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THE REACTIONS OF $N_3P_3Cl_4[NH(CH_2)_3NMe]$ WITH DIFUNCTIONAL FLUORO ALCOHOLS

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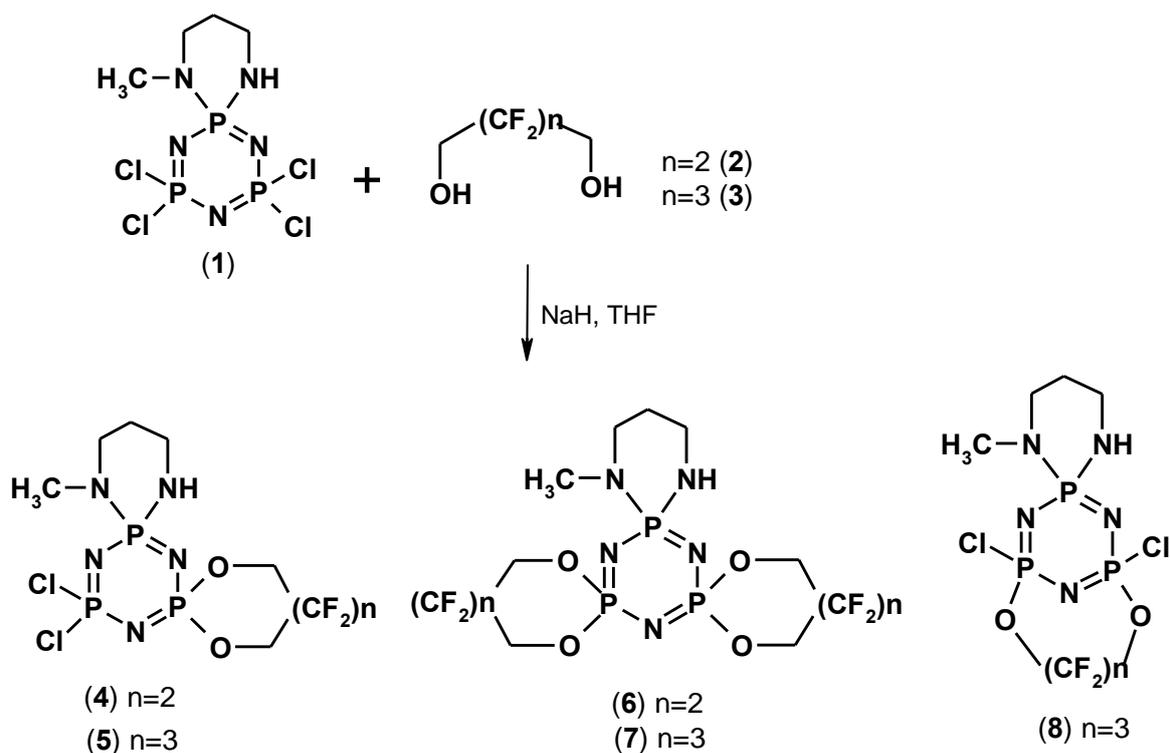
Abstract – The reactions of $N_3P_3Cl_4[NH(CH_2)_3NMe]$ (**1**) in one stoichiometry (1:1) with the sodium derivatives of the fluorinated diols 2,2,3,3-tetrafluorobutane-1,4-diol (**2**) and 2,2,3,3,4,4-hexafluoropentane-1,5-diol (**3**) in THF solution at room temperature yielded the following five products, whose structures (**4-8**) have been characterized by elemental analysis, mass spectrometry, FT-IR, 1H and ^{31}P NMR spectroscopy: the mono-spiro compound, $N_3P_3Cl_2[NH(CH_2)_3NMe](OCH_2CF_2CF_2CH_2O)$ (**4**), a di-spiro derivative $N_3P_3[NH(CH_2)_3NMe](OCH_2CF_2CF_2CH_2O)_2$ (**6**) and the mono-spiro compound, $N_3P_3Cl_2[NH(CH_2)_3NMe](OCH_2CF_2CF_2CF_2CH_2O)$ (**5**), its ansa isomer (**8**), a di-spiro derivative $N_3P_3[NH(CH_2)_3NMe](OCH_2CF_2CF_2CF_2CH_2O)_2$ (**7**). Besides, the thermal properties of the compounds (**1, 4-8**) were investigated by thermal analysis, namely by DSC and TGA.

INTRODUCTION

The reactions of phosphazenes with difunctional alcohols are widely studied.¹⁻⁴ The four types of products derived from the reactions of cyclotriphosphazenes with diols (spiro, ansa, open chain, and bridged compounds) are well established.⁵ Reaction of $N_3P_3Cl_6$ (trimer) with 1,2-ethane-, 1,3-propane- and 1,4-butane-diols (in the presence of pyridine to neutralize the HCl formed) predominantly gave spiro derivatives with 5-, 6-, 7-membered phosphate rings, respectively, whereas ansa derivatives were obtained only in small yields.⁶ A bridged derivative was observed as a minor product with butanediol, indicating that chain length was a contributing factor in determining derivative-type.⁵ It was also found that ansa-derivatives are formed using sodium salts of diols as reagents in polar solvents such as THF.^{7,8}

Reaction of $N_3P_3Cl_6$ with amino-alcohols, diamines and their -NMe derivatives showed a preference for spiro-derivatives, when the linking $-(CH_2)_n-$ group of the reagent consisted of $n = 2,3$ moieties.⁹ Bridged compounds are formed by the reactions of $N_3P_3Cl_6$ with diamines of increasing chain length ($n = 4, 5$).¹⁰ Guerch et al.¹¹ reported that for the forming of bridged compounds one needs at least chain lengths of five ($n > 5$). The reactions of a trimer with the sodium derivative of the fluorinated diol 2,2,3,3-tetrafluorobutane-1,4-diol (**2**) and 2,2,3,3,4,4-hexafluoropentane-1,5-diol (**3**) yield mono-spiro, di-spiro, tri-spiro, ansa, di-ansa and spiro-ansa products.⁶ The chemical and physical properties of phosphazenes change with the substituted side groups. So, it is possible to design materials with special properties such as inflammable textile fibers and advanced elastomers,¹² anticancer agents,¹³⁻¹⁵ hydraulic fluids and lubricants,^{16,17} electrical conductivity,¹⁸ fertilizers,^{19,20} and flame retardant properties.^{21,22} Over the past two decades, a considerable amount of research has been devoted to the synthesis and analysis of cyclic phosphazene trimers substituted with fluorinated groups as lubricants for magnetic recording media,²³⁻²⁷ for example computer hard disks, video and computer tapes, etc.

The reactions of (**1**) with 2,2,3,3-tetrafluorobutane-1,4-diol (**2**) and 2,2,3,3,4,4-hexafluoropentane-1,5-diol (**3**) giving compounds (**4**, **5**, **6**, **7**, **8**), respectively, (Scheme 1) is presented in this work. The new compounds (**4-8**) have been characterized by elemental analysis, mass spectrometry, FT-IR, 1H and ^{31}P NMR spectroscopy. The thermal properties of the compounds (**4-8**) were investigated by DSC and TGA.



Scheme 1

RESULTS AND DISCUSSION

NMR Spectra

Each of the compounds was characterized by ^1H and ^{31}P NMR spectroscopy. The ^1H NMR results are provided as part of the analytical data in the synthesis section for each new compound and the ^{31}P NMR chemical shifts and phosphorus–phosphorus coupling constants are summarized in Table 1.

Table 1. ^{31}P NMR parameters of compounds (1, 4-8)^a

Cpd	δPCl_2 ppm	[P(R)] [O(CH ₂ (CF ₂) ₂ CH ₂)O] [O(CH ₂ (CF ₂) ₃ CH ₂)O]	[PCl(R)] [O(CH ₂ (CF ₂) ₃ CH ₂)O]	[PNMe(CH ₂) ₃ NH]	$^2\text{J}(\text{PP})/\text{Hz}$	Ref
(1) ^b	23.2			12.8	39.5	31
(4) ^c	26.7	16.0		17.6	34.5; 80.7; 66.5	This work
(6) ^d		21.3		21.6	63.1	This work
(7) ^d		19.8		21.6	61.2	This work
(5) ^c	26.5	15.0		17.6	34.7; 79.8; 64.1	This work
(8) ^b			25.1	17.0	52.8	This work

^a 500MHz ^{31}P NMR measurements in CDCl_3 solutions at 298 K. Chemical shifts referenced to external H_3PO_4 .

^b ^{31}P NMR spectrum analysed as an A_2X spin system.

^c ^{31}P NMR spectrum analysed as an AMX spin system.

^d ^{31}P NMR spectrum analysed as an AB_2 spin system.

In the proton decoupled ^{31}P NMR spectrum of (4 and 5) peaks at 26.7 and 26.5 ppm were observed (Table 1) which are corresponding to the PCl_2 groups of fluoroalkoxide substituted phosphazene. These findings are in agreement with the literature.^{6,28} Looking at the NMR spectra one can see that the chemical shift of the phosphorous atoms of the spiro-ring depends on the nature of substituent. For example, when the substituted spiro group, such as $[-\text{OCH}_2(\text{CF}_2)_n\text{CH}_2\text{O}-]$, where $n=2,3$ chemical shift between 15.0-21.3 ppm is observed in the ^{31}P NMR spectrum, depending on the degree and type of the substituent. $\text{PCl}(\text{R})$ group of compound (8) give a signal at 25.1 ppm in the proton decoupled ^{31}P NMR spectrum. Two methods were used to quantify the products of the reactions of compounds (1) with various nucleophiles, one method compares the amounts of compounds that were isolated and purified, whereas the other method quantifies the relative amounts of each compound from the proton-decoupled ^{31}P NMR spectrum of the reaction mixture (Table 2). Compound (1) and (2) reacted to the compounds (4) and (6). In Figure 1 is shown the proton-decoupled ^{31}P NMR spectrum of the reaction mixture (Figure 1a),

obtained by the reaction of (1) and 2,2,3,3-tetrafluorobutane-1,4-diol (2), as well as the proton-decoupled ^{31}P NMR spectra of the isolated and separated compounds (4) (Figure 1b) and (6) (Figure 1c). The reaction of compound (1) with 2,2,3,3,4,4-hexafluoropentane-1,5-diol (3) resulted mono-spiro (5), di-spiro (7) and mono-ansa (8) products (Figure 2). In the spectrum of reaction mixture (2a) we observed four groups of the peaks belonging to starting material (1), mono-spiro, di-spiro and mono-ansa products (chemical shifts of the all compounds are given in Table 1). The amount of the mono-spiro, di-spiro and mono-ansa products are given in Table 2. Generally, the yield rates obtained from the ^{31}P NMR of the reaction mixture are higher than the calculated yields obtained after the isolation and purification of the products. It is likely that the quantitation of reaction products in the reaction mixture by ^{31}P NMR spectroscopy is more reliable than that after the isolation procedure, because the only sample preparation for the NMR investigation was to filter the reaction mixture, evaporate off the solvent under vacuum and dissolve the residue in CDCl_3 solution, whereas, during the chemical separation and purification procedure some material remains in the chromatographic column used for the separation of the individual compounds from the reaction mixture and is lost during purification processes (recrystallization etc.).

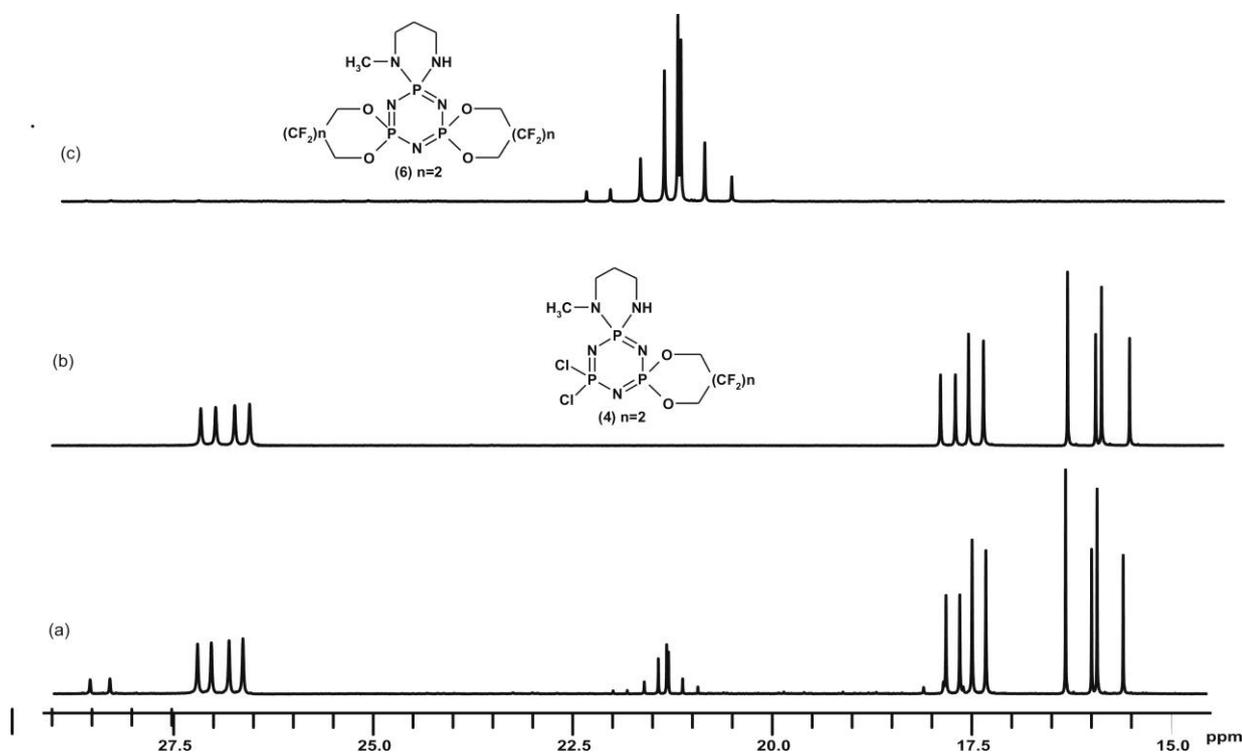


Figure 1. a) Proton-decoupled ^{31}P NMR spectrum of the reaction of compound (1) with 2,2,3,3-tetrafluorobutane-1,4-diol (2) at a 1:1 ratio in THF solution; the reaction mixture was filtered and solvent removed prior to dissolving in CDCl_3 . b) Proton-decoupled ^{31}P NMR spectrum of compound (4) c) Proton-decoupled ^{31}P NMR spectrum of compound (6).

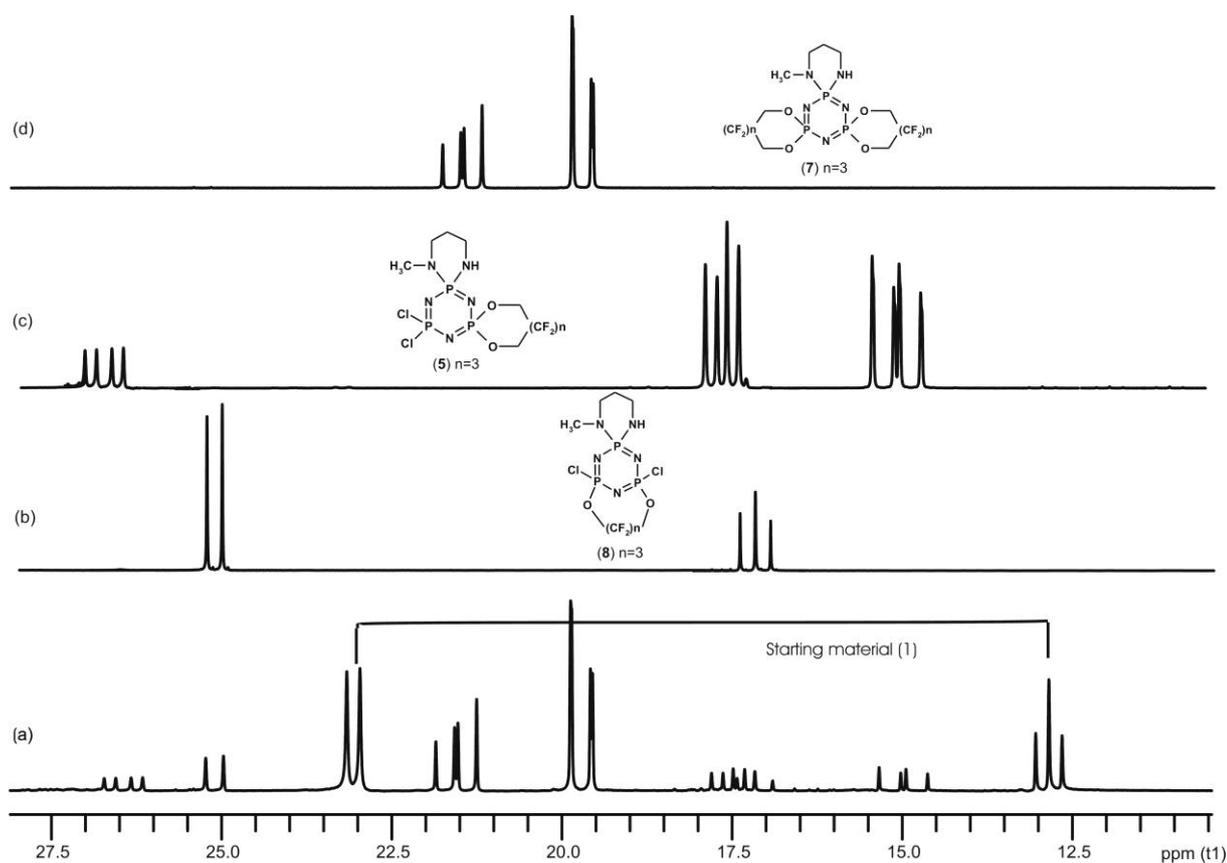


Figure 2. a) Proton-decoupled ^{31}P NMR spectrum of the reaction of compound (1) with 2,2,3,3,4,4-hexafluoropentane-1,5-diol (3) at a 1:1 ratio in THF solution; the reaction mixture was filtered and solvent removed prior to dissolving in CDCl_3 . b) Proton-decoupled ^{31}P NMR spectrum of compound (8) c) Proton-decoupled ^{31}P NMR spectrum of compound (5) d) Proton-decoupled ^{31}P NMR spectrum of compound (7).

Table 2. Quantitation of products of reactions of nucleophiles with compound (1)^a

Isolation procedure					^{31}P NMR of reaction mixture			
(Cpd. No); % yield (experimental)					(Cpd. No); % products			
Nucleophile ^a	starting material (1)	mono-spiro (4), (5)	di-spiro (6), (7)	mono-ansa (8)	mono-spiro (4), (5)	di-spiro (6), (7)	mono-ansa (8)	starting material (1)
(i) reactions of nucleophile with compound (1) in a ca.1:1 molar ratio								
$[\text{OH}(\text{CH}_2(\text{CF}_2)_2\text{CH}_2)\text{OH}]$ (2)	-	55	8	-	87	13	-	
$[\text{OH}(\text{CH}_2(\text{CF}_2)_3\text{CH}_2)\text{OH}]$ (3)	30	7	30	7	10	41	9	40

^aReactions of compound (1) with nucleophiles were effected as the sodium alkoxide in THF.

Thermal Analysis

The aim of the thermal analysis study was to investigate the influence of the degree and the type of the substituent on the thermal stability of the molecules. Therefore, in this study the unsubstituted trimer,

compound (1), the mono-spiro compounds (4 and 5), the di-spiro compounds (6 and 7), and the mono-ansa compound (8) were chosen for the comparison concerning to the thermal properties of the molecules.

The significant data obtained by the thermal analysis methods (TGA/DSC) are given in table 3. The melting points (T_m) of the compounds are determined using the DSC technique. The DSC data show that the melting points of the compounds increase with the substitution. Looking on the melting points of the all compounds, one can see that the mono-spiro compounds (4 and 5) show lower melting points (124 °C and 130 °C) than the di- substituted and mono-ansa substituted compounds. The lowering of the melting point might be due to the presence of H-bonding seen in the FT-IR spectra. Similar effects were observed also in other study.²⁹ The TGA of compounds was recorded between RT and 1000 °C under 50 ml/min N₂ flow. It was found that the starting point of the decomposition temperature (T_d) of the mono substituted compounds (4 and 5) is different from the decomposition of di-substituted ones. Comparing the onset temperature (T_{on}) of these molecules, the mono substituted compounds (4 and 5) are decomposing faster than the di-substituted ones, besides, the mono substituted analogues decomposes in several steps. In the thermogram of the compound (5) a loss of mass (6.86 %) is observed at around 70 °C correspond to the loss of 2 mol of water. The presence of the water in the molecule is confirmed by the FT-IR spectrum. The decomposition of mono-ansa compound (8) started already at 168 °C and ended at 268 °C as expected when one compared this with the mono substituted analogues (4 and 5), since the ring stress in mono-ansa compound (8) is higher than the mono substituted (4 and 5) ones.

Table 3. Significant results of thermal analysis

Compounds	DSC (T_m)	First mass loss in TGA (% wt Loss) (°C)	
		T_{on}	T_{dm}
Trimer	114	159	205
(1)	157	209	253
(4)	124	215	256
(6)	226	281	285
(5)	130	240	290
(7)	204	250	289
(8)	167	168	260

T_{on} : Onset temperature, starting point of the decomposition processes

T_{dm} : Maximum point of decomposition temperature

To resume, in this study, different derivatives of the spiro and ansa cyclotriphosphazenes containing different number of fluoro atoms were successfully synthesized and characterized using various spectroscopic techniques. Additionally, thermal properties of the compounds were determined using thermal analysis methods like TGA and DSC.

EXPERIMENTAL

1. Materials

Hexachlorocyclotriphosphazene (Otsuka Chemical Co. Ltd) was purified by fractional crystallization from hexane. Sodium hydride, 60 % dispersion in mineral oil (Merck), the latter removed by washing with dry heptane (Merck) followed by decantation. Hexane, heptane, ethylacetate, dichloromethane (Merck), 2,2,3,3-tetrafluoro-1,4-butanediol and 2,2,3,3,4,4-hexafluoropentane-1,5-diol, N-methyl-1,3-propane-di amine (Aldrich) were used as received. THF was distilled over a sodium–potassium alloy under an atmosphere of dry argon. All reactions were performed under a dry argon atmosphere. For column chromatography silica gel (230–400 mesh Merck) was used.

2. Methods

Elemental analyses were obtained using a Carlo Erba 1106 Instrument. Mass spectra were recorded on a Bruker MicrOTOF LC-MS spectrometer using the electrospray ionization (ESI) method; ^{35}Cl values were used for calculated masses. Analytical Thin Layer Chromatography (TLC) was performed on Merck silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230-400 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm in diameter and 60 cm in length). ^1H and ^{31}P NMR spectra were recorded in CDCl_3 solutions on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^1H NMR and 85 % H_3PO_4 as an external reference for ^{31}P . The FT-IR spectra were recorded with Bio-Rad 175 FTS. The spectrum resolution was 2 cm^{-1} and 16 scans were recorded for all samples. The spectra were recorded on the base of KBr pellet technique. The thermal analyses are performed on Mettler Toledo TGA/SDTA 851 and Mettler Toledo DSC 822 devices. The thermo gravimetric analyses are measured between 20 and 1000 °C with 10 °C/min and under the 50 mL/min N_2 flow. The DSC data recorded between RT and 350 °C. The heating rate was also 10 °C/min.

3. Synthesis

Reaction of compound (1) with 2,2,3,3-tetrafluorobutane-1,4-diol (2) to form (4), (6).

Compound (1)³¹ (2 g, 5.5 mmol) and 2,2,3,3-tetrafluoro butanediol (2) (0.9 g, 5.5 mmol) were dissolved in 70 mL of dry THF in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60 % oil suspension, 0.44 g, 11 mmol) in 10 mL of dry THF was quickly added to

the stirred solution under an argon atmosphere. The reaction was stirred for 23 h at rt and followed by TLC silica gel plates using *n*-hexane:EtOAc (3:2) and 2 compounds were observed. The reaction mixture was filtered to remove sodium chloride, the solvent removed under reduced pressure and the resulting colourless oil was subjected to column chromatography, using hexane:EtOAc (3:2) as eluent. The first product is the mono-spiro derivative (**4**) (mp 114-115 °C), Yield 1.37 g, 55 %. Anal. Calcd for C₈H₁₄Cl₂F₄N₅O₂P₃: C 21.26, H 3.12, N 15.49 %. Found: C 21.20, H 3.15, N 15.47 %. MS (ESI): *m/z*: calcd. for 452.05, Found: 453. ¹H NMR (CDCl₃ solution): δ 1.71-1.8 (m, 2H, -NHCH₂CH₂CH₂NCH₃-), 2.4 (broad, 1H, NH), 3.52 (d, 3H, NCH₃), 3.81-3.95(m, 2H, CH₃NCH₂), 4.13-4.2 (m, 2H, NCH₂), 4.3-4.56 (m, 4H, POCH₂(CF₂)₂OCH₂). IR (KBr, cm⁻¹), ν = 1200 (P=N), ν = 530 (P-Cl), ν = 700 (P-N), ν = 3235 (broad, N-H), ν = 1000 (N-C), ν = 1130 (C-C), ν = 2900 (C-H), ν = 839 (P-O), ν = 1111 (C-F), ν = 1150 (C-C), ν = 1087 (C-O) and ν = 2951-2817 cm⁻¹(C-H). The second product is the di-spiro derivative (**6**) (mp 221-222 °C), (Yield 0.25 g, 8 %). Anal. Calcd for C₁₃H₂₂F₈N₅O₄P₃ : C 28.02, H 3.98, N 12.57 %. Found: C 28.08, H 3.91, N 12.63 %. MS(ESI): *m/z*: calcd. for 557, Found: 558. ¹H NMR (CDCl₃ solution δ 1.71-1.81 (m, 2H, -NHCH₂CH₂CH₂NCH₃-), 2.42 (broad, 1H, NH), 3.52 (d, 3H, NCH₃), 3.81-3.94(m, 2H, CH₃NCH₂), 4.13-4.21 (m, 2H, NCH₂), 4.31-4.56 (m, 4H, POCH₂(CF₂)₂OCH₂). IR (KBr, cm⁻¹), ν = 1200 (P=N), ν = 530 (P-Cl), ν = 700 (P-N), ν = 3321 (broad, N-H), ν = 1000 (N-C), ν = 1130 (C-C), ν = 2900 (C-H), ν = 839 (P-O), ν = 1111 (C-F), ν = 1150 (C-C), ν = 1087 (C-O) and ν = 2951-2817 cm⁻¹(C-H). Both products were crystallized from *n*-hexane:dichloromethane (1:3) and obtained as white crystals.

Reaction of compound (**1**) with 2,2,3,3,4,4-hexafluoropentane-1,5-diol (**3**) to form (**5**), (**7**), (**8**).

Compound (**1**)³¹ (2 g, 5.5 mmol) and 2,2,3,3,4,4-hexafluoropentane-1,5-diol (**3**) (1.17 g, 5.5 mmol) were dissolved in 70 mL of dry THF in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60 % oil suspension, 0.44 g, 11 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction was stirred for 23 h at rt and followed by TLC silica gel plates using hexane: EtOAc (2:1) and 4 compounds were observed. The reaction mixture was filtered to remove sodium chloride, the solvent removed under reduced pressure and the resulting colourless oil was subjected to column chromatography, using *n*-hexane: EtOAc (2:1) as eluent. The first product is starting material (**1**) (0.6 g, 30 %). The second product is (**8**) mono-ansa derivative (mp 164-165 °C) (yield 0.19 g, 7 %). Anal. Calcd for C₉H₁₄Cl₂F₆N₅O₂P₃ : C 21.53, H 2.81, N 13.95 %. Found: C 21.60, H 2.78, N 13.97 %. MS (ESI): *m/z*: calcd for 501, Found: 501. ¹H NMR (CDCl₃ solution): δ 1.71-1.78 (m, 2H, -NHCH₂CH₂CH₂NCH₃-), 2.4 (broad, 1H, NH), 3.55 (d, 3H, NCH₃), 3.85-3.95 (m, 2H, CH₃NCH₂), 3.88-4.2 (m, 2H, NCH₂), 4.3-4.41 (m, 4H, POCH₂(CF₂)₃OCH₂). IR (KBr, cm⁻¹), ν = 1200 (P=N), ν = 530 (P-Cl), ν = 700 (P-N), ν = 3429 (sharp, N-H), ν = 1000 (N-C), ν = 1130 (C-C),

$\nu = 2900$ (C-H), $\nu = 839$ (P-O); $\nu = 1111$ (C-F), $\nu = 1150$ (C-C), $\nu = 1087$ (C-O) and $\nu = 2951-2817$ (C-H). The band at 3429 cm^{-1} assigned to the N-H vibration is very sharp and the frequency of the vibration is higher than the other compounds, which indicates that there is a no H-bond formed between the molecules. The third product is the mono-spiro derivative (**5**) (mp $122-123\text{ }^{\circ}\text{C}$) (Yield 0.2 g, 7 %). Anal. Calcd for $\text{C}_9\text{H}_{14}\text{Cl}_2\text{F}_6\text{N}_5\text{O}_2\text{P}_3$: C 21.53, H 2.81, N 13.95 %. Found: C 21.57, H 2.76, N, 13.99 %. MS(ESI): m/z : calcd for 501, Found 502.08. ^1H NMR (CDCl_3 solution): δ 1.7-1.8 (m, 2H, -NHCH₂CH₂CH₂NCH₃-), 2.4 (broad, 1H, NH), 3.52 (d, 3H, NCH₃), 3.81-3.98(m, 2H, CH₃NCH₂), 4.13-4.19 (m, 2H, NCH₂), 4.4-4.53 (m, 4H, POCH₂(CF₂)₃OCH₂). IR (KBr, cm^{-1}), $\nu = 1200$ (P=N), $\nu = 530$ (P-Cl), $\nu = 700$ (P-N), $\nu = 3344$ (broad, N-H), $\nu = 1000$ (N-C), $\nu = 1130$ (C-C), $\nu = 2900$ (C-H), $\nu = 839$ (P-O); $\nu = 1111$ (C-F), $\nu = 1150$ (C-C), $\nu = 1087$ (C-O) and $\nu = 2951-2817\text{ cm}^{-1}$ (C-H). The fourth product is di-spiro (**7**) (mp $210-211\text{ }^{\circ}\text{C}$) (Yield 1,06 g, 30 %), isolated as white powders and recrystallized from *n*-hexane-CH₂Cl₂ (1:2). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{F}_{12}\text{N}_5\text{O}_4\text{P}_3$: C 26.22, H 2.83, N 10.92 %. Found: C 26.24, H 2.80, N 10.87 %. MS(ESI): m/z : calcd for 641, Found: 642. ^1H NMR (CDCl_3 solution): δ 1.71-1.79 (m, 2H, -NHCH₂CH₂CH₂NCH₃-), 2.41 (broad, 1H, NH), 3.52 (d, 3H, NCH₃), 3.81-3.96(m, 2H, CH₃NCH₂), 4.14-4.20 (m, 2H, NCH₂), 4.4-4.55 (m, 4H, POCH₂(CF₂)₃OCH₂). IR (KBr, cm^{-1}), $\nu = 1200$ (P=N), $\nu = 530$ (P-Cl), $\nu = 700$ (P-N), $\nu = 3360$ (broad, N-H), $\nu = 1000$ (N-C), $\nu = 1130$ (C-C), $\nu = 2900$ (C-H), $\nu = 839$ (P-O); $\nu = 1111$ (C-F), $\nu = 1150$ (C-C), $\nu = 1087$ (C-O) and $\nu = 2951-2817$ (C-H).

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