) and 1.809 Å (**IIc**)] are much larger than normal values, unlike the situation with the carbon analogs [1.788 (**IIIa**) and 1.771 Å (**IIIC**)], where the accumulation of electron-acceptor substituents on the α-carbon atom destabi-

Table 2. Dependence of the calculated activation ($E^{\neq}$, kJ/mol) energy and heat (ΔH, kJ/mol) of the chlorotropic isomerization for the phosphorus **I, II** and carbon **III** systems on the degree of solvation n for solvates $\mathrm{M \cdot }n\mathrm{CHCl_3}$

Reaction, parameter	Mechanism	**Ia** $\rightleftarrows$ **Ic**		**IIa** $\rightleftarrows$ **IIc**		**IIIa** $\rightleftarrows$ **IIIc**	
		$n = 0$	$n = 2$	$n = 0$	$n = 2$	$n = 0$	$n = 2$
Direct	*a*	130	121	115	112	194	183
X→Z	*b*[a]	–	–	285	194	–	–
Reverse	*a*	90	69	65	54	167	159
Z→X	*b*[a]	–	–	235	136	–	–
ΔH	*a*	40	52	50	58	27	24

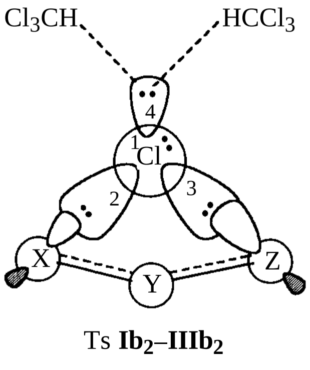
[a] Enthalpy of the substrate–intermediate transformation (ΔH^1, kJ/mol) by dissociation–recombination pathway *b*.

lizes the heteroallyl structure and leads to a thermodynamically more stable carbamoyl isomer $\mathrm{Cl_2C{=}NC(O)Cl}$ (**IIIc**) [2, 13].

Sigmatropic transition states of the phosphorus (**Ib, IIb**) and carbon (**IIIb**) analogs are structurally similar. The angle α at the transit chlorine atom is 60–70°, and the C–Cl bond length in the XClZ triad monotonically decreases in the order **Ib** > **IIb** > **IIIb** (Table 1). But elimination or addition of chlorine in the course of isomerization of phosphorus systems **I, II** occurs from the axial position of a square (**Ib**) or trigonal (**IIb**) phosphorus bipyramid, which considerably reduces energy consumption for rehybridization of the exchanging P,C centers compared with the C,C centers in carbon system **III**. This is explained by the fact that energy consumption for rehybridization [14] appears to contribute most to the activation barrier for the chlorotropic isomerization (Table 2). In the case of specific solvation, the charge on the transit chlorine atom in phosphorus systems **I, II** proves to be more mobile than in carbon system **III**, resulting in stronger polarization of P–Cl bonds in isomers **Ia, IIa** and of dative bonds of the transition states, as well as in stabilization of frontier orbitals in the systems in study (Table 3).

Intermediate state **IId** of dissociation–recombination izomerization pathway *b* for phosphazopentachloroethane is a separated ion pair in which the chloride ion is located near the benzodioxaphosphole fragment of the cation ($l_3 < l_4$), and bonds in the PNC triad are equalized but to a slightly lesser extent than in sigmatropic transition state **IIb** (Table 1). The heat ΔH^1 of the **IIa** (**IIb**) $\rightleftarrows$ **IId** transformation is several times higher than the activation barrier for pathway *a* (Table 2), implying that the chlorotropic isomerization of phospazopentachloroethanes can occur in no other way than by sigmatropic mechanism *a* and eliminating the necessity of consideration of the structures and energies of TS1 and TS2 for pathway *b* for which one whould expect an even stronger $E^{\neq}(\mathrm{TS1,TS2}) > \Delta H^1 \gg E^{\neq}(\mathrm{TS})$ inequality. If with acyclic phosphorus system **III** we find a theoretical possibility that the 1,3-chlorine migration follows dissociation–recombination pathway *b*, then with systems **I, III** this possibility is completely absent, since attempted localization of the separated ion pair for the isomerization of amidinium tetrachlorophosphorate **Ia** by pathway *b* results in decomposition of **Ia** with molecular chlorine evolution. Analogous procedure converts trichloromethyl isocyanate **IIIa** to a highly energetic structure Cl–Cl–C(Cl)NCO (cf. with the structure $\mathrm{H_2C{-}Cl{-}H}$ obtained by higher level computations [15]).

Analysis of delocalized molecular orbitals of the sigmatropic transition states for chlorotropic systems **Ib**–**IIIb** (Table 3) gives almost no way for distinguishing 1,3 migration of chlorine atom (its charge, –0.5 to –0.6 *e*, remains very close to that on the chlorine atom in one of the chlorotropic isomers in phosphorus systems **I, II**) and 1,3-migration of chloride ion (with formation of a tight ion pair and fairly strong $\mathrm{Cl^-} \rightarrow \mathrm{E}$ dative bonds, which reduces the charge on the chloride ion to the same value of –0.5 to –0.6 *e*). The formalism of localized bonds (localization was carried out according to Perkins–Stewart [16]), applied to transition states **Ib, Ib$_2$**–**IIIb**, and **IIIb$_2$**, shows that the second approach is preferable (Table 4). Actually, solvated sigmatropic transition state **Ib$_2$**–**IIIb$_2$** is characterized by three low-energy (–11 to –15 eV) localized orbitals that include lone electron pairs (LEPs) of the transit chloride ion, two of which form dative bonds with atoms of the PNC or CNC triads, and the third one is involved in interaction with chloroform molecules in the solvate [scheme (3)]:



(3)

Ts **Ib$_2$–IIIb$_2$**

Specific solvation of phosphacyclic system **I** leads to destabilization of both dative bonds in transition

Table 3. Calculated atomic charges (q_i, e), atomic coefficients (c_{ij}), and energies (ε_i, eV) of frontier orbitals of solvated amidinium tetrachlorophosphorate **Ia**$_2$ and dichlorophosphorane **IIa**$_2$ (MNDO–PM3), trichloromethyl isocyanate **IIIa**$_2$ (MNDO), their chlorotropic isomers **Ib**$_2$–**IIIb**$_2$, transition states **Ib**$_2$–**IIIb**$_2$, and intermediate **IId**$_2$ for the sigmatropic and dissociation–recombination mechanisms of the 1,3-chlorine shift in the PNC and CNC triads of solvates $M \cdot 2CHCl_3$[a]

Atom, parameter	q_i	c_{ij}		q_i	c_{ij}		q_i	c_{ij}	
		HOMO	LUMO		HOMO	LUMO		HOMO	LUMO
		Ia$_2$			TS **Ib**$_2$			**Ic**$_2$	
P	1.92 (1.91)	0.02	–0.57	1.82 (1.84)	–0.01	–0.55	1.78 (1.82)	0.04	–0.54
N	–0.34 (–0.34)	0.04	–0.17	–0.41 (–0.43)	0.03	–0.18	–0.52 (–0.53)	0.16	–0.22
C	0.06 (0.06)	0.01	–0.10	0.21 (0.18)	–0.02	–0.06	0.05 (0.07)	0.03	–0.09
Cl	–0.51 (–0.46)	–0.08	–0.32	–0.63 (–0.50)	–0.44	0.00	–0.04 (–0.04)	0.15	–0.02
ε_i		–10.52	–3.28		–10.39	–3.54		–10.54	–3.10
		(–10.62)	(–2.98)		(–10.44)	(–3.22)		(–10.37)	(–2.97)
		IIa$_2$			TS **IIb**$_2$/IM **IId**$_2$[b]			**IIc**$_2$	
P	2.03 (2.01)	0.00	–0.57	**2.01 (2.02)**	**0.00**	**0.49**	1.90 (1.90)	–0.04	–0.54
				1.95 (1.95)	–0.00	–0.55			
N	–0.52 (–0.52)	–0.07	–0.23	**–0.68 (–0.68)**	**–0.06**	**–0.25**	–0.80 (–0.79)	0.10	–0.30
				–0.56 (–0.58)	–0.00	–0.26			
C	0.04 (0.04)	0.01	0.09	**0.24 (0.24)**	**0.01**	**0.35**	0.12 (0.11)	0.02	0.13
				0.06 (0.06)	0.00	0.11			
Cl	–0.54 (–0.52)	0.02	0.00	**–0.62 (–0.58)**	**–0.02**	**–0.25**	–0.07 (–0.06)	0.00	–0.01
				–0.68 (–0.80)	–0.45	–0.01			
ε_i		–9.66	–2.79		**–9.91**	**–2.72**		–9.88	–2.28
		(–9.46)	(–2.49)		**(–9.70)**	**(–2.50)**		(–9.76)	(–2.11)
					–8.15	–4.49			
					(–7.09)	(–4.22)			
		IIIa$_2$			TS **IIIb**$_2$			**IIIc**$_2$	
C^1	0.43 (0.42)	–0.00	0.31	0.51 (0.48)	0.07	0.07	0.28 (0.28)	0.05	0.04
N	–0.40 (–0.40)	–0.75	0.00	–0.40 (–0.38)	–0.42	0.14	–0.28 (–0.29)	0.44	0.08
C^2	0.46 (0.46)	–0.17	–0.00	0.53 (0.52)	–0.07	0.16	0.41 (0.42)	–0.12	0.00
Cl	–0.14 (–0.14)	–0.20	0.40	–0.46 (–0.41)	0.15	0.24	–0.11 (–0.12)	0.19	–0.16
ε_i		–12.16	–1.42		–11.91	–2.88		–12.24	–1.47
		(–12.00)	(–1.20)		(–11.59)	(–2.54)		(–12.07)	(–1.28)

[a] Values in parentheses relate to nonsolvated structures, whose c_{ij} values are not given because they are to those for solvated structures. [b] Boldface-typed values relate to transition state **IIb**$_2$.

state **Ib**$_2$. In acyclic PNC and CNC systems **II, III** only one of dative bond [P ← Cl^- (**IIb**$_2$) or C^1 ← Cl^- (**IIIb**)] is destabilized, whereas the other [C ← Cl^- (**IIb**$_2$) or C^2 ← Cl^- (**IIIb**$_2$)] is stabilized. In all the three systems, the X ← Cl^- and Z ← Cl^- dative bonds include, alone with a LEP of the chloride ion, a small but finite fraction of orbitals of the partner phosphorus and/or carbon atoms.

Specific solvation results in that the difference in the orbital contributions of the dative bonds increases by 1–7% for the C ← Cl^- (**Ib**$_2$), P ← Cl^- (**Ib**$_2$, **IIb**$_2$), and C^1 ← Cl^- (**IIIb**$_2$) bonds, remains almost the same for the C ← Cl^- bond (**IIb**$_2$), and decreases for the C^2 ← Cl^- bond (**IIIb**$_2$). At the same time, the LEP orbital interacting with chloroform molecules is always stabilized. Therewith, the negative charge on the chloride ion increases by –0.04 to –0.13 e (Table 3), which reduces the activation barrier for the P,C and C,C chlorotropic isomerizations of the systems in study (Table 2). This reduction is very small (it is rather a tendency), on the background of the more noticeable shift of the equilibrium in phosphorus systems **I, II**, unlike carbon system **III**, where, according to experimental data, the equilibrium is practically completely shifted to the carbamoyl form [12, 17]. The latter circumstance allowed isolation of a pure *N*-dichloromethylidenecarbamoyl chloride [13].

Table 4. Compositions and energies of localized orbitals of the transition states of the phosphorus (**Ib$_2$** and **IIb$_2$**) and carbon (**IIIb$_2$**) systems, including LEPs of the transite chloride ion[a]

Comp. no.	Number of centers	Composition of orbital, %			Energy of orbital, eV	Type of bond
		Cl	P (C^1)	C (C^2)		
Ib$_2$	1.00 (1.00)	100 (100)	–	–	–52.98 (–51.73)	LEP1
	1.36 (1.51)	85 (79)	–	13 (18)	–13.18 (–13.52)	$C \leftarrow Cl$
	1.06 (1.11)	97 (95)	2 (4)	–	–12.95 (–13.98)	$P \leftarrow Cl$
	1.01 (1.00)	99 (100)	–	–	–11.54 (–11.41)	LEP4
IIb$_2$	1.00 (1.00)	100 (100)	–	–	–40.44 (–50.59)	LEP1
	1.01 (1.01)	99 (100)	–	–	–15.56 (–11.53)	LEP2
	1.10 (1.14)	95 (94)	3 (5)	–	–14.88 (–15.78)	$P \leftarrow Cl$
	1.34 (1.36)	86 (85)	0 (1)	12 (12)	–13.21 (–12.75)	$C \leftarrow Cl$
IIIb$_2$	1.00 (1.00)	100 (100)	–	–	–24.27 (–24.15)	LEP1
	1.39 (1.34)	84 (86)	–	13 (12)	–15.31 (–14.61)	$C^2 \leftarrow C$
	1.27 (1.37)	88 (84)	10 (3)	–	–14.59 (–14.61)	$C^1 \leftarrow C$
	1.01 (1.00)	100 (100)	–	–	–13.43 (–13.25)	LEP4

[a] Values in parentheses relate to nonsolvated structures.

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