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Interaction of phosphorus trichloride with triethylamine

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Heating of trichlorophosphine with triethylamine in acetonitrile (4 h at 80 °C) affords 2,2-bis(dichlorophosphino)-*N*,*N*-diethylethenamine in 38% yield and oligomeric product containing 60.5% of phosphorus.

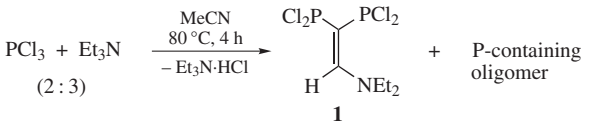
Coupling of phosphorus trichloride with organic amines and imines leads to various compounds containing phosphorus–nitrogen bond.[1] Phosphorus trichloride easily reacts with primary amines to form cyclodiphosphazanes $[ClP(\mu\text{-}NR)]_2$ as main products.[2,3] Reactions with secondary amines give alkylaminophosphines and alkylaminochlorophosphines depending on the reaction stoichiometry.[1] Reactions between phosphorus trichloride and organic imines (containing no NH groups) result in migration of double bond to form enamines and, further, 1,2-azaphospholenes and 1,2-azaphosphorines as their cyclization products.[4] The data describing stable adducts between PCl_3 and tertiary amines were documented previously.[5] The unstable complex of phosphorus trichloride with triethylamine has been detected at –78 °C in the form of a white powder which rapidly decomposed at room temperature.

In contrast to PCl_3, PBr_3 gives more stable donor–acceptor adducts with tertiary amines, which were isolated and characterized by X-ray analysis.[6]

System PCl_3–Et_3N–MeCN is used in the synthesis of heterocycles, where Et_3N serves as HCl scavenger whereas MeCN is a polar aprotic solvent.[7] However, there are no data in the literature on other reactions of this system, which may be due to higher reactivity of phosphorylation substrates and some difficulties in separation and identification of the products simultaneously containing PCl_2 and dialkylamino groups.

In the present work, we report interaction of PCl_3 with triethylamine in MeCN as a solvent under controlled conditions without traces of oxygen and moisture. Heating of these reactants in evacuated ampoule gives 2,2-bis(dichlorophosphino)-*N*,*N*-diethylethenamine **1** and phosphorus-containing (tentatively oligomeric) product (Scheme 1).†

Replacement of the solvent (MeCN) by hexane allows one to extract compound **1** from solid residue, which, on concentrating, precipitated as large pale-yellow crystals. The yield of **1** was 38% (calculated per 2 mol PCl_3). It is of note that compound **1** is



1

Scheme 1

impossible to recrystallize and store for a long time (1 week) at room temperature since it undergoes the further transformation. Control experiment showed that **1** also reacts with triethylamine in acetonitrile in the absence of PCl_3 to yield $Et_3N{\cdot}HCl$ and intractable brown oil. To the best of our knowledge, compound **1** was not isolated and characterized till now because of limited time and temperature ranges of its formation.

IR spectrum of **1** in Nujol contains strong absorption bands at 1601 (C=C), 1322 (C–N) and 490 cm^{-1} (P–Cl). The ^1H NMR spectrum in C_6D_6 displays two groups of ethyl protons: δ 0.47 (t, Me) and 2.1–2.6 (m, CH_2). The multiple resonances corresponding to the CH_2 group arise due to imposed spin–spin interactions of methylene protons with ^{31}P nuclei and methyl protons. The hydrogen atom at the double bond, $HC{=}C(PCl_2)_2$, is in low field at 7.51 ppm and gives triplet-like signal with $^3J_{P,H}$ 14 Hz. The ^{31}P NMR spectrum shows a very broad single resonance at 174.4 ppm in the field typical of (organyl)dichlorophosphines. The reason of broad resonance may be existence of rotation barrier around P–C bonds and possible reducing rotation barrier around carbon–carbon bond because of tautomeric effect (see below). The systems with two non-equivalent phosphorus atoms and low rotation barrier usually demonstrate a doublet of doublets at low temperature.[8]

Crystals of **1** suitable for X-ray analysis were obtained from hexane solution by slow cooling (Figure 1).‡

The C(1)–C(2) bond length of 1.389 Å is typical of conjugated systems. The distance between the nitrogen atom N(1) and sp^2

† Phosphorus trichloride (1.79 g, 13.0 mmol) was added to a solution of 2.23 g (22.0 mmol) of triethylamine in 10 ml of acetonitrile *in vacuo*. The mixture was heated at 80–85 °C for 4 h. During the reaction the precipitate including large crystals of triethylammonium hydrochloride and a fine suspension of bright yellow solid was formed. The solvent and remaining PCl_3 were removed *in vacuo*, a residue was extracted 3 times by hexane. Crystallization from hexane gave 0.74 g (2.47 mmol) of pale-yellow crystals of **1** (yield 38%). IR (Nujol, ν/cm^{-1}): 1601 (vs), 1355 (s), 1323 (s), 1287 (sm), 1256 (m), 1189 (m), 1159 (w), 1123 (w), 1094 (m), 1065 (m), 992 (m), 963 (m), 945 (m), 907 (m), 884 (m), 850 (sh), 808 (w), 789 (w), 757 (s), 688 (s), 550 (s), 490 (br. vs). ^1H NMR (400 MHz, C_6D_6) δ: 0.47 (t, 6H, *Me*CH_2N, $^3J_{H,H}$ 7 Hz), 2.1–2.6 (m, 4H, MeCH_2N), 7.51 (t, 1H, C=CH, $^3J_{H,P}$ 14 Hz). ^{13}C NMR (100 MHz, C_6D_6) δ: 13.0 (s, Me), 49.0 (br. s), 127.8 (t, CP_2, $^1J_{C,P}$ 23 Hz), 157.2 (d, *C*=CP_2, $^2J_{C,P}$ 17 Hz). $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6) δ: 174.4 (br. s).

Fine bright yellow suspension after stirrings in hexane was separated from large crystals of triethylammonium hydrochloride by decantation. Hexane was removed *in vacuo*. Solid residue was a light yellow powder, nonsoluble in common organic solvents, insensitive to oxygen and moisture. No changes in IR spectrum were found after washing the product with water. IR (Nujol, ν/cm^{-1}): 1570 (s), 1341 (m), 1160 (br. m), 1040 (br. m). Found (%): C, 20.8; H, 4.82; P, 60.47; Cl, 2.07.

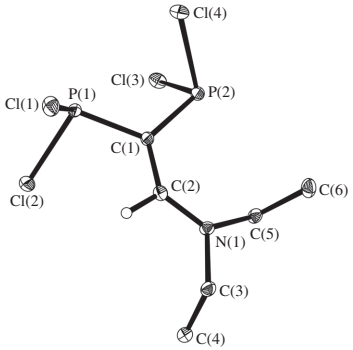
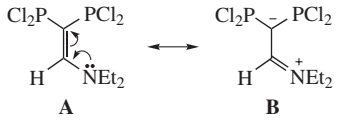


Figure 1 Molecular structure of **1**. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms of ethyl groups are omitted for clarity. Selected bond distances (Å) and angles (°): Cl(1)–P(1) 2.088(12), Cl(2)–P(1) 2.083(12), Cl(3)–P(2) 2.083(12), Cl(4)–P(2) 2.090(12), P(1)–C(1) 1.783(3), P(2)–C(1) 1.779(3), N(1)–C(2) 1.322(4), C(1)–C(2) 1.389(4); C(1)–P(1)–Cl(2) 101.79(11), C(1)–P(1)–Cl(1) 102.38(11), Cl(2)–P(1)–Cl(1) 96.39(5), C(1)–P(2)–Cl(3) 101.60(11), C(1)–P(2)–Cl(4) 100.24(11), Cl(3)–P(2)–Cl(4) 97.28(5), C(2)–N(1)–C(5) 124.3(3), C(2)–N(1)–C(3) 119.4(3), C(5)–N(1)–C(3) 116.1(2), C(2)–C(1)–P(2) 125.0(2), C(2)–C(1)–P(1) 119.7(2), P(2)–C(1)–P(1) 115.20(17), N(1)–C(2)–C(1) 133.2(3).

carbon N(1)–C(2) 1.322(4) Å is notably shorter than those between N(1) and sp^3 carbons: N(1)–C(3) 1.480(4) Å and N(1)–C(5) 1.467(4) Å. The N(1) atom has trigonal-planar geometry with the sum of the angles 359.8°. The torsion angles C(5)N(1)C(2)C(1) and N(1)C(2)C(1)P(2) are 5.0 and 14.7°, respectively. Thus, from the geometry of **1** it is obvious that chemical bonds C(1)–C(2) and N(1)–C(2) form a conjugated system as a result of interaction between lone electron pair of the nitrogen atom and π-component of double C(1)–C(2) bond.

The existence of ionic form **B** is in accordance with low rotation barrier around C=C bond.



A **B**

The lengths of P–Cl bond lie in a narrow range of 2.083(1)–2.090(1) Å. The angles in fragments C–P–Cl, and P–Cl bond lengths slightly differ. This may result from packing interactions between atoms P···P (3.52 Å), Cl···H (2.93 Å), Cl···Cl (3.47 Å) (Figure 2).

In order to estimate the energetic advantage of attractive interaction N→P in complex $Et_3N{\cdot}PCl_3$, we optimized its structure at the B3LYP/6-31G(d) level of theory. According to the NBO analysis, a possible model for the N→P nonbonding interaction might be a negative hyperconjugation of the lone

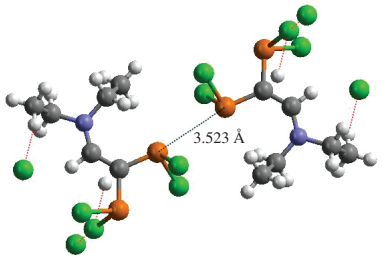


Figure 2 Short contacts in crystal of **1**.

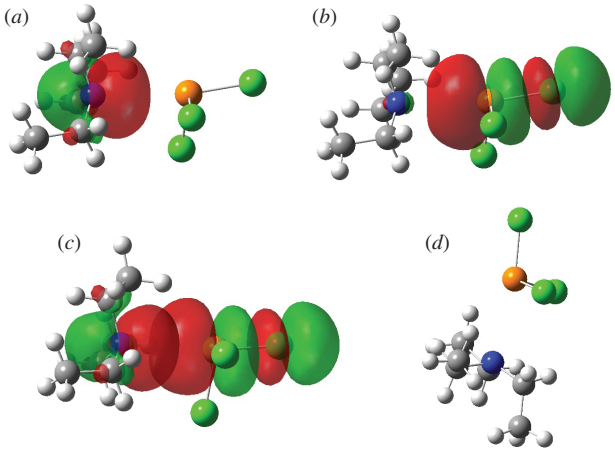
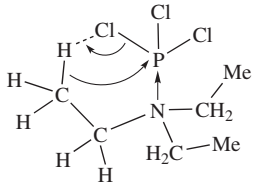


Figure 3 Details of NBO-analysis for the complex $Et_3N{\cdot}PCl_3$: (*a*) HOMO (lone electron pair of nitrogen), (*b*) LUMO (σ*P–Cl), (*c*) HOMO + LUMO and (*d*) general view of the complex.

electron pair at nitrogen with the anti-bonding orbital σ*(P–Cl) at the adjacent phosphorus (Figure 3).[11]

The complexation is energetically favorable by 3.1 kcal mol^{-1}. We assume that further elimination of hydrogen chloride occurs due to possibility of close contact between β-protons of ethyl group and chlorine atoms on simultaneous formation of the P–C bond.



It is confirmed by the fact that usual tertiary amines lacking β-hydrogen atoms do not react with PCl_3 in a similar way. In particular, long heating tribenzylamine with PCl_3 in acetonitrile does not give any products. On the contrary, reaction with 1,4-dimethylpiperazine under the same conditions leads to a dark-brown water-soluble product.§ Unfortunately, full characterization of this product appeared problematic.

Using THF instead of MeCN as a solvent also allowed us to obtain product **1**. However, its yield (^{31}P NMR data) was much less (⩽ 10%) at increase in the reaction time to 20 h.

Note that the reaction represented in Scheme 1 is not stoichiometric and is accompanied by formation of one more product

‡ *Crystal data for* **1**. $C_6H_{11}Cl_4NP_2$, M = 300.90, triclinic, space group $P\bar{1}$, at T = 100 K: a = 6.109(1), b = 7.982(1) and c = 13.670(2) Å, α = 94.246(2)°, β = 102.286(2)°, γ = 103.992(2)°, V = 626.4(2) $Å^3$, Z = 2, d_{calc} = 1.595 g cm^{-3}, μ = 1.158 mm^{-1}, $2\theta_{max}$ = 52°; 5187 reflections collected (2390 independent reflections, R_{int} = 0.0187), $R_1[I > 2\sigma(I)]$ = 0.0370, wR_2 (for all data) = 0.0908, GOOF = 1.113, largest difference peak and hole 0.617/–0.379 e $Å^{-3}$. X-ray diffraction intensity data were collected with a Bruker Smart Apex diffractometer (graphite-monochromated MoKα, λ = 0.71073 Å) using ω-scans. The structure was solved by direct methods and refined on F^2 using the SHELXTL software package.[9] All non-hydrogen atoms were located from Fourier syntheses of electron density and refined anisotropically. All hydrogen atoms except H(2A) were placed in calculated positions and refined in the riding model. SADABS was used to perform area-detector scaling and absorption corrections.[10]

CCDC 1012061 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

§ 1,4-Dimethylpiperazine (1.6 g, 14.0 mmol) was added to phosphorus trichloride (1.1 g, 8.0 mmol) in 10 ml of acetonitrile *in vacuo*. Heating the mixture for 10 h at 80 °C gave dark-brown solid. IR (Nujol, ν/cm^{-1}): 3494 (m), 3449 (m, NH), 2675–2200 (br., NH^+), 1328 (m), 1293 (m), 1196 (s), 1150 (s), 1117 (m), 1082 (s), 1067 (w), 1046 (w), 990 (s), 908 (s), 820 (m), 771 (s), 582 (m), 504 (w), 472 (s). Found (%): C, 25.62; H, 6.56; P, 28.95; Cl, 0.51.

being a bright yellow powder, insoluble in common organic solvents and water, stable to oxygen and moisture. IR spectrum of the powder contains wide absorption bands at 1600 (C=N) and 1340 cm^{-1} (P=N) lacking C–H vibrations. According to elemental analysis, this product contains much phosphorus (60.47%), carbon (20.8%), hydrogen (4.82%) and a little of chlorine (2.07%). Its heating *in vacuo* causes decomposition accompanied by the formation of white phosphorus in considerable quantity. We assume that this solid is a result of interaction between PCl_3 and acetonitrile in the presence of catalytic amounts of HCl formed in this reaction.

It is known that keeping the mixture of trichlorophosphine and acetonitrile for a long time in the presence of air at 0 °C leads to formation of addition–oxidation product $MeC(Cl)=N–P(O)Cl_2$.[12] In our hands, long keeping or heating this mixture *in vacuo* did not give any products.

In conclusion, we have obtained and characterized 2,2-bis-(dichlorophosphino)-*N*,*N*-diethylethenamine which surprisingly formed in the widely used system $Et_3N–PCl_3$–MeCN. However, this and related systems require further study.

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