Russian Chemical Bulletin, International Edition, Vol. 50, No. 2, pp. 279—286, February, 2001

Intramolecular electrophilic rearrangements in saturated acyclic systems. Reactivity of the zwitterion derived from triisopropylphosphine and ethyl 2-cyanoacrylate with respect to different types of electrophiles

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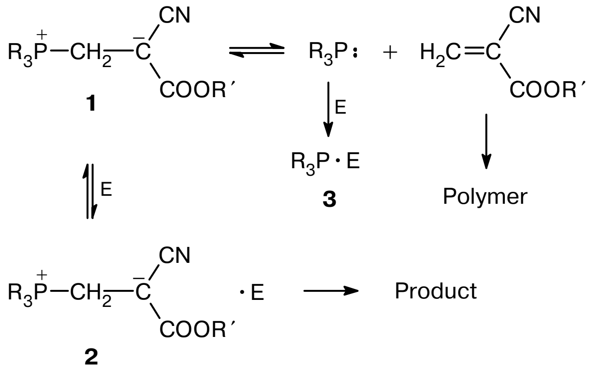
The reactions of the zwitterion derived from triisopropylphosphine and ethyl 2-cyanoacrylate with mercuric chloride and aryl isothiocyanates containing Cl atoms in the *ortho* positions of the benzene ring follow an unusual pathway because this zwitterion represents "latent" triisopropylphosphine due to the reversibility of the reaction of triisopropylphosphine with ethyl 2-cyanoacrylate. The molecular structures of the adducts of triisopropylphosphine with 2,6-dichloro- and 2,4,6-trichlorophenyl isothiocyanates were confirmed by X-ray diffraction study. Protonation of the adduct of triisopropylphosphine with 2,6-dichlorophenyl isothiocyanate occurred at the nitrogen atom, whereas methylation with methyl trifluoromethanesulfonate afforded an *S*-methylation product. The results of X-ray diffraction study of the resulting compounds are presented.

Key words: phosphorus-containing zwitterions, adduct of triisopropylphosphine with mercuric chloride, X-ray diffraction analysis, quantum-chemical calculations.

Phosphorus-containing zwitterions, which have been prepared recently by the reactions of trialkylphosphines with esters of 2-cyanoacrylic acid,[1,2] react with acids, alkyl halides,[3] alkyl isocyanates, and aryl isocyanates[2,4] as C-nucleophiles. However, these zwitterions in reactions with some electrophiles (**E**) react not only as carbanions, but also as the corresponding parent trialkylphosphines.[2] The present study was aimed at revealing the characteristic features of their behavior.

It is known that the formation of phosphorus-containing zwitterions of the type **1** from trialkylphosphines and highly electrophilic olefins is reversible[5] as a result of which the conversions discussed below afford either the reaction products *via* intermediate adducts of the type **2** or adducts of the type **3** (Scheme 1).

Scheme 1

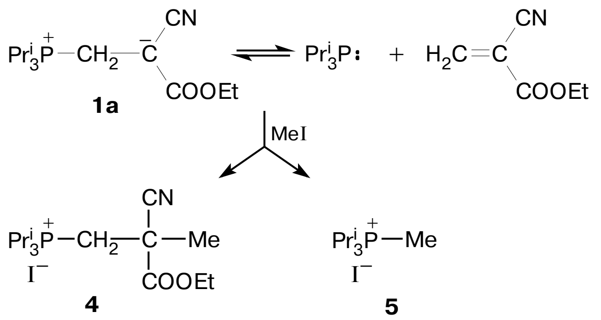


R = Pr, Pr^i, Bu; R′ = Me, Et; E is an electrophile

Actually, it appeared that one of the pathways of decomposition of zwitterion **1a** (R = Pr^i, R′ = Et) in solutions consists in its dissociation giving rise to triisopropylphosphine and ethyl 2-cyanoacrylate (Scheme 2). The latter undergoes polymerization, which is one of the driving forces for the shift of the equilibrium to the right. According to the ^{31}P NMR spectral data, a solution of zwitterion **1a** in THF immediately after preparation contained several percent of triisopropylphosphine. A solution in MeCN contained two phosphorus-containing compounds along with triisopropylphosphine. In pure CH_2Cl_2, no dissociation of zwitterion **1a** was observed, but it dissociated upon addition of organic bases. Storage of a solution of zwitterion **1a** in CH_2Cl_2 in a sealed tube for 10 months afforded a mixture of compounds rather than triisopropylphosphine. The mixture is characterized by the following chemical shifts (δ_P): 38.65 (30%, the starting zwitterion) and 44.43 (20%), 45.10 (~12%), 45.72 (~33%), and 57.79 (~5%) corresponding to compounds of unknown nature.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 269—275, February, 2001.

Scheme 2



δ_P 46.15 δ_P 46.68

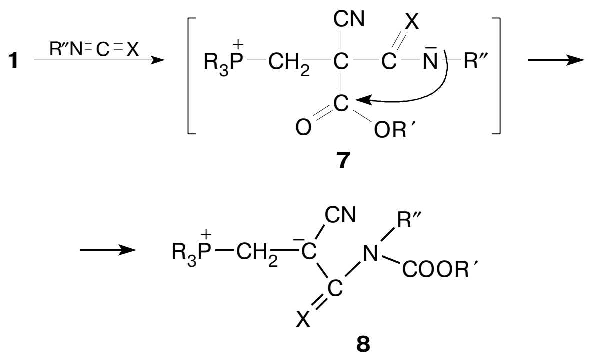
Taking into account the equilibrium (see Scheme 1), one would expect that the results of the reactions of zwitterion **1a** with electrophiles will be determined primarily by the affinity of the electrophile for the carbanionic center or trivalent phosphorus and by the stabilities of the resulting products. As to the stabilities of the latter, this implies both the possibility of their conversions into more stable new derivatives and their decomposition with regeneration of zwitterion **1** and electrophile **E** (see Scheme 1).

We examined MeI, $HgCl_2$, and a number of aryl isothiocyanates as electrophiles **E**. Alkyl halides are sufficiently reactive both with respect to zwitterion **1a** and tertiary phosphines.[3] Hence, we believed that both a *C*-methylation product of zwitterion **1a** and a methylation product of triisopropylphosphine can be prepared under appropriate reaction conditions. Actually, the reaction of zwitterion **1a** with MeI (100-fold excess) afforded (according to the ^{31}P NMR spectral data) two phosphonium salts in a ratio of 1 : 2.16 (*cf.* Ref. 3), *viz.*, derivative **4**[2] and triisopropyl(methyl)phosphonium iodide **5** as the major and minor products, respectively (see Scheme 2). The latter was isolated and identified by ^1H and ^{31}P NMR spectroscopy.

The published data give no grounds to assume that carbanions form stable adducts with $HgCl_2$. Hence, taking into account the available data on the stabilities of complexes of mercuric chloride with phosphines, it can be suggested that the equilibrium (see Scheme 1) is shifted towards triisopropylphosphine, which then reacts with $HgCl_2$. Actually, mixing of solutions of zwitterion **1a** and $HgCl_2$ in MeCN led to rapid precipitation of the crystalline adduct $Pr^i{}_3P \cdot HgCl_2$ (**6**), whereas the formation of the adduct with zwitterion **1a** was not observed.

The results of the reactions of zwitterion **1** with aryl isothiocyanates are less predictable. On the one hand, the reactions of zwitterions of the type **1** with alkyl(aryl) isocyanates and phenyl isothiocyanate gave rise to isomerization products **8** from the initially formed adducts **7** as a result of the nucleophilic attack of the *N*-anionic center on the carbon atom of the ethoxycarbonyl group[4] (Scheme 3).

Scheme 3



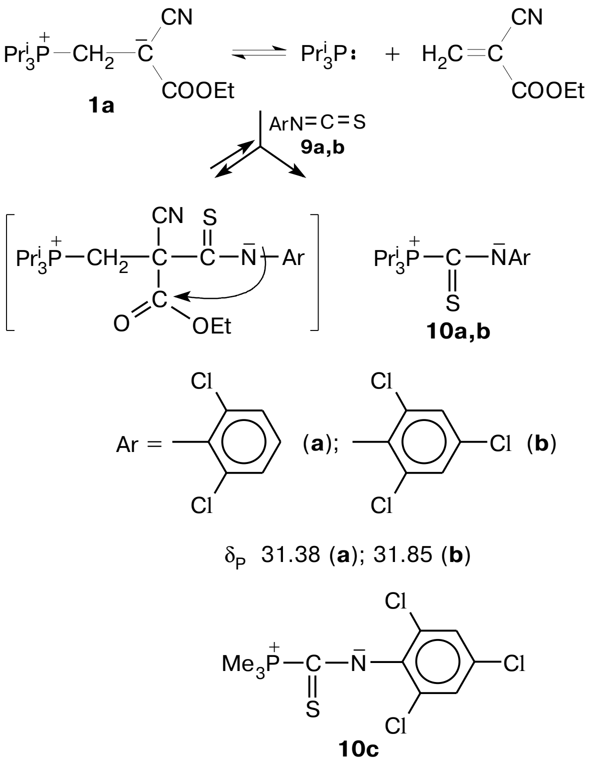
X = O, S

On the other hand, zwitterion **1a** reacted with tosyl isocyanate to form the adduct of the latter with triisopropylphosphine[2] rather than a product structurally similar to compound **8**. The explanation of this fact should be seeked for in the influence of the electronic and steric factors on the rates of the first and second reaction stages (see Scheme 3). The second stage should be particularly sensitive to the electronic and steric effects of the substituents in the nucleus of ArNCX. In the cited study,[2] the introduction of the highly electronegative *p*-$MeC_6H_4SO_2$ substituent relative to the NCO group led to substantial acceleration of the first reaction stage (according to the ^{31}P NMR spectral data, the formation of the adduct of zwitterion **1a** with tosyl isocyanate occurred within a few seconds after mixing of the reactants), thus hindering the second stage due apparently to a decrease in the nucleophilicity of the N atom in an intermediate of the type **7**.

In the present study, we found that the steric effects can also hinder the second stage of conversions according to Scheme 3. Thus the reaction of zwitterion **1a** with mesityl isocyanate led only to polymerization of the isocyanate, while zwitterion **1a** remained unchanged. Since it is evident that the scheme of anionic trimerization of the isocyanate involves the primary attack of the carbanion at the carbon atom of the isocyanate group, it should be concluded that the second stage of conversions according to Scheme 3 is hindered owing to which the chain propagation occurs according to the known scheme of trimerization of isocyanates.

On the other hand, 2,6-dichlorophenyl isothiocyanate and 2,4,6-trichlorophenyl isothiocyanate (**9a,b**) reacted with a solution of zwitterion **1a** in CH_2Cl_2 at ~20 °C over 25 days (or on heating in a toluene solution at 90 °C for 5 h) to form their adducts with triisopropylphosphine **10** in high yields. The reactions were not accompanied by polymerization of isothiocyanates. Based on the fact that heating of phenyl isothiocyanate with zwitterion **1a** afforded a rearrangement product of the type **8**,[4] it can be suggested that the *ortho*-Cl atoms hinder the nucleophilic attack of the N atom in adduct **7** both for electronic and steric reasons. The existence of the equilibrium (see Scheme 1) makes possible the formation of adducts **10** because (*cf.* Ref. 8) trialkylphosphines form rather stable adducts with isothiocyanates (Scheme 4).

Scheme 4



The structures of adducts **10a** and **10b** were confirmed by the data from elemental analysis and NMR spectroscopy. With the aim of obtaining data on the molecular structures of the zwitterions under consideration and, primarily, on the character of the charge distribution, we studied these compounds by X-ray diffraction analysis and performed quantum-chemical calculations of a model molecule **10c** (Table 1).

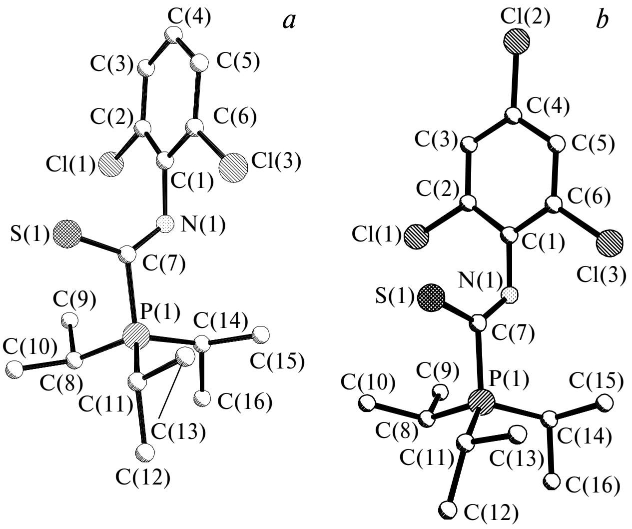


Fig. 1. Overall views and the atomic numbering schemes of zwitterionic molecules **10a** (*a*) and **10b** (*b*) based on X-ray diffraction data.

According to the X-ray diffraction data, the C(1)N(1)C(7)S(1)P(1) fragments in molecules **10a** and **10b** are planar and are arranged almost perpendicularly (to within 10°) relative to the plane of the phenyl ring (see Table 1, Fig. 1, *a* and *b*). The P atom is characterized by a slightly distorted tetrahedral coordination, the C(8)—P(1)—C(14) bond angle being increased to 114—115°. Apparently, this increase is determined by steric repulsions between the Cl(1) atom and the C(9) and C(15) methyl groups. The character of the distribution of the bond lengths indicates that the negative charges in these zwitterionic compounds are delocalized over the S and N atoms. Actually, the S(1)—C(7) and N(1)—C(7) bond lengths in molecules **10a** and **10b** (see Table 1) have values intermediate between those typical of single and double bonds (1.751 and 1.671 Å for S and 1.279 and 1.334 Å for N, respectively[10]).

With the aim of making a quantitative estimate of the charge distribution, we carried out quantum-chemical calculations for the model compound **10c**, which differs from molecule **10b** in that it contains the methyl groups instead of the isopropyl fragments. Optimization of the molecule (C_s symmetry) was carried out using the Gaussian 94W program package[11] within the framework of the density functional theory using the B3LYP functional[12] and the 6-31G* basis set.[13] The charges on the atoms were evaluated with the use of three different approaches, *viz.*, the charges were fitted to the electro-

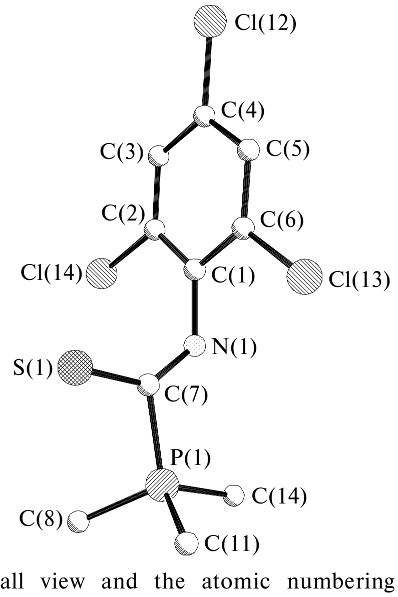


Fig. 2. Overall view and the atomic numbering scheme of zwitterionic molecule **10c** according to the data from B3LYP/6-31G* quantum-chemical calculations.

Table 1. Principal bond lengths (*d*), bond angles (φ), and torsion angles (τ) in compounds **10a**, **10b**, **11**, and **12** according to the data from X-ray diffraction studies and B3LYP/6-31G* quantum-chemical calculations for the model compound **10c**

Parameter	**10a***	**10b**	**11**	**12**	**10c**
Bond			*d*/Å		
P(1)—C(7)	1.840(3) (1.837(3))	1.841(2)	1.848(4)	1.849(1)	1.848
P(1)—C(8)	1.834(4) (1.825(4))	1.833(3)	1.827(4)	1.823(1)	1.822
P(1)—C(11)	1.828(4) (1.830(4))	1.821(3)	1.823(4)	1.823(1)	1.822
P(1)—C(14)	1.836(4) (1.830(3))	1.827(2)	1.810(4)	1.821(1)	1.825
S(1)—C(7)	1.693(3) (1.696(3))	1.696(2)	1.667(4)	1.756(1)	1.695
N(1)—C(1)	1.416(4) (1.403(4))	1.412(3)	1.438(5)	1.408(2)	1.398
N(1)—C(7)	1.293(4) (1.294(4))	1.293(3)	1.337(4)	1.268(2)	1.301
S(1)—C(17)				1.807(2)	
Bond angle			φ/deg		
C(11)—P(1)—C(14)	114.9(2) (114.5(2))	115.3(1)	114.8(2)	116.27(6)	108.4
C(11)—P(1)—C(8)	108.9(2) (108.4(2))	108.9(1)	109.9(2)	108.95(7)	108.2
C(14)—P(1)—C(8)	107.1(2) (107.7(2))	106.6(1)	108.6(2)	108.93(6)	108.5
C(11)—P(1)—C(7)	108.9(2) (109.4(2))	106.7(1)	107.3(2)	108.48(6)	109.6
C(14)—P(1)—C(7)	109.1(2) (107.9(2))	110.3(1)	110.2(2)	105.75(6)	112.2
C(8)—P(1)—C(7)	107.9(2) (108.6(2))	109.0(1)	105.6(2)	108.18(6)	109.6
C(7)—N(1)—C(1)	118.9(2) (117.9(2))	116.3(2)	121.4(3)	125.5(1)	120.3
C(6)—C(1)—C(2)	116.2(3) (115.7(3))	116.5(2)	117.4(3)	117.1(1)	116.0
C(6)—C(1)—N(1)	122.2(3) (120.8(3))	121.0(2)	121.7(3)	122.7(1)	121.8
C(2)—C(1)—N(1)	121.1(3) (123.3(3))	122.5(2)	120.8(3)	119.6(1)	121.8
N(1)—C(7)—S(1)	132.2(2) (130.7(2))	130.1(2)	125.1(3)	133.4(1)	136.5
N(1)—C(7)—P(1)	112.1(2) (113.5(2))	112.0(2)	116.5(3)	113.51(9)	109.8
S(1)—C(7)—P(1)	115.7(2) (115.8(2))	117.83(12)	118.2(2)	113.04(7)	113.7
Torsion angle			τ/deg		
C(7)—N(1)—C(1)—C(2)	−106.3(4) (−82.4(4))	−85.8(2)	−103.6(4)	−118.3(2)	93.9
C(8)—P(1)—C(7)—S(1)	68.9(3) (77.5(2))	88.5(2)	86.4(2)	79.01(8)	59.3

* The parameters of the second independent molecule in the crystal of **10a** are given in parentheses.

static potential distribution within the framework of the Merz—Singh—Kollman scheme,[14,15] the natural bond orbitals (NBO) were analyzed,[16] and the Mulliken analysis was performed.

As can be seen from Table 1, the geometric parameters of molecule **10c** (the data of B3LYP/6-31G* calculations; Fig. 2) are similar to those of compounds **10a,b** determined experimentally. Analysis of the charge distribution demonstrated that the positive charge in molecule **10c** is localized predominantly on the P atom regardless of the procedure used for calculations. However, the magnitudes of the charge are substantially

Table 2. Charges on the atoms in the model compound **10c** according to the data from B3LYP/6-31G* quantum-chemical calculations

Atom	ESP MK[a]	NBO analysis[b]	Mulliken
P(1)	0.79	1.63	0.74
S(1)	−0.57	−0.54	−0.50
N(1)	−0.39	−0.26	−0.30
C(7)	0.03	0.06	−0.02

[a] The charges were calculated by fitting them to the electrostatic potential distribution using the Merz—Singh—Kollman scheme.[14,15]

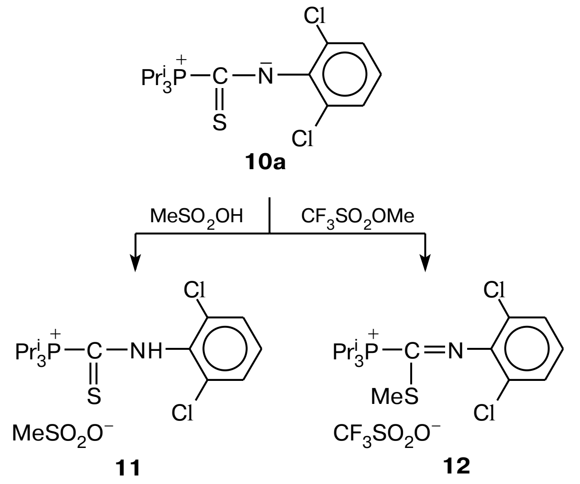
[b] The charges were calculated based on the NBO analysis.[16]

different (Table 2). As would be expected based on the results of analysis of the geometry, the negative charge is delocalized over the S(1)C(7)N(1) fragment. The charge distribution in S(1)C(7)N(1) (see Table 2) is nonuniform, the electrons being predominantly localized on the S atom, whereas the charge on the C(7) atom being virtually equal to zero.

Based on the analysis of the geometry and the charge distribution, it was suggested that the reactions of zwitterions of the type **10** with electrophiles can proceed to form both N- and S-derivatives depending on the nature of the reagents.

The reactions of zwitterion **10a** with methanesulfonic acid and methyl trifluoromethanesulfonate confirmed the above assumption. Thus only the N atom was protonated by the acid giving rise to amide **11**, whereas methyl triflate reacted with the zwitterion at the S atom to form imide **12** (Scheme 5).

Scheme 5



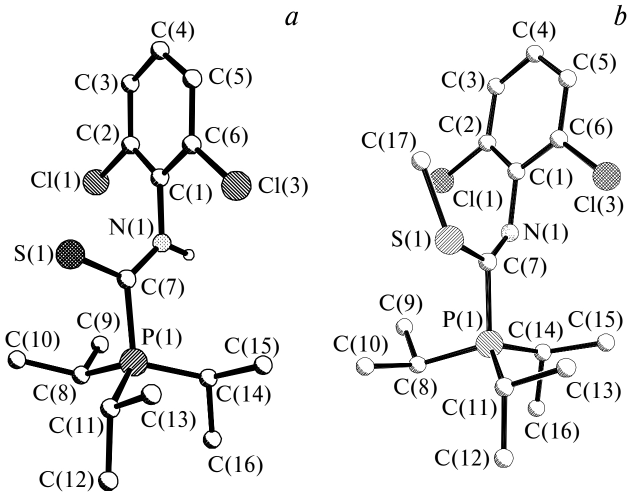


Fig. 3. Overall views and the atomic numbering schemes of the cations in the structures of **11** (*a*) and **12** (*b*) based on X-ray diffraction data. The counterions are omitted.

The structures of protonation and methylation products of zwitterion **10a** were established by NMR spectroscopy and X-ray diffraction analysis. X-ray diffraction study of compounds **11** and **12** demonstrated that the mutual arrangement of the PPr^i_3, N(1)C(7)S(1), and phenyl fragments and the distortion of the tetrahedral coordination (an increase in the C(8)—P(1)—C(14) angle) are retained (see Table 1, Fig. 3, *a* and *b*). It should be noted that the P(1)—C(7) bond lengths in compounds **11** and **12** are somewhat larger (1.849 Å) compared to the average value (1.840 Å) in molecules **10a** and **10b**. Analysis of the bond lengths in the N(1)—C(7)—S(1) fragments demonstrated that the average lengths of the single and double N(1)—C(7) and S(1)—C(7) bonds in electrophilic addition products **11** and **12** (1.30 and 1.71 Å, respectively) are virtually identical to the corresponding bond lengths in compounds **10a** and **10b** (1.293 and 1.696 Å, respectively). Based on this fact, it is reasonable to suggest that the N(1)—C(7) and S(1)—C(7) bonds in the latter compounds have approximately the one-and-a-half order.

To obtain the data on the multiplicities of the bonds in zwitterionic compounds **10a** and **10b**, we analyzed the electron density distributions ($\rho(r)$) according to Bader's topological theory[17] based on calculations for the model compound **10c** using the B3LYP/6-31G* method.

Within the framework of this theory, the character of chemical bonds can be described based on analysis of the positions and types of critical points in which the gradient of the electron density becomes equal to zero. The critical point (3, −1) is most important from the chemical standpoint. The presence of this point is indicative of the existence of a chemical bond. Analysis of $\rho(r)$ and its Laplacian ($\nabla^2\rho(r)$) at the critical point (3,−1) allows one to examine the character of the bond, whereas the ratio between the curvature components (ellipticity (ε)) lying in the plane perpendicular to the bond at the critical point (3, −1) is indicative of the deviation of $\rho(r)$ from the cylindrical symmetry and, consequently, of the multiplicity of the chemical bond.

Analysis of the $\rho(r)$, $\nabla^2\rho(r)$, and ε values at the critical point (3, −1) demonstrated that all bonds in the

Table 3. Principal topological characteristics at the critical point (3, −1) for a number of bonds in molecule **10c** according to the data from B3LYP/6-31G* quantum-chemical calculations

Bond	$\rho(r)$	$\nabla^2\rho(r)$	ε*
	a.u.		
C(7)—S(1)	0.21	−0.21	0.06
N(1)—C(7)	0.36	−0.91	0.22
N(1)—C(1)	0.31	−0.99	0.03
P(1)—C(7)	0.17	−0.43	0.08

* ε — Ellipticity.

model molecule **10c** are characterized by negative $\nabla^2\rho$ values in spite of the substantial positive charge on the P atom, which is typical of covalent interactions (Table 3). Comparison of the ellipticities in the N(1)C(7)S(1)P(1) fragment demonstrated that these values for the N(1)—C(1), S(1)—C(7), and P(1)—C(7) bonds are small, whereas its value for the N(1)—C(7) bond (0.22) is comparable with the corresponding value for the phenyl ring (0.25).

Therefore, in spite of the conclusion about the one-and-a-half order of the N(1)—C(7) and S(1)—C(7) bonds, which was made based on comparison of the geometric parameters of compounds **10a** and **10b** and of compounds **11** and **12**, the topological analysis demonstrated that the double bond in the zwitterionic compounds is essentially localized and, consequently, as has been noted previously,[18] the bond lengths in organometallic compounds are invariant with respect to fine electronic effects and not always can be used for the analysis of delocalization.

Analysis of the crystal packings demonstrated that the molecules are linked in dimers in all crystals under study through strong secondary intermolecular Cl...Cl interactions (Cl...Cl, 3.420(2)—3.514(2) Å; C—Cl...Cl, 156.41(5)—171.18(8)°). In the crystal of **11**, there is also a strong intermolecular N(1)—H(1N)...O(1) hydrogen bond between the basic molecule and the counterion.

Therefore, the importance of zwitterion **1a** and structurally similar adducts[1] is determined both by their reactivities and the reactivities of phosphines formed upon decomposition of the former. In the latter case, zwitterion **1a** serves as a source of triisopropylphosphine, which is of particular practical interest because it is much easier to handle with stable crystalline zwitterion **1a** than with triisopropylphosphine or other tertiary phosphines.

Experimental

The NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.26 MHz for ^{1}H and 162.02 MHz for ^{31}P) relative to Me_4Si and 80% H_3PO_4 for ^{1}H and ^{31}P, respectively. The reactions were performed under an atmosphere of dry nitrogen. The solvents were thoroughly purified and dried before use. The data from elemental analysis are given in Table 4.

Table 4. Data from elemental analysis

Compound	Found/Calculated (%)					Molecular formula
	C	H	N	S	Hg	
6	24.93 25.03	5.01 4.87	—	—	46.32 46.47	$C_9H_{21}Cl_2HgP$
10a	53.02 52.75	6.87 6.64	3.89 3.85	8.79 8.80	—	$C_{16}H_{24}Cl_2NPS$
10b	48.19 48.19	6.10 5.81	3.49 3.51	8.23 8.04	—	$C_{16}H_{23}Cl_3NPS$
11	42.71 44.35	6.15 6.13	2.65 3.04	13.80 13.93	—	$C_{17}H_{28}Cl_2NO_3PS_2$
12	40.99 40.91	5.18 5.15	2.56 2.65	11.90 12.13	—	$C_{18}H_{27}Cl_2F_3NO_3PS_2$

Zwitterion 1a was prepared according to a procedure reported previously.[2]

The reaction of zwitterion 1a with MeI. Zwitterion **1a** (1 g, 3.51 mmol) was mixed with MeI (30 mL). After 3 h, the precipitate that formed was filtered off, washed with ether, and crystallized from a 1 : 5 CH_2Cl_2 : THF mixture. Less soluble salt **5** was obtained in a yield of 120 mg, m.p. >260 °C. ^{31}P NMR ($CDCl_3$), δ: 46.68 (*cf.* lit. data[6] for salt **5**: m.p. >360 °C, δ_P 46.3). ^{1}H NMR ($CDCl_3$), δ: 1.48 (dd, 18 H, $C\underline{H}_3CH$, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 9.2 Hz); 2.00 (d, 3 H, CH_3P, J_{HP} = 12.4 Hz); 2.97 (m, 3 H, $C\underline{H}CH_3$). The filtrate was concentrated. The residue was recrystallized from acetone. Salt **4** was obtained in a yield of 0.54 g, m.p. 138—140 °C. ^{31}P NMR ($CDCl_3$), δ: 46.15 (*cf.* lit. data[2] for compound **4**: m.p. 139—140 °C).

The adduct of triisopropylphosphine with mercuric chloride (6). A solution of $HgCl_2$ (480 mg, 1.75 mmol) in MeCN (3 mL) was added to a solution of zwitterion **1a** (500 mg, 1.75 mmol) in MeCN (3 mL). After 15 min, the precipitate that formed was filtered off and crystallized from CH_2Cl_2. The yield was 600 mg (80%), m.p. 232—235 °C. ^{31}P NMR (acetone-d), δ: 78.49 ($^1J_{PHg}$ = 1720 Hz). ^{1}H NMR (acetone-d), δ: 1.47 (dd, 18 H, $C\underline{H}_3CH$, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 9.2 Hz); 3.11 (m, 3 H, $C\underline{H}CH_3$).

Zwitterions 10a,b. ***A.*** A twofold excess of isothiocyanate **9a** or **9b** was added to a solution of zwitterion **1a** in CH_2Cl_2. After 25 days, ether was added and the precipitate that formed was filtered off and crystallized from acetone.

***N*-(2,6-Dichlorophenyl)triisopropylphosphoniothiocarbonylamide (10a).** The yield was 90%, m.p. 127—142 °C (with decomp.). ^{31}P NMR ($CDCl_3$), δ: 31.39. ^{1}H NMR ($CDCl_3$), δ: 1.57 (dd, 18 H, $C\underline{H}_3CH$, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.2 Hz); 3.11 (m, 3 H, $C\underline{H}CH_3$); 6.89 (t, 1 H, Ph, $^3J_{HH}$ = 8.0 Hz); 7.27 (d, 2 H, Ph, $^3J_{HH}$ = 8.0 Hz).

***N*-(2,4,6-Trichlorophenyl)triisopropylphosphoniothiocarbonylamide (10b).** The yield was 89%, m.p. 120—136 °C (with decomp.). ^{31}P NMR ($CDCl_3$), δ: 31.85. ^{1}H NMR ($CDCl_3$), δ: 1.55 (dd, 18 H, $C\underline{H}_3CH$, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.2 Hz); 3.09 (m, 3 H, $C\underline{H}CH_3$); 7.27 (s, 2 H, Ph).

B. A solution of zwitterion **1a** (0.3 g, 1.0 mmol) and 2,6-dichlorophenyl isothiocyanate (0.36 g, 1.75 mmol) in toluene (1 mL) was heated at 80—90 °C for 5 h. The reaction mixture was cooled and the precipitate that formed was filtered off, washed with a 1 : 1 ether—acetone mixture, and crystallized from acetone. The yield was 0.34 g (85%), m.p. 127—142 °C (with decomp). The NMR spectral data are analogous to those reported above.

Table 5. Principal crystal-structural data and details of the refinement of compounds **10a**, **10b**, **11**, and **12**

Parameter	**10a**	**10b**	**11**	**12**
T/K	293		110	
Crystal habitus	Prism			
Crystal dimensions/mm	0.20×0.20×0.40	0.20×0.20×0.40	0.05×0.05×0.15	0.20×0.30×0.40
Composition	$C_{16}H_{24}Cl_2NPS$	$C_{16}H_{23}Cl_3NPS$	$C_{16}H_{25}Cl_2NPS \cdot SO_3CH_3$	$C_{17}H_{27}Cl_2NPS \cdot SO_3CF_3$
Diffractometer	«Siemens P3»		«Bruker SMART-1000»	
Radiation	Mo-Kα (λ = 0.71072 Å)			
a/Å	11.908(5)	11.398(4)	8.340(1)	7.7746(6)
b/Å	13.762(5)	12.271(5)	8.156(1)	20.1849(15)
c/Å	22.963(10)	14.248(5)	31.450(5)	15.3711(11)
β/deg	96.50(4)	103.85(3)	90.08(3)	96.708(2)
V/Å^3	3739.0(26)	1934.8(12)	2139.2(3)	2395.7(3)
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	
Z	8	4	4	4
d_{calc}/г · см$^{-3}$	1.294	1.369	1.430	1.465
μ/мм$^{-1}$	0.538	0.660	0.591	0.555
Scanning mode	θ/2θ	θ/2θ	ω with a step of 0.3°, frames were exposed for 10 s each	ω with a step of 0.3°, frames were exposed for 20 s each
2θ$_{max}$/deg	26.06	27.05	27.46	30.04
Number of independent reflections	7252	4093	4874	6846
Number of reflections with $I > 2s(I)$	6057	3585	2520	5750
$R_1(F)$	0.0635	0.0462	0.0498	0.0326
w$R_2(F^2)$	0.1657	0.1305	0.0832	0.0844
GOF	1.130	1.083	0.997	1.089

[*N*-(2,6-Dichlorophenyl)thiocarbamoyl]triisopropylphosphonium methosulfate (11). Methanesulfonic acid (24 mg, 0.25 mmol) was added to a solution of zwitterion **10a** (80 mg, 0.22 mmol) in $CDCl_3$ (1 mL) and the NMR spectrum was recorded. Then the reaction mixture was poured into ether (10 mL). The precipitate that formed was crystallized from THF. The yield of salt **11** was 90 mg (88%), m.p. 110—112 °C. ^{31}P NMR ($CDCl_3$), δ: 45.93. ^1H NMR ($CDCl_3$), δ: 1.58 (dd, 18 H, $C\underline{H}_3CH$, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.2 Hz); 2.63 (s, 3 H, CH_3SO_2); 3.65 (m, 3 H, $C\underline{H}CH_3$); 7.08—7.42 (m, 3 H, Ph); 13.05 (br.s, 1 H, NH). The NMR spectra of the reaction mixture are identical to those of crystalline salt **11**.

[*N*-(2,6-Dichlorophenyl(methylthio)imidocarbamoyl]triisopropylphosphonium trifluoromethanesulfonate (12). Methyl triflate (34 mg, 0.21 mmol) was added to a solution of zwitterion **10a** (70.5 mg, 0.19 mmol) in $CDCl_3$ (1 mL). After 1 h, the reaction mixture was poured into hexane (20 mL). The precipitate that formed was crystallized from acetone. The yield of salt **12** was 90 mg (88%), m.p. 161—162 °C. ^{31}P NMR ($CDCl_3$), δ: 53.19. ^1H NMR ($CDCl_3$), δ: 1.50 (dd, 18 H, $C\underline{H}_3CH$, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.2 Hz); 2.07 (s, 3 H, CH_3S); 3.17 (m, 3 H, $C\underline{H}CH_3$); 7.03—7.32 (m, 3 H, Ph). The ^1H and ^{31}P NMR spectra of the reaction mixture are identical to those of the crystalline *S*-methylation product.

Reaction of zwitterion 1a with mesityl isocyanate. A solution of zwitterion **1a** (0.34 g, 1.2 mmol) and mesityl isocyanate (0.29 g, 1.8 mmol) in CH_2Cl_2 (1 mL) was kept at ~20 °C for 14 days. The precipitate that formed was filtered off (170 mg). According to the ^{31}P NMR spectral data, the filtrate contained triisopropylphosphine oxide (δ_P 58.35) along with the initial zwitterion **1a** (δ_P 39.24).

X-ray diffraction study. The X-ray diffraction data sets for compounds **10a** and **10b** were collected on a four-circle Siemens P3 diffractometer at ~20 °C. The X-ray data sets for compounds **11** and **12** were collected on a Bruker Smart 1000 diffractometer equipped with a CCD detector at 110 K. The principal crystal-structural data and details of the refinement of compounds **10a**, **10b**, **11**, and **12** are given in Table 5.

All structures were solved by the direct method and refined by the full-matrix least-squares method based on F^2 with anisotropic thermal parameters for nonhydrogen atoms using the SHELXTL PLUS 5.0 program package. The positions of the hydrogen atoms of the CH_3 groups in the structures of **10a** and **10b** were calculated geometrically and included in the refinement using the riding model with fixed isotropic displacement parameters $1.5U_{eq}$, where U_{eq} is the equivalent isotropic displacement parameters of the corresponding C atoms. The remaining H atoms were located from difference Fourier syntheses and refined isotropically. The final R factors are given in Table 5.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 98-03-33-117a, 00-03-32807a, and 00-15-97359) and by DFG (Aktenreichen 436 RUS 17/44/99).

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Received April 12, 2000;
in revised form October 6, 2000