Novel cyclophosphazene monomers and their polymerization behavior

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Chapter 2

NOVEL OLEFIN-SUBSTITUTED CHLOROCYCLOTRIPHOSPHAZENES: SYNTHESIS AND CHARACTERIZATION

2.1 Abstract

The synthesis and characterization of three new alkenyl substituted tetrachlorocyclophosphazenes with direct P-C linkages is discussed. The reaction of vinylbenzylmagnesium chloride with $(NPCl_2)_3$ gives a styrene derivative with formula $(NPCl_2)_2NPMe(CH_2C_6H_4CH{=}CH_2)$ (STP) in high yields. ^{13}C NMR studies show that the benzyl group acts as an efficient spacer between the double bond and inorganic ring. A new olefin-substituted chlorocyclotriphosphazene $(NPCl_2)_2NP^iPr\{C[OC(O)Me]{=}CH_2\}$ (VAcP) and an unique bicyclotriphosphazene $[(NPCl_2)_2NP^iPr]_2C(OH)Me$ (PCP) have been prepared from the reaction of MeC(O)Cl and $(NPCl_2)_2NP^iPrH$ in the presence of Et_3N. Exclusive formation of VAcP could be achieved by using an excess of both Et_3N and MeC(O)Cl. The elimination reaction of $(NPCl_2)_2NP(^iPr)C(Me)_2OSO_2Me$ with DBU affords a propene derivative and an ansa compound with formula $N_3P_3Cl_3(^iPr)\{C(Me)_2CH{=}C(Me)O\}$ (ANSA). All the chlorine atoms in the styrene and propene derivative can be replaced by dimethylamino groups. The fully amino-substituted styrene derivative undergoes spontaneously polymerization. This phenomenon is not observed for the analogous propene compound.

2.2 Introduction

Much attention has been paid to the synthesis of olefin-substituted cyclophosphazenes [1-9]. These phosphazene monomers have proven to be very suitable for radical (co)polymerization reactions resulting in hybrid inorganic-organic polymers. In contrast to the well-known polyphosphazenes in which the backbone consists of alternating phosphorus and nitrogen atoms, these polymers have a carbon chain backbone with the cyclophosphazene rings as side groups. As a result of the incorporation of these inorganic substituents the polymers show an enhanced flame retardancy [4,10,11]. Another advantage of the presence of the phosphazene rings is the high degree of incorporated functionalities, viz. the remaining phosphorus-halogen centres. The facile replacement of the halogen atoms by various nucleophiles (e.g. alcohols, amines) makes it possible to modify the properties and applications of the polymers to a great extent [12].

As already discussed in Section 1.3.2 most of the synthesized organo-substituted chlorocyclotriphosphazenes have the polymerizable group linked to the phosphorus atom by a phosphorus-oxygen bond rather than by a phosphorus-carbon bond [4,5,11]. In the cases where a P-C bond is present, fluorocyclotriphosphazene rings have been used [1,2,13].

In this Chapter the synthesis of some novel chlorocyclotriphosphazene monomers is described. The reaction of vinylbenzylmagnesium chloride in the presence of methyl iodide and $(NPCl_2)_3$ resulted in a new styrene substituted chlorocyclotriphosphazene in high yields. The styrene moiety is linked to the phosphazene ring via a CH_2 group. It will be shown that the benzyl group acts as an effective insulator between the double bond and the phosphazene ring.

In search of novel routes for the synthesis of chlorocyclotriphosphazene precursors with polymerizable groups linked to the inorganic ring by a P-C bond, we also investigated the use of hydridocyclotriphosphazenes. From literature it is known that hydridophosphazenes act as nucleophiles in addition reactions due to their polar phosphorus-hydrogen bond. By utilizing this route it is possible to link phosphazene rings to a wide variety of functional groups as olefins, thiocyanates, ketones and aldehydes [14]. In all cases the phosphorus attacks at the electron deficient carbon centre. Alternatively, hydridophosphazenes can react with alkyl lithium reagents to generate phosphazeno anions [15].

In our approach we allowed to react the hydridocyclophosphazene $(NPCl_2)_2NP^iPrH$ with MeC(O)Cl. This resulted in the formation of a new 1,1-disubstituted alkene, $(NPCl_2)_2NP^iPr\{C[OC(O)Me]=CH_2\}$. In addition a compound with formula $[(NPCl_2)_2NP^iPr]_2C(OH)Me$ could be isolated, which is the first representative of a new class

of compounds in which two cyclophosphazene rings are bridged by one carbon atom. A mechanism for the formation of both compounds is proposed.

The synthesis of the last monomer that will be discussed is another 1,1-disubstituted olefin, viz. the propene derivative $(NPCl_2)_2NP^iPrC(Me)=CH_2$, which has been synthesized via an elimination reaction of a hydroxyl or sulphonium substituted cyclotriphosphazene with DBU. Apart from the expected propene monomer a small amount of another compound was detected in the reaction mixture. This side-product was identified as an ansa derivative. However, the underlying reaction mechanism is not yet understood.

Finally the remaining chlorine atoms in the styrene and propene derivative were replaced with dimethylamine groups. This allows to investigate to what extent the electron withdrawing effect of the phosphazene ring is reduced by the introduction of electron donating substituents.

2.3 Experimental

Measurements

NMR spectra were recorded on a Varian Gemini-200 spectrometer operating at 199.98 (^{1}H), 50.29 (^{13}C) and 80.95 (^{31}P) MHz. $CDCl_3$ (^{1}H and ^{13}C) was used as internal standard. $(NPCl_2)_3$ in $CDCl_3$ was applied as external reference for ^{31}P spectra. High temperature ^{1}H NMR experiments were performed on a Varian Unity 500 spectrometer operating at 499.86 MHz. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen.

Materials and procedures

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen using standard Schlenck techniques. Hexachlorocyclotriphosphazene (1) was kindly provided by Shin Nisso Kako Co. and purified by recrystallization from n-hexane (Merck). Iodomethane (Merck) and 3-vinylbenzyl chloride (70%, remainder 4-isomer, Aldrich) were used as received. Vinylbenzylmagnesium chloride (2), 1-hydrido-1-isopropyltetrachlorocyclotriphosphazene (3) and gem-isopropyl(hydroxypropyl)tetra-chlorocyclotriphosphazene (PAC) were synthesized according to literature [6,16,17]. Triethylamine (Et_3N, Merck) was dried on KOH and distilled from KOH under nitrogen. Tetrahydrofuran (THF, Janssen) was distilled from sodium/benzophenone under nitrogen prior to use. Diethyl ether (Janssen) was distilled from $CaCl_2$ and stored on sodium wire. Acetonitrile (Janssen) was dried on molecular sieves 3 Å (Merck). All other reagents and solvents were used as received.

Synthesis

$(NPCl_2)_2NPMe(CH_2C_6H_4CH=CH_2)$ (STP)

To a stirred solution of 10.0 g (28.8 mmol) of 1 and 2.25 ml (36.1 mmol) of CH_3I in 80 ml of THF, cooled to 0 ^oC, was added quickly 77 ml of a 0.6 M solution of vinylbenzylmagnesium chloride in THF. Stirring of the reaction mixture at 0 ^oC was continued for 3 days. After removal of the solvent, diethyl ether was added to precipitate the magnesium salts, which were removed by filtration. The ether was evaporated under reduced pressure and the crude product was purified by flash chromatography (silica gel 230-400 mesh, eluant hexane/ethyl acetate 4:1) to yield 7.1 g (17.4 mmol, 60%) of a white solid with mp 125.0-126.5 ^oC (uncorrected). Anal. Calc.: C, 29.37; H, 2.95; Cl, 34.68%. Found: C, 29.35; H, 3.04; Cl, 34.63%. ^1H NMR: δ 1.72 (dt, 3 H, Me, $^2J_{PH}$ 14.1 Hz, $^4J_{PH}$ 2.1 Hz), 3.20 (dt, 2 H, $-CH_2-$, $^2J_{PH}$ 13.7 Hz, $^4J_{PH}$ 2.8 Hz), 5.52 (dd, 2 H, $=CH_2$), 6.70 (dd, 1 H, -CH=), 7.27 (m, 4 H, ArH); $^{13}C\{^1H\}$ NMR: δ 19.2 (dt, Me, $^1J_{PC}$ 93.7 Hz, $^3J_{PC}$ 4.0 Hz), 40.7 (dt, $-CH_2-$, $^1J_{PC}$ 85.6 Hz, $^3J_{PC}$ 3.0 Hz), 114.3 ($=CH_2$), 125.4-137.8 (ArC), 136.3 (-CH=); $^{31}P\{^1H\}$ NMR: A_2B type, δ 18.1 (PCl_2), 37.2 ($POrg_2$), $^2J_{PP}$ unresolved.

$(NP(NMe_2)_2)_2NPMe(CH_2C_6H_4CH=CH_2)$ (STPN)

To a stirred solution of 0.5 g (1.2 mmol) of STP in 12.5 ml of acetonitrile was added 2.5 ml (19.7 mmol) of a 40% solution of dimethylamine in water. The solution was heated to 60 ^oC and stirred for 1 day. After removal of the solvent, diethyl ether was added and washed with demineralized water. After drying on $MgSO_4$ and evaporation of the ether, a clear colorless liquid was obtained. The oil slowly solidified to yield 0.23 g (41 % of theory) of a white solid. Recrystallization from ether afforded crystals with mp 56.0-57.5 ^oC. ^1H NMR: δ 1.5 (d, 3 H, Me, $^2J_{PH}$ 13.2 Hz), 2.47 (m, 24 H, NMe_2), 3.0 (d, 2 H, $-CH_2-$, $^2J_{PH}$ 14.5 Hz), 5.17 (d, 1 H, $=CH_2$, $^3J_{HH}$ 11.11 Hz), 5.69 (d, 1 H, $=CH_2$, $^3J_{HH}$ 17.52 Hz), 6.64 (dd, 1 H, -CH=, $^3J_{HH}$ 11.11 Hz, $^3J_{HH}$ 17.52 Hz), 7.27 (m, 4 H, ArH); $^{13}C\{^1H\}$ NMR: δ 21.5 (d, Me, $^1J_{PC}$ 94.0 Hz), 36.5 (d, NMe_2, $^2J_{PC}$ 17.6 Hz), 42.4 (d, $-CH_2-$, $^1J_{PC}$ 88.8 Hz), 113.4 ($=CH_2$), 124.0-137.0 (ArC), 136.8 (-CH=); $^{31}P\{^1H\}$ NMR: A_2B type, δ 24.4 ($PNMe_2$), 29.9 ($POrg_2$), $^2J_{PP}$ 14.9 Hz.

$(NPCl_2)_2NP^iPr\{C[OC(O)Me]=CH_2\}$ (VAcP)

Acetyl chloride (0.9 ml, 12 mmol) was added slowly to a stirred solution of 1.0 g (3 mmol) of 3 and 1.7 ml (12 mmol) of Et_3N in 50 ml of diethyl ether, cooled to 0 ^oC. The

reaction mixture was then stirred for 18 hours and the temperature was allowed to rise to room temperature. The precipitated salts were removed by filtration. The yellow ether solution was washed with 25 ml of demi-water, dried on $MgSO_4$ and stirred with activated carbon. The ether was evaporated under reduced pressure and the crude product was distilled (bp 140 ^{o}C/0.1 mm Hg) to yield 0.75 g (1.85 mmol, 59%) of a colorless oil, which became a solid upon standing with mp 34.0-36.0 ^{o}C. Anal. Calcd for $C_7H_{12}Cl_4N_3O_2P_3$: C, 20.76; H, 2.99; Cl, 35.02%. Found: C, 21.01; H, 3.07; Cl, 34.85%. ^{1}H NMR ($CDCl_3$): δ 1.19 (dd, 6 H, Me, $^{3}J_{PH}$ 20.7 Hz, $^{3}J_{HH}$ 7.1 Hz), 2.07 (m, 1 H, CH), 2.23 (s, 3 H, C(O)Me), 5.81 (dd, 1 H, =CH_2, $^{2}J_{HH}$ 2.4 Hz, $^{3}J_{PH}$ 31.7 Hz), 5.99 (dd, 1 H, =CH_2, $^{2}J_{HH}$ 2.7 Hz, $^{3}J_{PH}$ 10.5 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 14.0 (Me), 20.8 (-C(O)Me), 28.4 (dt, CH, $^{1}J_{PC}$ 97.7 Hz, $^{3}J_{PC}$ 4.0 Hz), 119.2 (d, =CH_2, $^{2}J_{PC}$ 20.4 Hz), 148.2 (d, CH=, $^{1}J_{PC}$ 146.5 Hz), 167.7 (C(O)). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): A_2B type, δ 19.4 (PCl_2), 30.5 ($POrg_2$), $^{2}J_{PP}$ unresolved.

$[(NPCl_2)_2NP^{i}Pr]_2CMeOH$ (PCP)

A solution of 0.16 g (0.5 mmol) of 3 and 50 µl (0.36 mmol) of Et_3N in 10 ml of THF was cooled to -40 ^{o}C. Acetyl chloride (40 µl, 0.56 mmol) was added quickly to the stirred solution and the temperature was allowed to rise slowly to room temperature. After stirring for 18 h at that temperature the solvent was evaporated, and diethyl ether was added to precipitate the salts. After filtration the ether was removed in vacuo, and the crude product, which consisted of 3, VAcP, and PCP, was further purified by flash chromatography (silica gel 60 mesh 230-400, eluant hexane/THF 85:15, elution order 3, PCP, and VAcP). Yield 0.05 g (0.07 mmol, 29%) of a white solid with mp 174-176 ^{o}C (uncorrected). Anal. Calcd for $C_8H_{18}Cl_8N_6OP_6$: C, 14.05; H, 2.65; Cl, 41.48%. Found: C, 13.91; H, 2.74; Cl, 41.47%. ^{1}H NMR: δ 1.27 (dd, 6 H, Me, $^{3}J_{PH}$ 20.0 Hz, $^{3}J_{HH}$ 7.1 Hz), 1.33 (dd, 6 H, Me, $^{3}J_{PH}$ 19.3 Hz, $^{3}J_{HH}$ 7.1 Hz), 1.80 (t, 3 H, Me, $^{3}J_{PH}$ 15.1 Hz), 2.50 (b,1 H, COH), 2.65 (m, 2 H, CH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 16.2 (CHMe), 16.6 (CHMe), 20.6 (C(OH)Me), 29.3 (dt, CHMe , $^{1}J_{PC}$ 83.6 Hz, $^{3}J_{PC}$ 3.0 Hz), 29.3 (t, COHMe , $^{1}J_{PC}$ 64.5 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): A_2B type, δ 19.0 (PCl_2), 48.2 ($POrg_2$), $^{2}J_{PP}$ unresolved.

$(NPCl_2)_2NP^{i}PrC(Me)_2OSO_2Me$ (PMES)

To a stirred solution of 3.8 g (10.0 mmol) of PAC and 2.2 ml (28.4 mmol) of methanesulfonyl chloride in 25 ml of diethyl ether was added slowly 4 ml (28.8 mmol) of Et_3N. After stirring for half an hour at room temperature the solution was refluxed for 2 hours and filtered to remove the precipitated salts. After filtration the ether was washed with 20 ml water and the water layer was in return extracted twice with 10 ml of ether. The combined ether layers were dried on $MgSO_4$, filtered and stirred with activated carbon. The ether was evaporated under reduced pressure and yielded 3.37 g (7.4 mmol, 73% of theory) of a light yellow oil which crystallized on standing. Recrystallization from pentane resulted in a white solid with mp 79.0-80.5 ^{o}C (uncorrected). Anal. Calc.: C, 18.40; H, 3.53; Cl, 31.03; S, 7.02%. Found: C, 18.68; H, 3.50; Cl, 31.06; S, 7.06%. ^{1}H NMR: δ 1.29 (dd, 6 H, Me, $^{3}J_{PH}$ 19.0 Hz, $^{3}J_{HH}$ 7 Hz), 1.93 (d, 6 H, Me, $^{3}J_{PH}$ 15.6 Hz), 2.3 (m, 1 H, -CH-), 3.1 (s, 3 H, Me); $^{13}C\{^{1}H\}$ NMR: δ 16.1 (Me), 22.1 (Me), 26.7 (d, -CH-, $^{1}J_{PC}$ 88.1 Hz), 41.1 (S-Me), 89.4 (d, -C-, $^{1}J_{PC}$ 108.1 Hz,); $^{31}P\{^{1}H\}$ NMR: A_2B type, δ 19.4 (PCl_2), 46.1 ($POrg_2$), $^{2}J_{PP}$ unresolved.

$(NPCl_2)_2NP^{i}PrC(Me)=CH_2$ (PP)

A solution of 2.2 g (4.8 mmol) of PMES and 1.5 ml (10 mmol) of DBU in 15 ml of acetonitrile was refluxed for 27 hours. After removal of the solvent in vacuo, 75 ml of diethyl ether was added. The ether solution was washed with 20 ml of water and the water layer was extracted twice with 50 ml of ether. The combined ether layers were dried on $MgSO_4$, filtered and stirred with activated carbon. The ether was evaporated under reduced pressure and the crude product was purified by flash chromatography (silica gel 230-400 mesh, eluant hexane/THF 9:1) to yield a light yellow oil, which became a solid after some time. The ^{31}P NMR spectrum showed that the crude product was composed of PP (about 95% of the total peak area) and ANSA (about 5%). The two products were separated from each other by flash chromatography (silica gel 230-400 mesh, eluant hexane/THF 9:1). Recrystallization from pentane yielded 0.63 g (1.75 mmol, 36% of theory) of PP as a white solid with mp 48.5-50.5 ^{o}C. Anal. Calc.: C, 19.97; H, 3.35; Cl, 39.29%. Found: C, 20.27; H, 3.38; Cl, 39.19%. ^{1}H NMR: δ 1.14 (dd, 6 H, Me, $^{3}J_{PH}$ 19.6 Hz, $^{3}J_{HH}$ 7.1 Hz), 1.98 (d, 3 H, Me, $^{3}J_{PH}$ 13.6 Hz), 2.0 (m, 1 H, -CH-), 5.85 (d, 1 H, $=CH_2$, $^{3}J_{PH,trans}$ 44.0 Hz), 5.97 (d, 1 H, $=CH_2$, $^{3}J_{PH,cis}$ 21.5 Hz); $^{13}C\{^{1}H\}$ NMR: δ 14.1 (Me), 17.9 (d, Me, $^{2}J_{PC}$ 13.1 Hz), 27.5 (dt, -CH-, $^{1}J_{PC}$ 92.7 Hz, $^{3}J_{PC}$ 4 Hz), 129.6 (d, $=CH_2$, $^{2}J_{PC}$ 9.1 Hz), 136.6 (dd, -C=, $^{1}J_{PC}$ 109.8 Hz, $^{3}J_{PC}$ 3 Hz); $^{31}P\{^{1}H\}$ NMR: A_2B type, δ 18.2 (PCl_2), 40.2 ($POrg_2$), $^{2}J_{PP}$ unresolved.

$N_3P_3Cl_3(^iPr)\{C(Me)_2CH=C(Me)O\}$ (ANSA)

Recrystallization from pentane gave ANSA with mp 109.0-110.5 ^oC. Anal. Calc.: C, 28.26; H, 4.48; Cl, 27.80%. Found: C, 28.53; H, 4.68; Cl, 27.36%. ^1H NMR: δ 1.24 (dd, 3 H, CHMe, $^3J_{PH}$ 19.6 Hz, $^3J_{HH}$ 7.0 Hz), 1.29 (dd, 3 H, CHMe, $^3J_{PH}$ 18.1 Hz, $^3J_{HH}$ 7.1 Hz), 1.33 (d, 3 H, CMe, $^3J_{PH}$ 15.9 Hz), 1.49 (d, 3 H, CMe, $^3J_{PH}$ 15.2 Hz), 1.92 (m, 3 H, Me), 2.1 (m, 1 H, -CH-), 4.82 (m, 1 H, -CH); $^{13}C\{^1H\}$ NMR: δ 16.1 (CHMe), 16.5 (CHMe), 23.1 (Me), 23.9 (Me), 25.0 (Me), 25.8 (d, -CH-, $^1J_{PC}$ 93.6 Hz), 44.0 (d, -C-, $^1J_{PC}$ 72.7 Hz), 120.4 ($=CH_2$), 148.0 (d, -C=, $^2J_{PC}$ 10.0 Hz); $^{31}P\{^1H\}$ NMR: AXY type with multiplets at 51.8 and 24.5 ppm.

$(NPCl_2)_2NP^iPrC(Me)=CH_2$ (PPN)

Into a round bottom flask cooled with ice was condensed about 1.5 ml (22.6 mmol) of dimethylamine. A solution of 0.50 g (1.4 mmol) of PP in 5 ml of acetonitrile which was cooled in ice was added to the amine. The solution was stirred for 1 day. After removal of the solvent, diethyl ether was added and the salts removed by filtration. The colored ether solution was then stirred with activated carbon. After removal of the carbon by filtration, the ether was evaporated. A clear colorless oil was obtained, which slowly solidified to yield 0.39 g (1 mmol, 71% of theory) of white crystals with mp 58-65 ^oC. Anal. Calc.: C, 42.51; H, 9.18; Cl, 24.80%. Found: C, 42.08; H, 8.93; Cl, 24.03%. ^1H NMR: δ 1.05 (dd, 6 H, Me, $^3J_{PH}$ 17.3 Hz, $^3J_{HH}$ 7.0 Hz), 1.8 (m, 1 H, -CH-), 1.93 (d, 3 H, Me, $^3J_{PH}$ 11.6 Hz), 2.57 (m, 24 H, NMe_2), 5.5 (d, 1 H, $=CH_2$, $^3J_{PH,trans}$ 37.7 Hz), 5.8 (d, 1 H, $=CH_2$, $^3J_{PH,cis}$ 17.5 Hz); $^{13}C\{^1H\}$ NMR: δ 15.1 (-Me), 19.3 (d, $-CH_3$, $^2J_{PC}$ 11.4 Hz), 28.1 (dt, -CH-, $^1J_{PC}$ 99.3 Hz, $^3J_{PC}$ 4 Hz), 36.7 (d, NMe_2, $^2J_{PC}$ 10.2 Hz), 124.9 (d, $=CH_2$, $^2J_{PC}$ 7.6 Hz), 142.8 (d, -C=, $^1J_{PC}$ 107.0 Hz); $^{31}P\{^1H\}$ NMR: A_2B type, δ 23.8 ($PNMe_2$), 33.8 ($POrg_2$), $^2J_{PP}$ 15.4 Hz.

2.4 Results and discussion

2.4.1 STP

As already mentioned in Section 1.3.2, the influence of the strong electron withdrawing phosphazene ring on the double bond of the phosphazene monomer has to be kept as small as possible in order to avoid complications during the polymerization reaction. A very efficient way to achieve this is the use of an insulating spacer group, e.g. phenyl, as was observed for the α-methylstyryl- and styrylfluorocyclophosphazenes (Fig. 2.1) [10,13].

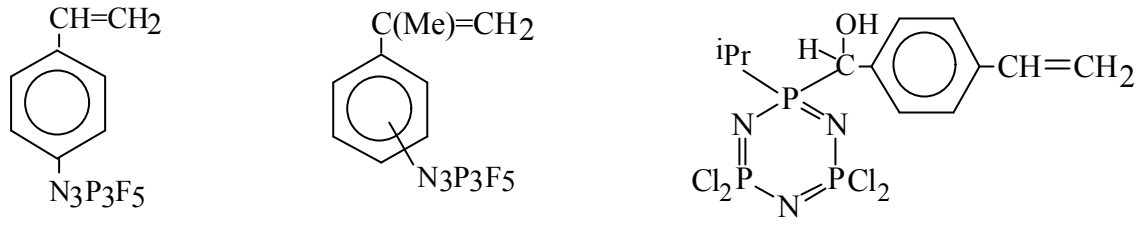
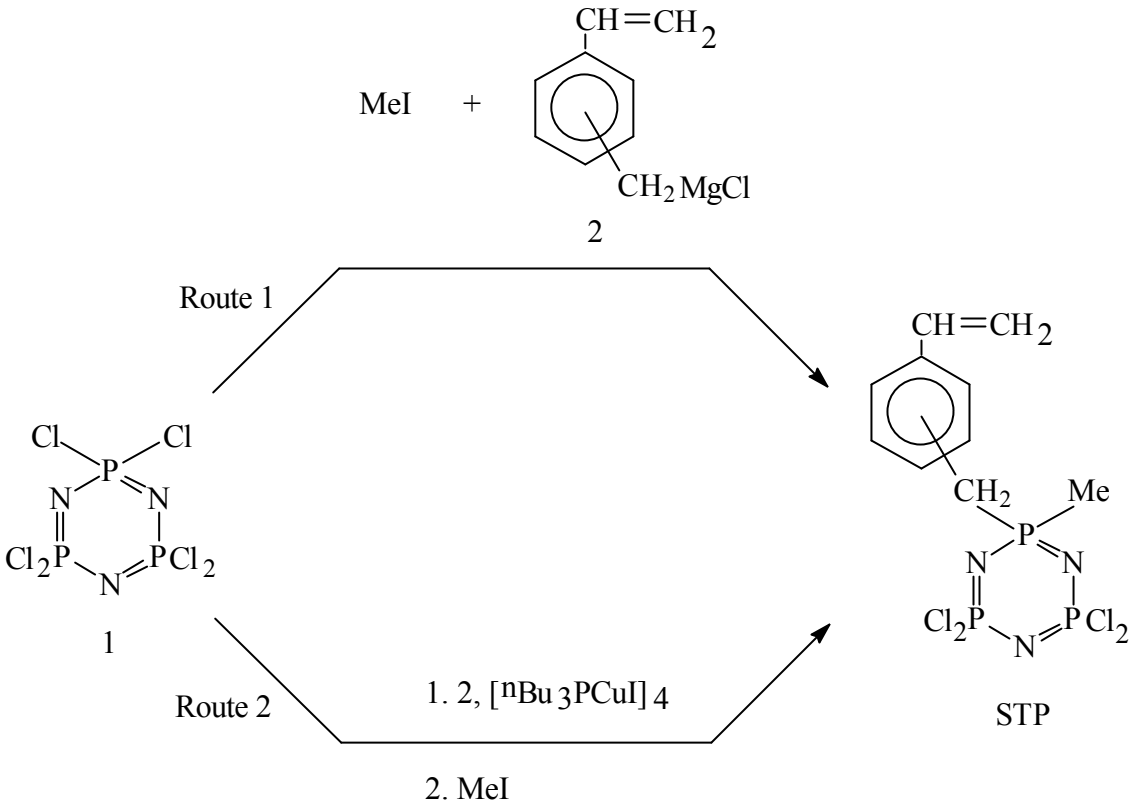


Figure 2.1 Structures of some styrene derivatives

Until now only one other styrene based chlorocyclophosphazene with a direct P-C linkage has been reported (see Fig. 2.1). But due to the presence of a hydroxyl group, which induced cross-linking, the corresponding homopolymer is not stable for long periods of time [7]. However, from NMR data and copolymerization studies it is clear that the benzyl group acts as an excellent spacer between the double bond and phosphazene ring. For this reason we tried to synthesize a chlorocyclophosphazene with a benzyl group as spacer between the double bond and the ring, but without the presence of groups which could give cross-link reactions.

For the synthesis of gem-dialkyl substituted chlorocyclotriphosphazenes with a P-C linkage two routes are generally followed as outlined in Chapter 1 [6,18,19]. The first method involves the addition of a Grignard reagent to a solution of $(NPCl_2)_3$ in THF, which can afford a monoalkylsubstituted cyclophosphazene [18]. Following the second route an intermediate phosphazenocuprate is formed which is allowed to react further with for instance an alkyl halide to give a gem-dialkylsubstituted cyclophosphazene.

We have applied these two methods for the preparation of gem-methyl(vinylbenzyl)tetrachlorocyclotriphosphazene (STP) as shown in Scheme 2.1. Both routes lead to the exclusive formation of STP in good yield. This was confirmed by the ^{31}P NMR spectra of the crude reaction mixtures (see Figure 2.2) which show no



Scheme 2.1 Reaction routes for the synthesis of STP

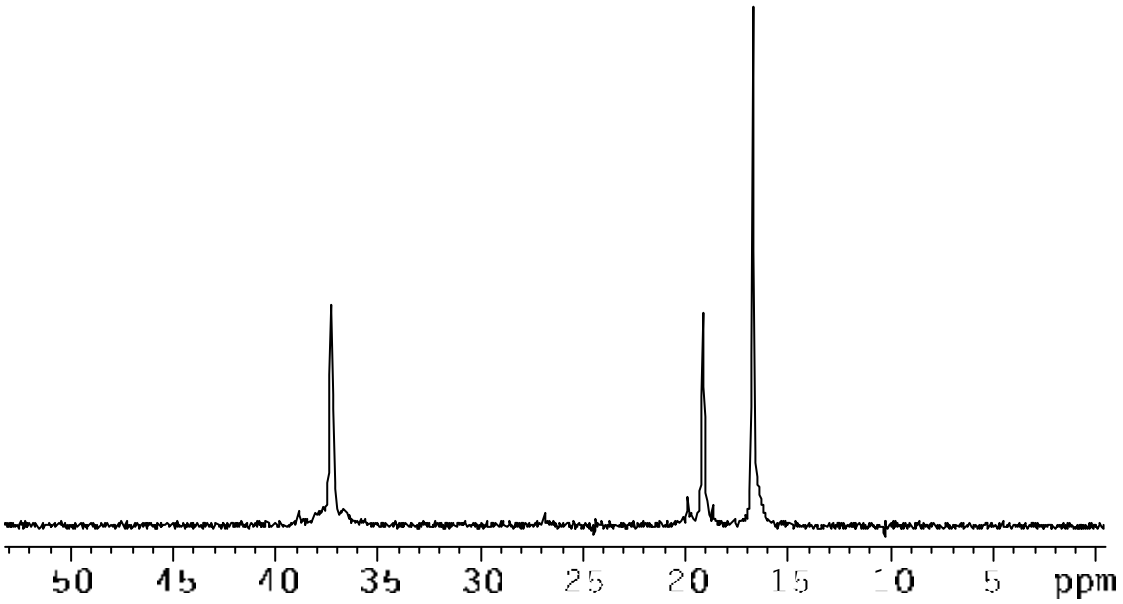


Figure 2.2 Proton decoupled ^{31}P NMR spectrum of the reaction mixture of route 1

resonance signals of other ring products than 1 (19.9 ppm) and STP (18.1 ppm PCl_2, 37.2 ppm Porg).

Due to its facile synthetic procedure, route 1 is favoured above route 2. The only drawback of route 1 is that polymerization occurs under the normal reaction conditions employed when the Grignard reagent is allowed to react with $(NPCl_2)_3$. This side reaction is caused by a metallophosphazene intermediate formed via the metal-halogen exchange mechanism (see Fig. 2.3 and Section 1.2.2) [18]. This nucleophilic compound can act as an anionic initiator for the polymerization of styrene. To avoid this polymerization the normal reaction procedure was slightly modified by adding the Grignard reagent to a solution of $(NPCl_2)_3$ and methyl iodide. In this way the highly reactive alkyl halide (MeI) functions as a 'trapping' agent and reacts quickly with any metallophosphazene that is formed during the reaction.

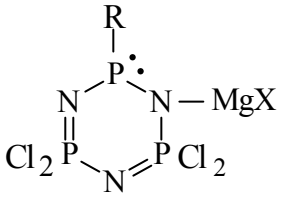


Figure 2.3 Proposed metallophosphazene intermediate in route 1

As a 7:3 mixture of m- and p- vinylbenzyl chloride was used, NMR was used to check whether the same isomer ratio was obtained for STP. Close examination of the aryl regions in the ^{1}H and ^{13}C NMR spectra of both vinylbenzyl chloride and STP gave no indication that the ratio of meta to para isomer was changed when going from vinylbenzyl chloride to STP.

^{13}C NMR chemical shifts are very sensitive to the electron density at the nucleus and can be used to investigate the polarity of the vinyl function to predict the reactivity of the monomer in polymerization reactions. In particular the ß-carbon ($=CH_2$) chemical shift is a good indicator for this purpose.

The ^{13}C NMR spectra of vinylbenzyl chloride and STP showed only one absorption for each of the carbon atoms of the double bond. This means that the vinyl groups of the meta and para isomers are the same from an electronic point of view. The δ $^{13}C(=CH_2)$ value of STP at 114.3 ppm is comparable with that of vinylbenzyl chloride (114.6 ppm) and only slightly shifted downfield compared with that of styrene (113.7 ppm). This means that the double bond is efficiently shielded from the strong electron withdrawing phosphazene ring. Therefore it is

reasonable to assume that the two isomers of STP behave similar compared with styrene in polymerization reactions. This is supported by the observation of Allen et al., that in copolymerization experiments with styrene and the pure para and meta derivatives of $N_3P_3F_5C_6H_4C(Me)=CH_2$ no significant difference in polymerization behavior for each of the isomers was found [10].

2.4.2 VAcP

Apart from the monomer with a spacer group between the phosphazene and double bond, we also prepared cyclophosphazene derivatives belonging to another class of monomers. This class consists of 1,1-disubstituted alkenes with the phosphazene directly bonded to the double bond. Here an alternative method is used to compensate for the electronegative effect of the phosphazene ring by the introduction of an electron donating organic group on the same carbon atom of the double bond. So far only derivatives with fluorocyclotriphosphazene rings have been synthesized (Fig. 2.4) [20,21].

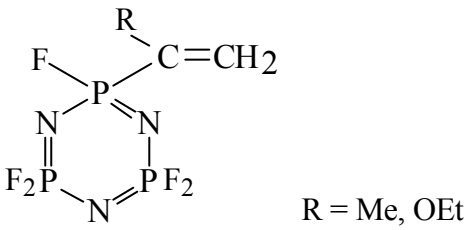


Figure 2.4 1,1-Alkenylfluorophosphazenes

In our case we used reactive hydridochlorocyclophosphazenes as an entry to the synthesis of monomers described above [14,15,17].

The reaction of gem-isopropylhydridotetrachlorocyclotriphosphazene (3) with an excess of acetyl chloride and Et_3N in diethyl ether at ambient temperature yields gem-isopropyl-2-(α-acetoxyvinyl)tetrachlorocyclotriphosphazene (VAcP) as only product, as determined from ^{31}P NMR spectra of crude reaction mixtures. The compound VAcP, which is sensitive to hydrolysis (formation of acetic acid), could be fully characterized by NMR methods and an X-ray structure determination (Fig. 2.5). The molecular structure is discussed in more detail in Chapter 3. From Figure 2.5 it can be clearly seen that the α-carbon atom (C4) of the vinyl acetate derivative is quite inaccessible for the approach of another alkene. This means that in particular 1,1-disubstituted alkenes will suffer from the steric hindrance caused by the bulky acetoxy group and the phosphazene ring.

A comparison of the ^{13}C NMR spectra of both vinyl acetate and VAcP shows the strong electron withdrawing character of the phosphazene ring. For vinyl acetate the ß-carbon of the vinyl group has a resonance signal at 96.8 ppm, while the $\delta\ ^{13}C(=CH_2)$ value of VAcP shows a large downfield shift to 119.2 ppm. For the α-carbon of the vinyl group also a downfield shift observed from 141.8 for vinyl acetate to 148.2 ppm for the VAcP monomer. Despite the fact that the carbon atoms of the double bond have become more electron deficient in comparison with vinyl acetate, the $\delta\ ^{13}C(=CH_2)$ value of 119.2 ppm is intermediate with that of MMA (124.7 ppm) and styrene (113.7 ppm).

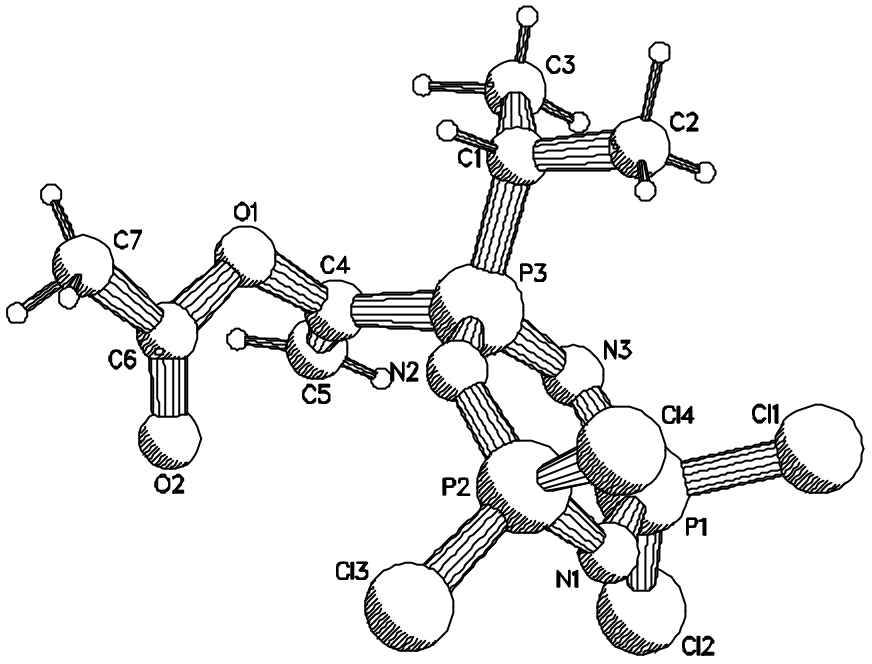
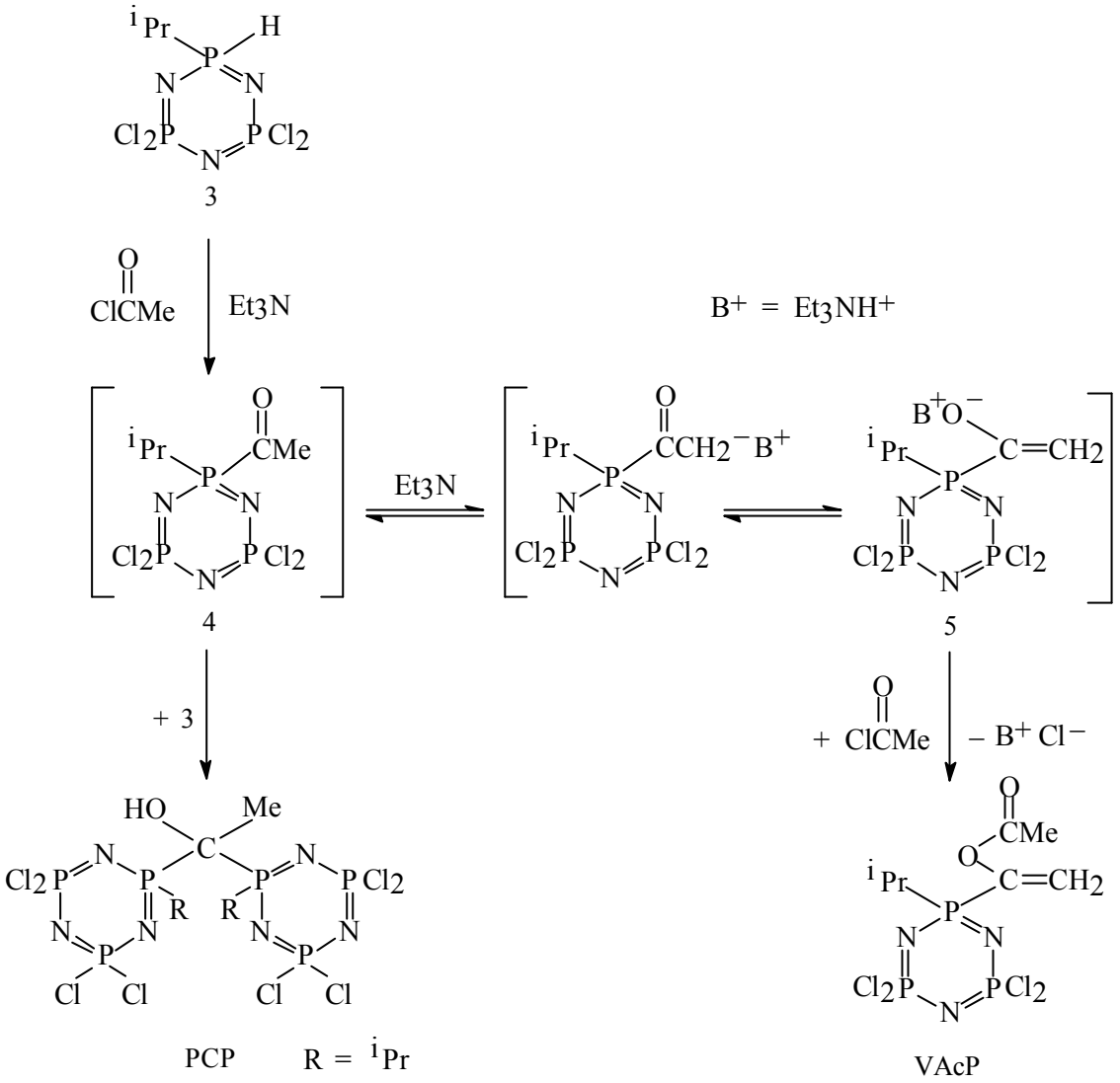


Figure 2.5 Molecular structure of the vinyl acetate derivative (VAcP)

To explain the formation of VAcP, two points should be considered. First, the presence of the α-acetoxyvinyl group directly bonded to the organo-substituted phosphorus atom suggests that two acid chloride molecules are involved in the reaction with 3. Secondly, it is known that hydridocyclophosphazenes can act as nucleophiles, which implies that these compounds are capable to nucleophilic addition reactions at carbonyl functionalities [14,15,22]. For that reason it is very probably that the formation of an acetyl derivative (4, see Scheme 2.2) can be considered as the first step of the reaction sequence.

Due to the presence of the strong electron withdrawing phosphazene ring in combination with the electronegative carbonyl group, the acidity of the methyl protons in 4 is increased compared to acid chloride or ester. Abstraction of hydrogen with a base



Scheme 2.2 Reaction mechanism for the synthesis of VAcP and PCP

results in the formation of the enolate intermediate 5. Subsequent reaction of 5 with a second molecule of acetyl chloride leads to the formation of PCP.

To obtain some evidence for the reaction scheme proposed, 3 was allowed to react with 1.1 equiv. of acetyl chloride and 0.7 equiv. of Et_3N in THF at -40 ^{o}C. Under these reaction conditions the ^{31}P NMR spectrum of the crude reaction mixture showed that only a small quantity of VAcP was formed together with a relatively large amount of another product with resonance signals at 48.2 and 19.0 ppm. These resonances could be assigned to the novel compound PCP in which two cyclophosphazene rings are bridged by one carbon atom. The

bicyclophosphazene was fully characterized by means of NMR (^{1}H, ^{13}C and ^{31}P) and elemental analyses.

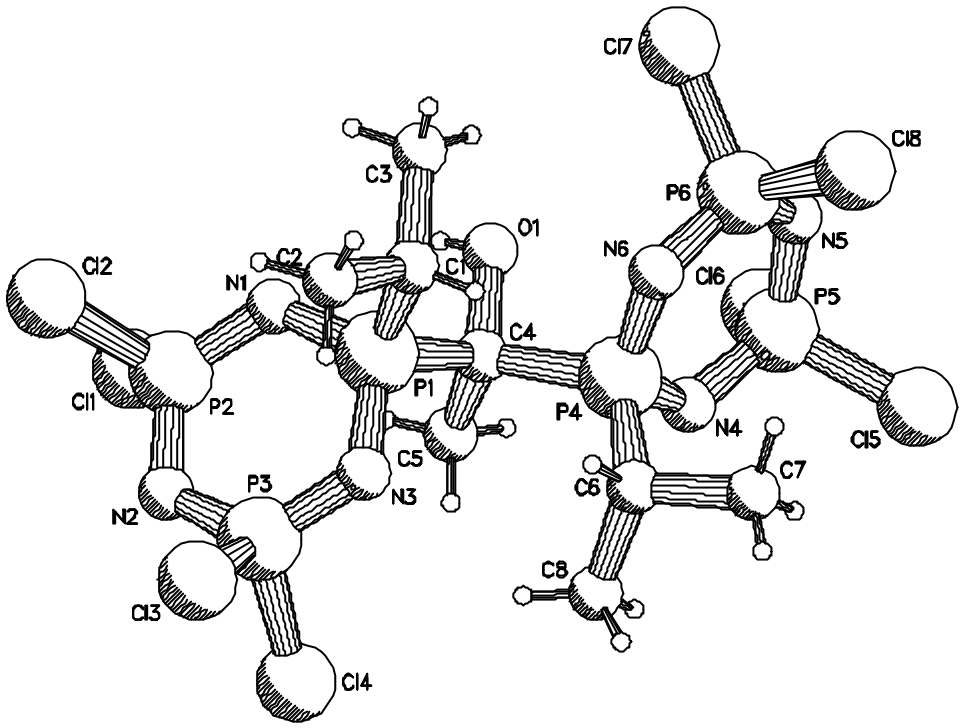


Figure 2.6 PLUTO drawing of the carbon-bridged bicyclophosphazene (PCP)

Furthermore the structure of $N_6P_6Cl_8(^iPr)_2C(Me)OH$ was confirmed by a single-crystal X-ray structure determination (Fig. 2.6) which will be considered in more detail in Chapter 3.

The formation of PCP follows the proposed mechanism and explains the influence of the amount of base and acetyl chloride on the reaction pathways. When excess Et_3N and acetyl chloride is used, the equilibrium between 4 and 5 is shifted to the right, and any 5 that is formed will react directly with acetyl chloride to give VAcP. Moreover, the excess acetyl chloride will convert all hydridophosphazene immediately into 4. Consequently, there is no or very little hydridophosphazene available for side reactions. This is in agreement with the observation that under these circumstances only resonance signals of VAcP are found in the ^{31}P NMR spectrum of the crude reaction mixture and no traces of PCP can be detected. When an excess of hydridophosphazene is present an alternative pathway is possible during which 4 reacts with a second molecule of hydridophosphazene to give the bicyclic compound PCP.

In the proton decoupled ^{13}C NMR spectrum of the bicyclophosphazene derivative (PCP) two singlet resonances (16.2 and 16.6 ppm) are observed in the methyl carbon region of the isopropyl group. As this phenomenon can not be the result of a P-C coupling, the two methyl groups of the isopropyl group must be magnetically inequivalent. This effect is also seen in the ^1H NMR spectrum of PCP. Where for VAcP the methyl resonances (1.19 ppm) appear as a

double doublet ($^{3}J_{PH}$ 20.7 Hz, $^{3}J_{HH}$ 7.1 Hz), for PCP two separate double doublets at 1.27 and 1.33 ppm are observed (Fig. 2.7). The observed inequivalence arises from the fact that the isopropyl group is bonded to a so-called prochiral phosphorus centre. As a result the two methyl groups become diasteriotopic.

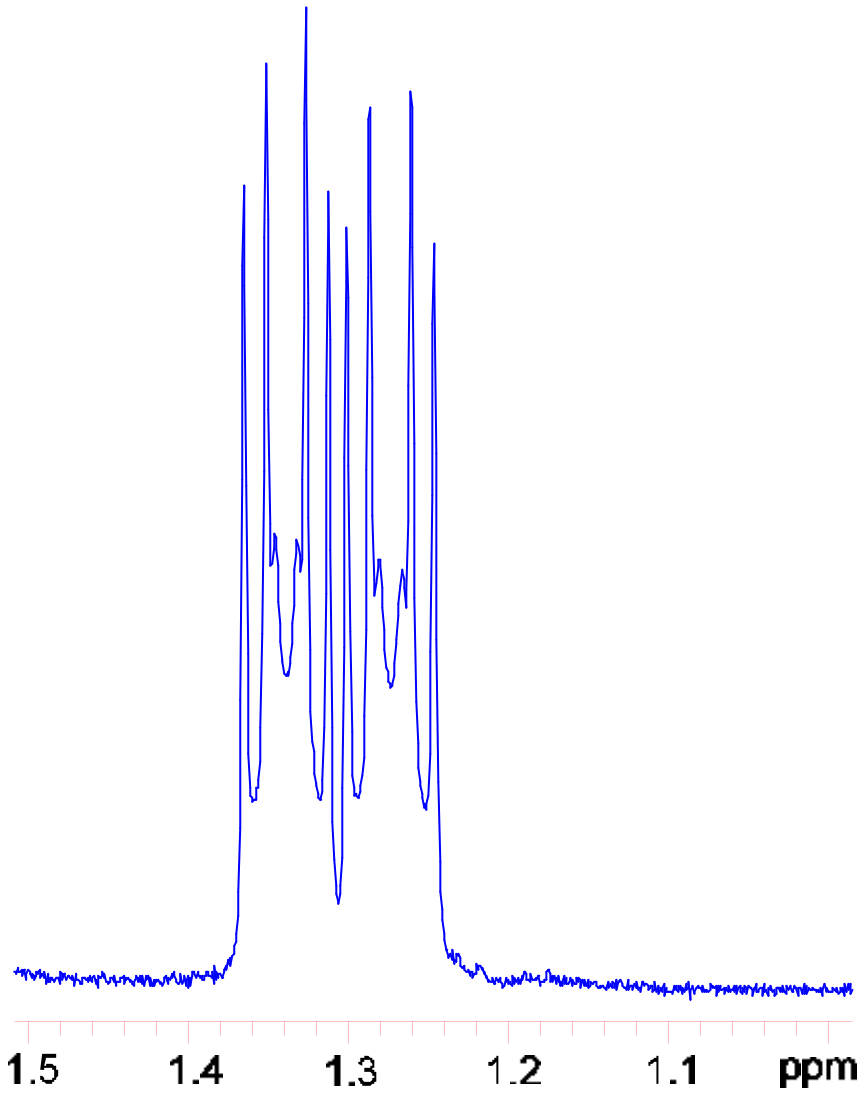
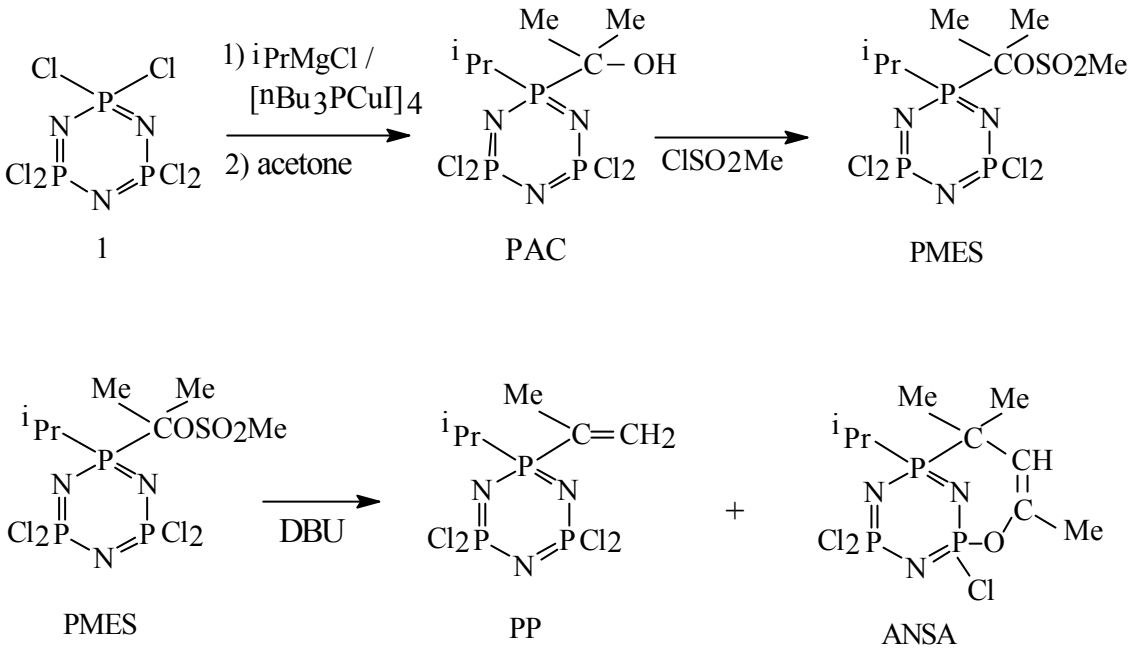


Figure 2.7 The alkyl region in the 500 MHz ^{1}H NMR spectrum of the PCP derivative

2.4.3 PP

In VAcP the acetoxy substituent counterbalances the electronegative effect of the phosphazene ring. To investigate to what extent the acetoxy group reduces the electron deficiency of the double bond, a monomer with a methyl group on the double bond was synthesized according to Scheme 2.3.



Scheme 2.3 Reaction scheme for the synthesis of PP

The first step involves the synthesis of the well-known (hydroxypropyl)tetrachloro-cyclotriphosphazene (PAC) via the reaction of a phosphazenocuprate and acetone [6]. Dehydration of this alcohol derivative can afford the desired propenylcyclophosphazene (PP). A large number of procedures have been described for the conversion of alcohols to olefins of which some require the use of a dehydrating agent such as $KHSO_4$, KOH or anhydrous $CuSO_4$ [22-24]. Secondary and tertiary alcohols are also dehydrated on refluxing with hexamethylphosphoric triamide (HMPT) [25]. This last method is however not applicable for PAC as dimethylamine is formed during the dehydration reaction which can react with the PCl_2 groups [12,26].

Attempts to prepare PP via the direct thermal dehydration of PAC were only partly successful. The ^{31}P NMR spectra of the reaction mixtures showed that only small amounts of the propene derivative (resonances at 18.2 and 40.2 ppm) were formed. The major fraction appeared to be starting material (18.6 and 50.3 ppm), together with an unknown compound

with resonances at 17.7 and 56.5 ppm. A small amount of this unknown compound is also present in the reaction mixture after the first step. No attempts were made to isolate this product.

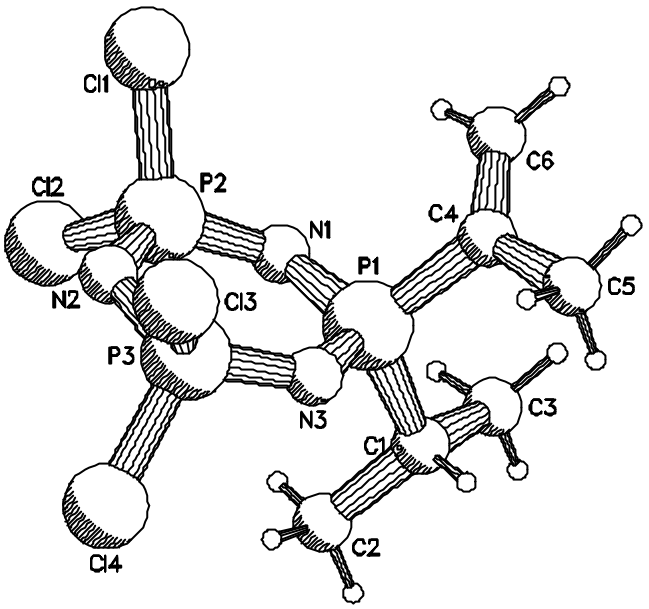


Figure 2.8 Molecular structure of the propene derivative (PP)

The low yields of propenylcyclophosphazene obtained with this direct method prompted us to transform the hydroxyl group to a better leaving group. Reaction of PAC with methanesulfonyl chloride yields $(NPCl_2)_2NP^iPrC(Me)_2OSO_2Me$ (PMES). Subsequent elimination of the sulphonium group on refluxing in acetonitrile in the presence of the base DBU proceeds smoothly to give $(NPCl_2)_2NP^iPrC(Me)=CH_2$ (PP). The molecular structure of this compound is shown in Figure 2.8 and will be described in more detail in Chapter 3. In the ^{13}C NMR spectrum of PP a large downfield shift to 129.6 ppm is observed for the absorption of the ß-carbon of the vinyl group. For VAcP the $\delta\ ^{13}C(=CH_2)$ value is 119.2 ppm which reflects the larger electron donating capacity of the acetoxy substituent as the phosphazene group is identical in both compounds. For the compound $N_3P_3F_5C(Me)=CH_2$ a ß-carbon shift of 131.6 ppm has been reported, which is close to the value in PP [27].

Apart from the expected propene derivative a small quantity of another compound was present in the reaction mixture. This compound appeared to be an ansa derivative, of which the X-ray structure is presented below (Fig. 2.9). In the ^{31}P NMR spectra of the crude reaction mixtures no resonance signals of compounds other than PP, PMES and ANSA are detected.

The formation of ANSA is not observed during the thermal dehydration reaction of PAC. The underlying reaction pathway leading to the formation of ANSA is believed to proceed via reaction of acetone with PMES. The proposed mechanism is shown in Scheme 2.4. The origin of traces of acetone in the reaction mixture is presumably the result of some hydrolysis of PMES.

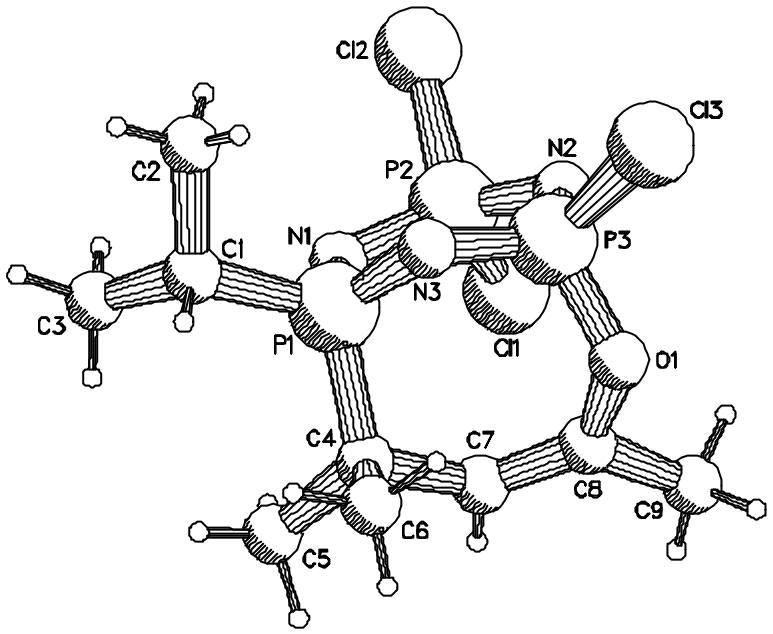
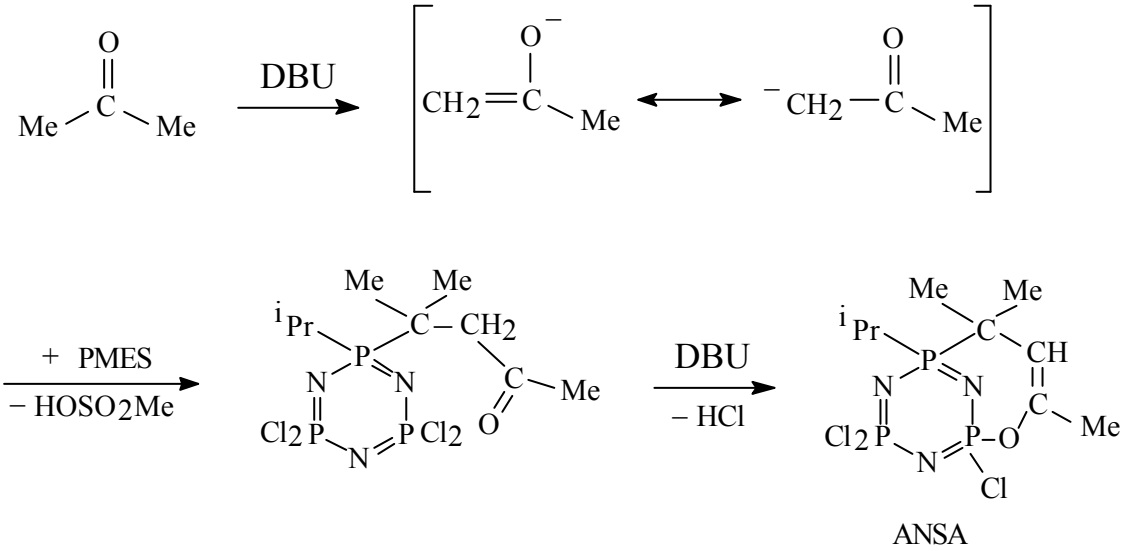


Figure 2.9 X-Ray structure of the ANSA derivative



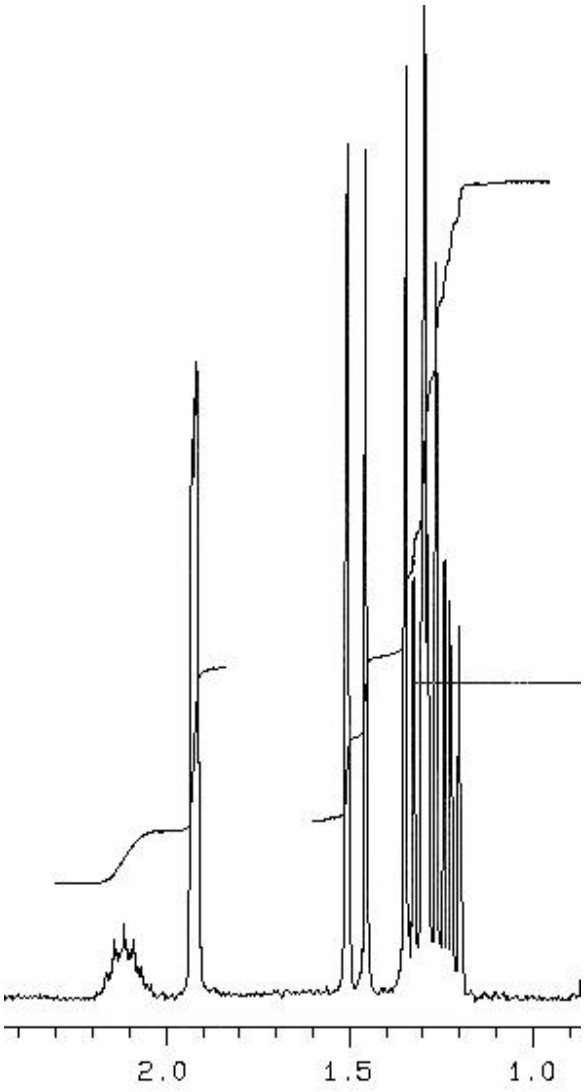


Figure 2.10 The alkyl region in the ^{1}H NMR spectrum of the ANSA derivative

Examination of the ^{1}H NMR spectrum of ANSA (Fig. 2.10) reveals that the two methyl groups (C2 and C3) of the isopropyl substituent are not magnetically equivalent. Whereas for similar phosphazene compounds with an isopropyl ligand only one double doublet is observed due to P-H ($^{3}J_{PH}$) and H-H ($^{3}J_{HH}$) coupling, the methyl groups in ANSA appear as two partly overlapping double doublets (1.24 and 1.29 ppm). The inequivalence of C2 and C3 becomes also manifest in the proton decoupled ^{13}C NMR spectrum where two resonance signals at 16.1 and 16.5 ppm are found. The observed inequivalence can be explained from the fact that the isopropyl group is attached to an asymmetrical phosphorus atom (P1). As a result the two methyl groups are diastereotopic. The C5 and C6 methyl groups are also magnetically

inequivalent and appear as two separate doublets at 1.33 and 1.49 ppm ($^3J_{PH}$ 15.9 and 15.2 Hz, respectively) in the ^1H NMR spectrum and as two singlets in the ^{13}C NMR spectrum.

2.4.4 Dimethylaminolysis of STP and PP

The remaining chlorine atoms in STP and PP can be replaced smoothly by dimethylamine in acetonitrile. The fully amino-substituted derivatives STPN and PPN are both crystalline compounds and show a remarkable good solubility in both polar and apolar solvents. The molecular structure of STPN will be discussed in Chapter 3.

The influence of the electron donating dimethylamine groups on the double bond was investigated by ^{13}C NMR. In Table 2.1 the ß-carbon shift for the vinyl group of the various synthesized cyclophosphazene monomers is listed along with their organic analogues. For STP no significant difference is observed when compared with STPN (114.3 and 113.4 ppm, respectively). This reflects the efficiency of the benzyl group as an electronic insulating spacer.

However, in the case of PP the introduction of dimethylamine groups to the phosphazene ring has a marked influence on the electron distribution in the vinyl group. The electron donating capacity of the amines is reflected in a higher electron density at the ß-carbon in PPN (124.9 ppm) when compared with the value of PP (129.6 ppm).

Table 2.1 Selected olefin ^{13}C chemical shifts

compound	- C =	= CH_2
STP	136.3	114.3
STPN	136.8	113.4
VAcP	148.2	119.2
PP	136.6	129.6
PPN	142.8	124.9
$N_3P_3F_5C(Me)=CH_2$	134.1	131.6
vinyl acetate	141.8	96.8
styrene	136.9	113.7
MMA	136.9	124.7

chemical shifts are reported in ppm

During the purification of STPN it was observed that the monomer is capable of spontaneous polymerization. However, as the polymer product was not soluble in any solvent

this means that cross-linking has occurred. Since only one polymerizable functionality is present in the monomer cross-linking implies that N-methyl groups at the phosphazene ring are in some way responsible for the cross-linking process. When copolymerizing STPN with styrene under free radical conditions these reactions afforded also insoluble polymers.

From literature it is known that radical (co)polymerization reactions with organofunctional borazine monomers (shown in Figure 2.11) yield cross-linked materials as well [28]. To explain the observed cross-linking behavior a mechanism was proposed which involves chain transfer to polymer. In this case the radical centre derived from the vinyl group abstracts a N-methyl hydrogen atom. The newly formed radical then adds to another vinyl group leading to the observed cross-linking. It is likely that for STPN a similar process takes place.

For PPN the cross-linking is not observed. Probably the larger steric hindrance at the double bond prevents the monomer from homopolymerization.

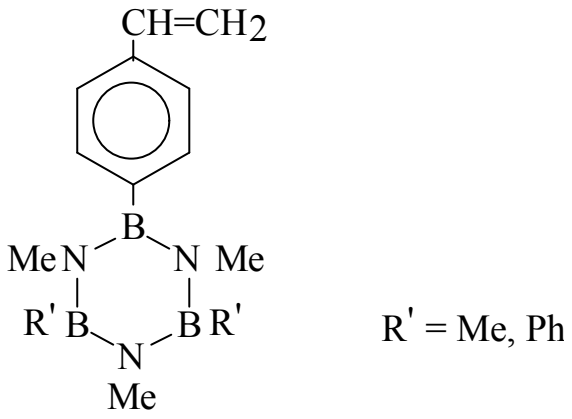


Figure 2.11 Organofunctional borazine monomers

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