Preparation of Urethane and Urea Derivatives of $(NPCl_2)_3$. Crystal Structure of a Spirocyclic Phosphazene with a Phosphacyanuric Loop *

Adri A. van der Huizen, Pieter L. Buwalda, Theo Wilting, Harm Pol, Andries P. Jekel, Auke Meetsma and Johan C. van de Grampel

Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Reactions of $(NPCl_2)_3$ with NaNCO in the presence of aliphatic alcohols have been investigated. Using an equimolar amount of NaNCO in refluxing acetonitrile, high yields of mono(urethane) derivatives $N_3P_3Cl_5(NHCO_2R)$ were obtained. Disubstitution is mainly non-geminal. Reactions of $(NPCl_2)_3$ with AgNCO and methanol in acetonitrile follow a quite different pattern and lead to the formation of three products with basically geminal structures, *e.g.* *gem*-$N_3P_3Cl_4(OR)(NHCO_2R)$, *gem*-$N_3P_3Cl_4(NHCO_2R)_2$, and a spiro derivative $(NPCl_2)_2NP[N(CO_2R)C(O)NHC(CH_3)N]$. The crystal structure of the last compound (R = CH_3) has been determined. The difference between the reaction pathways observed for NaNCO and AgNCO is discussed in terms of S_N2 and S_N1 mechanisms, respectively. An improved synthesis of $(NPCl_2)_2NP(NH_2)(NCO)$ and its reactions with alcohols and amines are described.

It is well established that reactions of fluoro- or chloro-cyclophosphazenes and cyclothiaphosphazenes with thiocyanate salts (KSCN, NH_4SCN) provide an excellent route to isothiocyanato derivatives of these inorganic ring systems.[1-6] Similar attempts involving reactions of $(NPBr_2)_3$ with AgNCO in order to prepare isocyanato derivatives were unsuccessful.[7] However, alternative methods have led to the isolation of stable isocyanatocyclophosphazenes. The reaction of *gem*-$N_3P_3Cl_4(NH_2)_2$ with $COCl_2$ in chlorobenzene[8]† or preferably in acetonitrile[9] leads to the formation of *gem*-$N_3P_3Cl_4(NH_2)(NCO)$. Roesky and Janssen[10] described the synthesis of $N_3P_3F_5(NCO)$ and $N_4P_4F_7(NCO)$ *via* the reaction of the monoamido derivatives with chlorosulfonylisocyanate.

Here we describe a direct route to urethane-substituted cyclophosphazenes by the reaction of $(NPCl_2)_3$ **1** with NaNCO in the presence of an alcohol. A very different reaction pathway was observed, when NaNCO was replaced by AgNCO. The specific effect of the Ag^+ ion will be discussed. From the reaction mixtures obtained with AgNCO in nitrile solvents a number of geminally substituted derivatives were isolated. The crystal structure of one of these compounds, a spiro derivative, will be discussed in detail. The reaction of $(NPCl_2)_2NP(NH_2)_2$ **2** with $COCl_2$ was reinvestigated leading to a high-yield synthesis of $(NPCl_2)_2NP(NH_2)(NCO)$ **3**. It is shown that this compound is a very useful precursor for the preparation of mono(urethane)- or mono(urea)-substituted cyclophosphazenes.

Experimental

Procedures and Materials.—All reactions were carried out under dry, oxygen-free nitrogen using inert gas-vacuum techniques and Schlenk-type glassware. The compound $(NPCl_2)_3$ **1** was obtained from Shin Nisso Kaku Co. and used without purification, NaNCO was commercial grade and dried *in vacuo* at 150 °C prior to use and AgNCO and $(NPCl_2)_2NP(NH_2)_2$ **2** were prepared according to literature methods, refs. 11 and 12, respectively. All absolute alcohols were analytical grade and obtained from Merck. The alcohol $HOCH_2[CHOC(CH_3)_2OCH_2]$ was synthesised as described in ref. 13. Acetonitrile (Merck) was distilled from P_2O_5 and stored under dry nitrogen.

Proton NMR spectra ($CDCl_3$ solutions, unless otherwise mentioned) were recorded on a Bruker WH90 spectrometer, operating at 90 MHz using $SiMe_4$ as an internal reference, ^{31}P NMR spectra ($CDCl_3$ solutions, unless otherwise mentioned) on a Nicolet NT200 (80.99 MHz) or on a Varian VXR300 (121.42 MHz) spectrometer, and chemical shifts are referenced to external $(NPCl_2)_3$ (δ19.9, $CDCl_3$ solution). The HPLC experiments were carried out using a Waters system consisting of two 6000A pumps, combined with a R401 RI detector. Separations were performed on Lichrosorb Si 60/10 columns (length 30 cm, outside diameter 22 mm). Mass spectra were obtained on an AEI MS9 spectrometer. Elemental analyses were performed at the Analytical Department of this University.

Preparation of Compounds $(NPCl_2)_2NPCl(NHCO_2R)$ **4–7** {R = CH_3, C_2H_5, $CH_2CH{=}CH_2$ *or* $CH_2[CHOC(CH_3)_2OCH_2]$}.—A mixture of compound **1** (1.74 g, 0.0050 mol), NaNCO (0.33 g, 0.0051 mol) and the appropriate alcohol ROH (0.0060 mol) was suspended in acetonitrile (25 cm^3). After refluxing for 3 h the mixture was allowed to cool to room temperature. By subsequent filtration and removal of the solvent *in vacuo* a viscous oil was obtained. Recrystallization from light petroleum (b.p. 60–80 °C) yielded a pure white crystalline product.

$(NPCl_2)_2NPCl(NHCO_2CH_3)$ **4** (0.0040 mol, 80%): m.p. 145–146 °C (Found: C, 6.25; H, 1.05; Cl, 45.80; N, 14.25. $C_2H_4Cl_5N_4O_2P_3$ requires C, 6.20; H, 1.05; Cl, 45.90; N, 14.50%); δ_H 3.81 (3 H, s, CH_3) and 6.6 [1 H, br d, NH, ^2J(PH) 14.6]; δ_P (A_2B type) 8.1 (PClNH) and 22.4 (PCl_2), ^2J(PP) 57.4 Hz.

$(NPCl_2)_2NPCl(NHCO_2C_2H_5)$ **5** (0.0040 mol, 80%): m.p. 136–138 °C (Found: C, 9.10; H, 1.55; Cl, 44.10; N, 13.60. $C_3H_6Cl_5N_4O_2P_3$ requires C, 9.00; H, 1.50; Cl, 44.30; N, 14.00%); δ_H 1.29 [3 H, t, CH_3, ^3J(HH) 7.2], 4.25 [2 H, q, CH_2, ^3J(HH) 7.2] and 6.6 [1 H, br d, NH, ^2J(PH) 14.5]; δ_P (A_2B type) 7.8 (PClNH) and 22.4 (PCl_2), ^2J(PP) 57.2 Hz.

$(NPCl_2)_2NPCl(NHCO_2CH_2CH{=}CH_2)$ **6** (0.0030 mol, 60%):

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

† The authors erroneously assigned non-geminal structures.

m.p. 91–93 °C (Found: C, 11.65; H, 1.50; Cl, 42.60; N, 13.35. $C_4H_6Cl_5N_4O_2P_3$ requires C, 11.65; H, 1.45; Cl, 43.00; N, 13.60%); δ_H 4.66 [2 H, d, OCH_2, ^3J(HH) 5.6], 5.2–5.4 (2 H, m, $=CH_2$), 5.7–6.1 (1 H, m, CH) and 6.9 [1 H, d, NH, ^2J(PH) 13.2]; δ_P (A_2B type) 7.8 (PClNH) and 22.3 (PCl_2), ^2J(PP) 57.3 Hz.

$(NPCl_2)_2NPCl\{NHCO_2CH_2[CHOC(CH_3)_2OCH_2]\}$ **7** (0.0047 mol, 94%): m.p. 106–107.5 °C; compound decomposes with liquefaction on standing, no satisfactory analytical data could be obtained; δ_H 1.33 (3 H, s, CH_3), 1.41 (3 H, s, CH_3), 3.5–4.5 (5 H, m, CH_2CHCH_2) and 7.1 [1 H, d, NH, ^2J(PH) 15.1]; δ_P(A_2B type) 7.8 (PClNH) and 22.3 (PCl_2), ^2J(PP) 57.6 Hz.

Reactions of Compound **1** *with* AgNCO *in the Presence of* CH_3OH.—To a solution of compound **1** (1.00 g, 0.0029 mol) in acetonitrile (60 cm^3) was added AgNCO (1.72 g, 0.0115 mol) and methanol ($n \times 0.0029$ mol; n = 1, 5, 10, or 100). After 2.5 h of reflux the mixture was allowed to cool and the solvent removed *in vacuo*. The residue was extracted three times with diethyl ether (50 cm^3). After removal of the ether the remaining solid was freed from salts by flash chromatography (silica gel 230–400 mesh, column length 20 cm, internal diameter 3 cm, diethyl ether as eluent). Separation of reaction products (not for n = 1) was achieved by HPLC with tetrahydrofuran–hexane (1:2) as eluent. The following results were obtained.

n = 1: ^{31}P NMR spectroscopy showed the reaction product to consist of one major compound with traces of **10** (see below). Recrystallization from diethyl ether yielded white crystals of $(NPCl_2)_2NP[N(CO_2CH_3)C(O)NHC(CH_3)N]$ **8** (0.0012 mol, 41%), m.p. (decomp.) 220–222 °C (Found C, 13.85; H, 1.65; Cl, 32.65; N, 18.8. $C_5H_7Cl_4N_6O_3P_3$ requires C, 13.85; H, 1.65; Cl, 32.70; N, 19.35%); δ_H 2.27 (3 H, s, OCH_3), 3.96 [3 H, d, CCH_3, ^4J(PH) 1.2], NH not visible; δ_P (A_2B type) − 4.0 (PN_2) and 23.2 (PCl_2), ^2J(PP) 46.5 Hz.

n = 5: Separation by means of HPLC yielded three fractions (A–C). Fraction A was recrystallized from diethyl ether and yielded white crystals of $(NPCl_2)_2NP(OCH_3)(NHCO_2CH_3)$ **10** (0.0007 mol, 24%), m.p. 139–141 °C (Found C, 9.60; H, 1.80; Cl, 36.85; N, 14.70. $C_3H_7Cl_4N_4O_3P_3$ requires C, 9.45; H, 1.85; Cl, 37.15; N, 14.65%); δ_H 3.71 [3 H, d, CH_3, ^3J(PH) 13.8], 3.76 (3 H, s, CH_3) and 6.05 [1 H, br d, NH, ^2J(PH) 9.6]; δ_P (A_2B type) 3.0 (PO,N) and 24.7 (PCl_2), ^2J(PP) 60.8 Hz. Fraction B could not be obtained in an analytically pure state. Identification as $(NPCl_2)_2NP(NHCO_2CH_3)_2$ **11** was confirmed by mass spectrometry {m/z 423 (M^+, 5), 359 (M^+ − $2CH_3OH$, 26) and 324 (M^+ − $2CH_3OH$ − ^{35}Cl, 100%)} and ^{31}P NMR spectroscopy [δ_P (A_2B type) −5.6 (PN_2) and 23.4 (PCl_2), ^2J(PP) 59.2 Hz]. Fraction C yielded the spiro compound **8** (0.0009 mol, 31%).

n = 10: The reaction products were not separated from each other; the composition of the reaction mixture is given in Fig. 1.

n = 100: Only compound **10** appeared to be present in the reaction mixture.

Preparation of $(NPCl_2)_2NP(NH_2)(NCO)$ **3**.*—Phosgene gas ($COCl_2$), obtained by slow evaporation of freshly condensed phosgene (about 30 cm^3), was passed through a solution of compound **2** (20.0 g, 0.0647 mol) in acetonitrile (500 cm^3), dried on 3 Å molecular sieves) at −20 °C. After evaporation of the phosgene (about 0.5 h) the mixture was allowed to warm to room temperature and stirred for 2 h at that temperature. After evaporation *in vacuo* the remaining product was extracted four times with diethyl ether (100 cm^3). After evaporation of the ether the product was recrystallized from a pentane–diethyl ether mixture, yielding white crystals of $(NPCl_2)_2NP(NH_2)$-(NCO) **3** (0.0518 mol, 80%), m.p. 74–76 °C (Found: Cl, 42.60. $CH_2Cl_4N_5OP_3$ requires Cl, 42.35%); δ_P (A_2B type) −3.2 (PN_2) and 21.5 (PCl_2), ^2J(PP) 59.0 Hz.

* **CAUTION**: This reaction should be performed in a well ventilated fumehood since highly toxic phosgene is involved.

Reaction of Compound **3** *with some Aliphatic Alcohols and Amines*.—The appropriate alcohol or amine (0.0015 mol) in acetonitrile (10 cm^3) was added dropwise to a stirred solution of compound **3** (0.5 g, 0.0015 mol) in acetonitrile (10 cm^3) at room temperature (alcohol) or −50 °C (amine). After stirring for 12 (alcohol) or 1 h (amine) at that temperature the solvent was removed under vacuum. Recrystallization from a pentane–diethyl ether (urethane derivatives) or a tetrahydrofuran–pentane mixture (urea derivatives) yielded white crystalline products.

$(NPCl_2)_2NP(NH_2)(NHCO_2CH_3)$ **12** (0.0009 mol, 60%): m.p. 182–184 °C (Found: C, 6.55; H, 1.70; Cl, 38.60; N, 18.80. $C_2H_6Cl_4N_5O_2P_3$ requires C, 6.55; H, 1.65; Cl 38.65; N, 19.10%); δ_H(CD_3CN) 3.79 (3 H, s, CH_3), 3.9 (2 H, br, NH_2) and 7.0 (1 H, br, NH); δ_P (A_2B type) 2.4 (PN_2) and 18.6 (PCl_2), ^2J(PP) 50.2 Hz.

$(NPCl_2)_2NP(NH_2)(NHCO_2C_2H_5)$ **13** (0.0009 mol, 60%): m.p. 140–142 °C (Found: C, 9.40; H, 2.05; Cl, 37.05; N, 18.20. $C_3H_8Cl_4N_5O_2P_3$ requires C, 9.45; H, 2.10; Cl, 37.25; N, 18.40%); δ_H 1.32 [3 H, t, CH_3, ^3J(HH) 7.1], 3.4 (2 H, br, NH_2), 4.26 [2 H, q, CH_2, ^3J(HH) 7.1] and 6.3 [1 H, br d, NH, ^2J(PH) 9.5]; δ_P (A_2B type) 2.7 (PN_2) and 21.9 (PCl_2), ^2J(PP) 52.7 Hz.

$(NPCl_2)_2NP(NH_2)(NHCO_2CH_2CH{=}CH_2)$ **14** (0.0011 mol, 73%): m.p. 106–107 °C (Found: C, 12.10; H, 2.10; Cl, 36.10; N, 17.60. $C_4H_8Cl_4N_5O_2P_3$ requires C, 12.25; H, 2.05; Cl, 36.10; N, 17.85%); δ_H 3.4 (2 H, br, NH_2), 4.62 [2 H, d, CO_2CH_2, ^3J(HH) 11.0], 5.1–5.4 (2 H, m, $=CH_2$), 5.6–6.2 (1 H, m, CH) and 6.38 [1 H, d, NH, ^2J(PH) 11.0]; δ_P (A_2B type) 2.7 (PN_2) and 22.0 (PCl_2), ^2J(PP) 52.3 Hz.

$(NPCl_2)_2NP(NH_2)(NHCONHCH_3)$ **15** (0.0006 mol, 40%): m.p. 171–172 °C (Found: C, 6.50; H, 2.05; Cl, 38.40; N, 22.25. $C_2H_7Cl_4N_6OP_3$ requires C, 6.55; H, 1.95; Cl, 38.75; N, 22.80%). δ_H(CD_3OD) 2.70 (3 H, s, CH_3), NH and NH_2 not visible; δ_P([$^2H_8$]tetrahydrofuran, A_2B type) 5.0 (PN_2) and 20.2 (PCl_2), ^2J(PP) 48.6 Hz.

$(NPCl_2)_2NP(NH_2)[NHCON(CH_3)_2]$ **16** (0.0011 mol, 73%): m.p. 154–155 °C (Found: C, 9.70; H, 2.45; Cl, 37.00; N, 22.00. $C_3H_9Cl_4N_6OP_3$ requires C, 9.50; H, 2.40; Cl, 37.35; N, 22.10%). δ_H(CD_3CN) 2.85 (6 H, s, CH_3), 3.8 (2 H, br, NH_2) and 5.90 (1 H, br, NH); δ_P([$^2H_8$]tetrahydrofuran, A_2B type) 6.7 (PN_2) and 21.4 (PCl_2), ^2J(PP) 47.2 Hz.

Crystal Structure Determination of Compound **8**.—A colourless crystal (dimensions 0.10 × 0.18 × 0.32 mm), obtained by recrystallization from hexane, was used for data collection (CAD-4F diffractometer).

Crystal data. $C_5H_7Cl_4N_6O_3P_3$, M = 433.83, triclinic, space group $P\bar{1}$ (no. 2), a = 7.348(2), b = 10.510(4), c = 10.910(3) Å, α = 96.88(3), β = 107.19(2), γ = 98.77(3)°, U = 774.3(4) Å^3 (by least-squares refinement on 22 setting angles in the range 6.70 < θ < 15.30°), λ = 0.710 73 Å, Z = 2, F(000) = 432, D_c = 1.86 g cm^{-3}, μ(Mo-Kα) = 10.9 cm^{-1}. Reduced-cell calculations did not indicate any higher lattice symmetry.[14]

Data collection. Intensity data for 2970 reflections were collected at room temperature in the range 1.99 < θ < 25.0° (h 0–8; k −12 to 12; l −12 to 12), using graphite-monochromated Mo-Kα radiation and the ω–2θ technique with ω scan width = (0.95 + 0.35 tan θ)°. Three reference reflections measured every 2 h [300, root-mean-square deviation (r.m.s.d.) 2; $0\bar{4}\bar{1}$, r.m.s.d. 1.8; 005, r.m.s.d. 1.8%) showed no indication of crystal decomposition. The intensities were corrected for scale variation and for Lorentz and polarization effects, but not for absorption. The variance $\sigma^2(I)$ was calculated based on counting statistics and the term (P^2I^2), where P (=0.034) is the instability constant as derived from the excess of variance in the reference reflections.[15] The data set was averaged to a set of 2736 unique reflections, of which 2060 satisfied the criterion $I \geqslant 2.5\sigma(I)$.

Structure analysis and refinement. The structure was solved by direct methods with GENTAN[16] and refined on F by block-

diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms located on a Fourier difference map were included in the final refinement with one overall isotropic thermal parameter. Convergence was reached at $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.037$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o^2|]^{\frac{1}{2}} = 0.046$, $w = 1/\sigma^2(F)$. A final Fourier difference map did not show any significant features (minimum and maximum residual electron density -0.38 and 0.41 e Å^{-3}, respectively). The final fractional atomic coordinates for the non-hydrogen atoms are given in Table 1. Scattering factors were taken from Cromer and Mann,[17] anomalous dispersion factors from Cromer and Liberman.[18] All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL,[16] EUCLID,[19] and a locally modified version of the program PLUTO.[20]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Reactions of Compound **1** *with Cyanate Salts.*—The most general method of synthesis of phosphorus-bonded isocyanates involves the reaction of both phosphorus-(III) and -(V) halides with metal cyanates.[21] For instance, with PCl_3 a stepwise replacement of chloro ligands by isocyanate groups can be achieved.[22]

Comparable with the behaviour of $(NPBr_2)_3$,[7] compound **1** showed a remarkably low reactivity towards the metal cyanates NaNCO and AgNCO. Addition of phase-transfer reagents (crown ethers or NBu^t_4Br) gave no significant improvement. In refluxing nitromethane or acetonitrile degradation of the NP ring system took place.

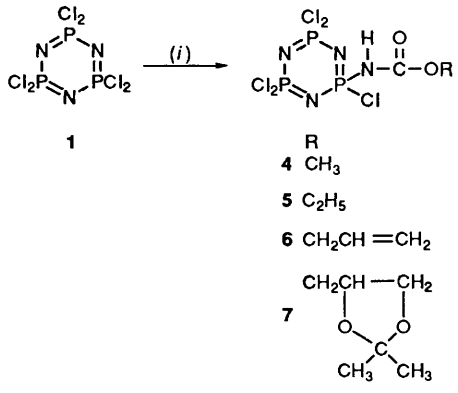
Reactions of Compound **1** *with* NaNCO *in the Presence of Aliphatic Alcohols.*—The reaction of compound **1** with an equimolar amount of NaNCO* in the presence of 1 or more equivalents of alcohol invariably led to the formation of mono-(urethane) derivatives **4**–**7** (Scheme 1). Products **4**–**6** were isolated as air- and moisture-stable, crystalline compounds; **7** slowly loses acetone when exposed to air owing to the acidic amide proton. Apparently, alcohol serves as an efficient isocyanate trap in these addition reactions. The best solvent appeared to be rigorously dried acetonitrile. After 3 h of reflux yields up to 90% can be obtained. The reaction of **1** with NaNCO in the presence of ethylene glycol appeared not to be selective. Only 25% of the expected urethane $(NPCl_2)_2$-$NPCl(NHCO_2CH_2CH_2OH)$ was isolated, although, according to the ^{31}P NMR spectrum of the reaction mixture, no starting material was left. Apart from considerable amounts of insoluble material, also the spirocyclic compound $(NPCl_2)_2NP(OCH_2$-$CH_2O)$[23] could be isolated.

As indicated by ^{31}P NMR spectra of the crude reaction mixtures, the analogous reactions with 2 equivalents of the alkali-metal cyanate salt gave, besides appreciable amounts of the mono(urethane) species, predominantly non-geminal di-substituted cyclophosphazenes. The specific formation of non-geminal products may be associated with an S_N2 type substitution mechanism, consistent with reactions of organic halides with cyanates carried out under comparable conditions.[24,25]

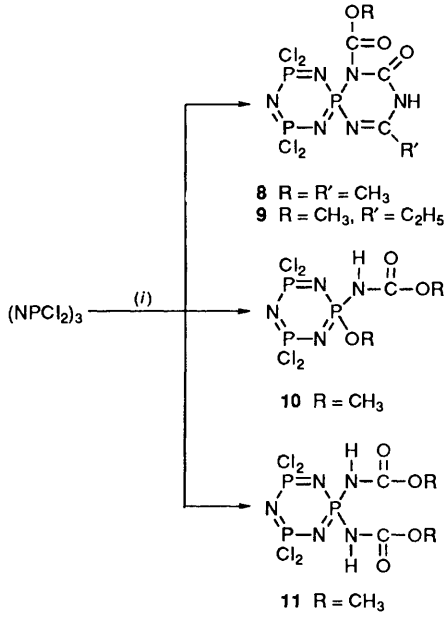
The reaction leading to urethane derivatives is strictly limited to aliphatic alcohols. In reactions with phenols, NaNCO acts as a base and alcoholysis of the P–Cl bonds is observed. Also ureas could not be synthesised by the reaction of compound **1** with NaNCO in the presence of a primary or secondary amine, as direct aminolysis of the P-Cl bonds occurs.

* Some of the experiments were repeated with KNCO as reagent; no changes in reaction features or isolated products were observed.

Reactions of Compound **1** *with* AgNCO *in the Presence of Aliphatic Alcohols.*—In general, three products were obtained in the reaction of compound **1** with AgNCO and ROH in nitrile solvents (Scheme 2). The relative yields of these products are strongly dependent on the number of equivalents of alcohol. This is illustrated in Fig. 1, showing the relative amounts of the three products obtained in the reaction system **1**, AgNCO,



Scheme 1 (*i*) NaNCO, ROH, CH_3CN



Scheme 2 (*i*) AgNCO, ROH, R'CN

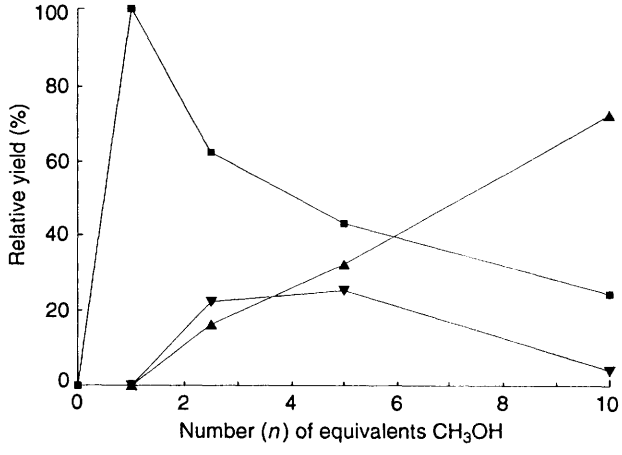


Fig. 1 Relative yields (from ^{31}P NMR spectra) of compounds **8** (■), **10** (▲) and **11** (▼) *versus* the number (*n*) of equivalents of CH_3OH used in the reaction $(NPCl_2)_3 + 4\,AgNCO + n\,CH_3OH$

CH_3OH (molar ratio 1:4:*n*) in MeCN. Similar results were obtained when the mono(urethane) derivative $N_3P_3Cl_5(NHCO_2CH_3)$ **4** was used as starting material for a reaction in the presence of methanol and AgNCO.

Mechanism of the Reactions in the Presence of AgNCO.—From the results given above, it can be assumed that the first two steps of the reaction sequence with AgNCO refer to the formation of a mono(urethane) derivative. The strictly geminal nature of the products **8**–**11** (Scheme 2) points to a regioselective action towards the urethane-substituted P atom in $N_3P_3Cl_5(NHCO_2R)$. It is well known that, unlike Na^+ or K^+, the Ag^+ ion is capable of promoting S_N1 type transition states by withdrawal of halide ions.[26] We therefore assume that withdrawal of Cl^-, aided by the electron-donating character of the urethane nitrogen atom, leads to the formation of a phosphazenium ion (Scheme 3).

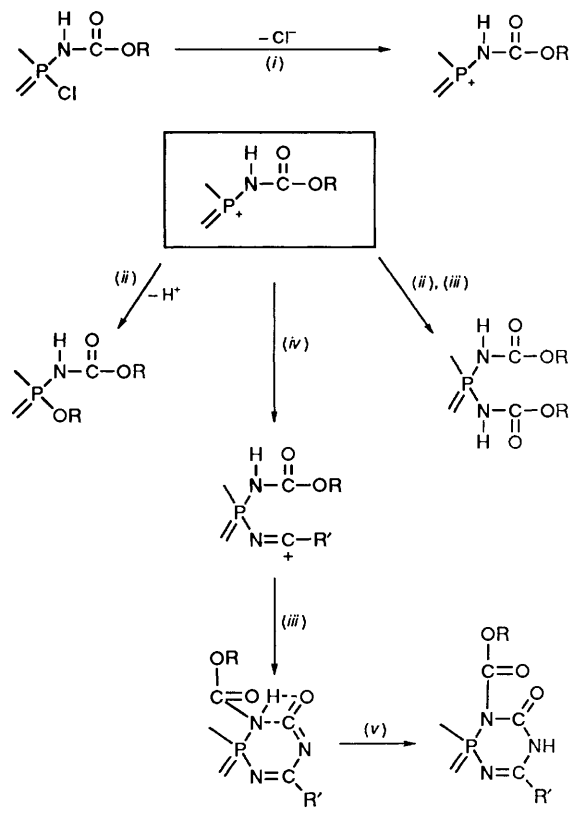
This ion can be expected to react with the alcohol to give directly the geminal alkoxyurethane derivative **10** (R = CH_3), which is by far the major product in the presence of an excess of alcohol (Fig. 1). Another reaction mode is the attack of the phosphazenium cation by (nitrile) solvent molecules (resembling the Ritter reaction[27] with carbonium ions) followed by neutralization with NCO^- anions. Ring closure by nucleophilic addition of the carbamato NH moiety to the NCO part followed by a rearrangement leads to the spiro compound. The participation of the solvent could be demonstrated by changing from acetonitrile to propionitrile. In the latter case an ethyl-substituted spiro derivative **9** (R = CH_3, R′ = C_2H_5) (NMR and mass spectroscopic evidence) was formed instead of the methyl analogue **8** (R = R′ = CH_3). As shown in Fig. 1 the formation of spiro compounds predominates at low alcohol concentrations; it is obvious that at higher concentrations the formation of the alkoxyurethane derivative becomes more manifest.

Reaction of the intermediate cation with NCO^- and subsequent addition of alcohol leads to the formation of the geminally substituted bis(urethane) derivative **11** (R = CH_3). Compound **11** is also formed as minor compound (yield about 2%) in the reaction of **1** with 2 equivalents of NaNCO and methanol. Despite many efforts it was not possible to isolate an analytically pure sample of **11**; identification, therefore, is based on NMR and mass spectra.

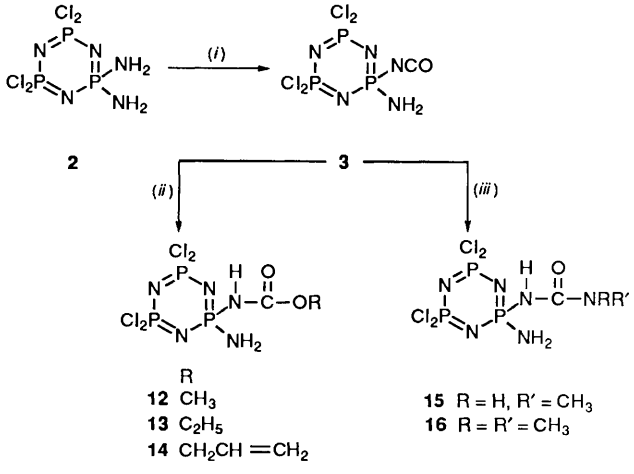
Synthesis and Reactivity of $(NPCl_2)_2NP(NH_2)(NCO)$ **3**.—The procedure of Tesi and Zimmer-Galler[8] for the preparation of compound **3** did not lead in our case to reproducible results. Instability of **3** towards water (hydrolysis to **2**) and HCl [formation of $(NPCl_2)_2NPCl(NH_2)$] appeared to be the main cause for low and varying yields. In our approach we used phosgene purified by a condensation–evaporation procedure (see Experimental section), small amounts of triethylamine and dry acetonitrile as solvent. From ^{31}P NMR spectra, large amounts of amine appear to induce oligomerization of **3**. Equimolar reactions of **3** with primary alcohols (Scheme 4) in acetonitrile led to the corresponding urethane derivatives in 60–80% yield. Analogous results were obtained for reactions with the amines, CH_3NH_2, $C_2H_5NH_2$, $(CH_3)_2NH$ and $C_6H_5NH_2$. The urea derivatives formed, however, were difficult to purify. Satisfactory analytical data could be obtained only for compounds **15** and **16**.

The reaction mode of compound **3** towards amines differs from that of the intermediate $(NPCl_2)_2NPCl(NCO)$, as in the latter case amino substitution takes place at the PCl_2 centres. This difference in behaviour can be ascribed by the presence of the electron-donating NH_2 group, which suppresses the reactivity of the PCl_2 centres in nucleophilic substitution, but enhances at the same time the reactivity of the NCO group.

Molecular Structure of Compound **8**.—The molecular structure and the atom numbering scheme adopted is shown in Fig.



Scheme 3 (*i*) S_N1 type reaction initiated by Ag^+; (*ii*) ROH; (*iii*) NCO^-; (*iv*) R′CN; (*v*) rearrangement



Scheme 4 (*i*) $COCl_2$, $(C_2H_5)_3N$, CH_3CN; (*ii*) ROH; (*iii*) RR′NH

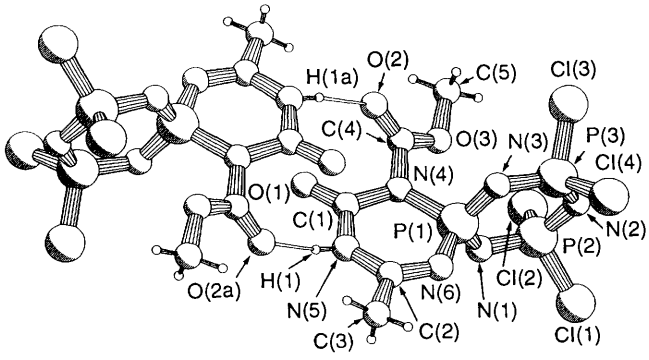


Fig. 2 A PLUTO drawing of the dimeric entity of compound **8** illustrating the puckering and the numbering scheme adopted

Table 1 Final fractional atomic coordinates for non-H atoms of compound **8** and their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cl(1)	0.493 9(2)	0.229 0(1)	0.144 89(9)
Cl(2)	0.715 0(2)	0.225 0(1)	−0.054 0(1)
Cl(3)	0.168 1(2)	−0.077 2(1)	−0.378 5(1)
Cl(4)	−0.075 6(2)	−0.061 6(1)	−0.193 4(1)
P(1)	0.171 0(1)	0.313 18(9)	−0.217 48(8)
P(2)	0.446 0(1)	0.210 40(9)	−0.046 84(9)
P(3)	0.140 8(2)	0.045 93(9)	−0.233 54(9)
O(1)	0.223 3(4)	0.573 8(2)	−0.434 4(2)
O(2)	0.257 5(4)	0.326 3(3)	−0.537 7(2)
O(3)	0.443 1(4)	0.272 7(3)	−0.356 3(2)
N(1)	0.360 3(4)	0.329 2(3)	−0.095 7(3)
N(2)	0.329 2(5)	0.067 6(3)	−0.112 2(3)
N(3)	0.070 0(4)	0.166 8(3)	−0.288 4(3)
N(4)	0.222 7(4)	0.392 0(3)	−0.336 0(3)
N(5)	0.047 5(5)	0.554 0(3)	−0.297 4(3)
N(6)	0.015 9(5)	0.388 5(3)	−0.176 7(3)
C(1)	0.169 1(5)	0.511 3(3)	−0.362 0(3)
C(2)	−0.033 1(5)	0.491 2(3)	−0.217 8(3)
C(3)	−0.182 3(6)	0.552 5(4)	−0.180 5(4)
C(4)	0.307 3(5)	0.329 5(3)	−0.422 9(4)
C(5)	0.536 8(7)	0.199 5(5)	−0.432 6(4)

Table 2 Selected data (distances in Å, angles in °) on the geometry

Cl(1)–P(2)	1.985(2)	P(3)–N(3)	1.588(3)
Cl(2)–P(2)	1.985(2)	O(1)–C(1)	1.224(4)
Cl(3)–P(3)	1.944(2)	O(2)–C(4)	1.189(5)
Cl(4)–P(3)	2.008(2)	O(3)–C(4)	1.335(5)
P(1)–N(1)	1.577(3)	O(3)–C(5)	1.428(6)
P(1)–N(3)	1.556(3)	N(4)–C(1)	1.419(5)
P(1)–N(4)	1.751(3)	N(4)–C(4)	1.406(5)
P(1)–N(6)	1.605(4)	N(5)–C(1)	1.372(5)
P(2)–N(1)	1.584(3)	N(5)–C(2)	1.386(5)
P(2)–N(2)	1.541(3)	N(6)–C(2)	1.298(5)
P(3)–N(2)	1.561(4)	C(2)–C(3)	1.474(6)
N(1)–P(1)–N(3)	113.8(2)	P(1)–N(4)–C(4)	119.5(2)
N(4)–P(1)–N(6)	102.9(2)	C(1)–N(4)–C(4)	115.0(3)
Cl(1)–P(2)–Cl(2)	101.29(7)	C(1)–N(5)–C(2)	127.6(3)
N(1)–P(2)–N(2)	119.1(2)	P(1)–N(6)–C(2)	124.2(3)
N(2)–P(3)–N(3)	121.4(2)	N(4)–C(1)–O(1)	125.0(3)
Cl(3)–P(3)–Cl(4)	101.93(7)	N(4)–C(1)–N(5)	113.9(3)
P(2)–N(1)–P(1)	124.8(2)	O(1)–C(1)–N(5)	121.0(3)
P(2)–N(2)–P(3)	118.0(2)	N(5)–C(2)–N(6)	124.7(4)
P(1)–N(3)–P(3)	122.4(2)	N(5)–C(2)–C(3)	113.9(3)
P(1)–N(4)–C(1)	125.2(2)	N(6)–C(2)–C(3)	121.4(3)

2. The triclinic unit cell contains two discrete molecules of the compound. Each asymmetric unit contains one complete molecule with no atoms at special positions. The six-membered rings P(1) to N(3) and P(1) to N(6) [angle between their normals 88.3(1)°] are almost planar with maximum deviations from the mean plane of 0.048(1) [P(2)] and 0.077(2) Å [P(1)], respectively. The OCH_3 group is located over the phosphazene ring. The sequence of the P–N bond lengths in the phosphazene part shows an unexpected asymmetry. In general in compounds of this type six P–N bonds are found more or less in three pairs. These would appear to be, in order of increasing lengths, P(2)–N(1), P(3)–N(3) < P(2)–N(2), P(3)–N(2) < P(1)–N(1), P(1)–N(3), provided the group electronegativity of the P(1) centre is smaller than that of P(2), P(3). In compound **8**, however, the 'pairs' of bonds run in order of increasing length (average values) as P(2)–N(2), P(3)–N(2) < P(1)–N(1), P(1)–N(3) < P(2)–N(1), P(3)–N(3), where P(2)–N(1) and P(3)–N(3) are essentially equal in length but the bond distances in the two other pairs differ by 0.02 Å. Another interesting feature of this structure is the presence of a more or less double N–P bond [N(6)–P(1) 1.605 Å] in the spiro loop (Table 2). Extended π-electron delocalization, involving the phosphazene ring and the C(2)–N(6)–P(1) unit, may induce the asymmetry mentioned above. The C–N bonds can be compared with those observed in organic N-containing heterocycles.[27] Between the molecules weak hydrogen bonding is observed: H(1)···O(2) ($-x$, $1-y$, $-1-z$) 2.22(3) Å (sum of the van der Waals radii[28] 2.72 Å), the angle N(5)–H(1)···O(2) 156(3)°, forming dimeric units in the solid state.

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