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SYNTHESIS AND CHARACTERIZATION OF SOME FUSED TRICYCLIC SPERMIDINE DERIVATIVES OF CYCLOTRIPHOSPHAZENE

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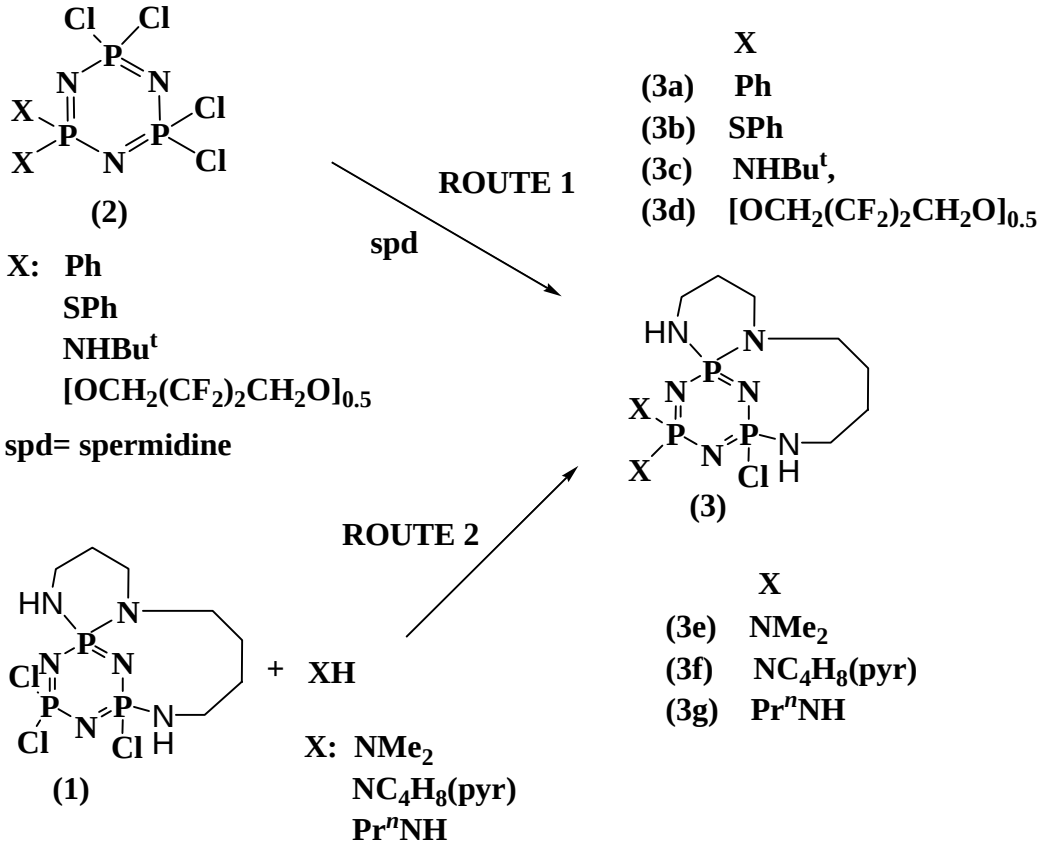
Abstract – A number of derivatives of 6-chloro-2, 2-X_2-1, 3, 5, 7, 11, 16-hexa aza-4,6-diphosphatricyclohexadeca-2, 4, 6-triene {X=SPh, $[OCH_2(CF_2)_2CH_2O]_{0.5}$, pyr, NMe_2, $NHPr^n$, Ph, $NHBu^t$} have been synthesised using two different reaction routes (1, 2) giving rise to penta-substituted-mono-chloro-compounds. The remaining chlorine atom in these products was reluctant to react with neutral nitrogen nucleophiles. The structures of the compounds were determined by elemental analysis, mass spectrometry and by ^1H and ^{31}P-NMR spectrocsopy.

INTRODUCTION

The reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with the tri-functional biogenic amine, spermidine, in aprotic solvents give rise to bridged dimers, $(N_3P_3Cl_5)spd(N_3P_3Cl_4)$, (spd = trifunctional spermidine residue)[1] and in protic solvents such as $CHCl_3$ gives a monomeric fused tricyclic derivative, $N_3P_3Cl_3(spd)$ (**1**).[2] The nine-membered spiro-cis-ansa spermidine derivatives have interesting features (e.g.conformational polymorphism and chirality,[3] reactions occurring with retention of configuration[4]). In this paper; we report the syntheses of novel fused tricyclic derivatives (3b-g), which can be approached by either introducing different substituents X into $N_3P_3Cl_6$ (Routes 1 in Scheme1), followed by spermidine or by reaction of a cyclophosphazene derivative with spermidine followed by further nucleophilic substitution (Route 2 in Scheme1).



Scheme 1

RESULTS AND DISCUSSION

Route 1 starts with a geminal di-substituted chlorocyclotriphosphazene, $N_3P_3Cl_4X_2$, (**2**) {X= Ph, SPh, $NHBu^t$ or $[OCH_2(CF_2)_2CH_2O]_{0.5}$}, which is allowed to react with spermidine to give penta-substituted mono-chloro-derivatives, $N_3P_3ClX_2$(spd) (**3**) or by route 2 starting with $N_3P_3Cl_3$(spd) (**1**) followed by nucleophilic attack by XH. When X is a neutral amine (e.g. X= NMe_2, pyr, $NHPr^n$) compounds of type (**3**) result, as it appears that the remaining bridge-head chlorine atom is exceedingly reluctant to react with this type of reagent. However, with oxygen nucleophiles, *e.g*. NaOMe, the bridge-head chlorine atom can also be replaced to yield e.g. $N_3P_3(OMe)_3$(spd)[4] and, interestingly, does so with retention of configuration, which is rather rare in such systems.[5] The apparent inertness of the bridge-head chlorine seemed rather surprising, as it contains the PCl(NHR) moiety, which has a propensity to react by a proton abstraction / chloride ion elimination reaction mechanism,[6] e.g. $N_3P_3Cl_5(NHBu^t)$ giving geminal $N_3P_3Cl_4(NHBu^t)_2$.

Details of the synthesis and analysis of compounds (**1, 3a-g**) is provided as supplementary information. The structures of the compounds were determined by elemental analysis, mass spectrometry and by ^1H and ^{31}P-NMR spectrocsopy. The proton decoupled ^{31}P-NMR spectra of compounds (**1, 3a-g**) show that the three different phosphorus nuclei are non-equivalent (analysed as AMX or ABX spin systems, as

appropriate) with characteristic chemical shifts for the P(Nspiro) and P(NHR)Cl moieties in penta-substituted mono-chloro-derivatives, $N_3P_3ClX_2$(spd), of 9-13 and 27-31 ppm, respectively. A crystal structure published by Cameron et al.[2b] shows that 6,2,2-trichloro-1,3,5,7,11,16-hexaaza-4,6-diphosphatricyclohexadeca-2,4,6-triene (**1**) has a fused tricyclic structure. As the pattern of proton coupled ^{31}P-NMR spectra of compounds **(3a-d),** is closely similar for the derivatives obtained by routes 1 and 2, it is concluded that all these spermidine substituted phosphazenes contain the same fused tricyclic system containing a spiro-ansa moiety. Furthermore, proton coupled ^{31}P-NMR spectra of compounds **(3e-g)** show that the nucleophiles had replaced the chlorine atoms of the PCl_2 group. The three bond-coupling constants of the P(NHR)Cl group ($^3J_{PH}$: ≈ 7.4 Hz of **3a-d** and $^3J_{PH}$: ≈ 7.3 Hz of **3e-g)** are similar to that for compound **1** ($^3J_{PH}$: ≈ 7.6Hz). The ^{31}P NMR spectral data of tricyclic spermidine derivatives of cyclotriphosphazatriene (**1, 3a-g**) are given in Table 1.

Table 1. ^{31}P NMR Parameters For Tricyclic Spermidine Derivatives of Cyclotriphosphazatriene

Cpd	δ (^{31}P NMR)[ppm]					^{2}J(PP) [Hz]		
	P(Nspiro)	P(NHR)X	X	PY_2 or PYZ	Y and/or Z			
	1	2		3		1,2	1,3	2,3
1[a,b]	9.2	26.7	Cl	25.94	Cl	42.2	41.55	57.00
3a [a,c]	12.2	28.7	Cl	22.72	Ph	22.55	22.15	19.75
3b [a,c]	11.52	29.46	Cl	49.35	SPh	37.63	6.07	16.55
3c [a,b]	12.03	30.02	Cl	11.56	$NHBu^t$	40.14	44.75	47.56
3d [a,c]	11.9	30.16	Cl	19.15	$[OCH_2(CF_2)_2CH_2O]_{0.5}$	41.76	66.82	71.82
3e [a,c]	14.13	31.6	Cl	28.79	NMe_2	40.17	43.36	41.72
3f [a,c]	14.10	31.74	Cl	20.47	Pyr	41.24	41.94	41.39
3g [a,c]	13.23	31.58	Cl	20.06	$NHPr^n$	39.91	44.95	45.24

a) 202,4 MHz ^{31}P NMR measurements in $CDCl_3$ solutions at 298K with chemical shifts given with respect to 85% H_3PO_4 as an external reference

b) Calculated as an ABX spin system

c) Calculated as an AMX spin system

These synthetic investigations show that the reluctance of derivatives (**1**) to react further with amines is not due to steric hindrance or an excess of electron density at the phosphorus atom of the remaining P-Cl bond, but must be due to some mechanistic features. Depending on the electron-releasing capacity of the X group, in conjunction with that of the three amino groups from the spermidine residue, either a faster S_N1 reaction[7] is likely to occur, if X is a secondary amino group, NR_2, or in the case where X is a primary amino group, NHR, a more likely reaction route will be via a proton abstraction/chloride elimination mechanism and the 3-co-ordinate trigonal planar, very reactive, phosphorus species will react with any nucleophile present.[6] In the case of compound **(1)**, where the X in PClX is represented by OMe, this grouping is sufficiently stable to be isolated.[3] No mono-substitution by such amino groups has been so far observed, possibly, because the presence of four amino residues in the N_3P_3 triggers an S_N1 reaction[6b] at the stage of the $PCl(NR_2)$ moiety, which is faster than the preceeding S_N2 reaction.

EXPERIMENTAL

1.Materials

Hexachlorocyclotriphosphazene (a gift from the Shin Nisso Kako Co. Ltd.) was purified by fractional crystallization from *n*-hexane. In addition to Spermidine (Fluka 99.0%) and 2,2, 3,3-tetrafluoro-1,4-butanediol (Acros, 98 %), the following chemicals were obtained from Merck; THF (≥ 99.0 %), *n*-hexane (> 96%), EtOAc (≥ 99.5 %), NaH (60 % dispersion in mineral oil), CH_2Cl_2 (≥ 99.0 %), Me_2NH (40 % aqueous solution), Bu^tNH_2 (> 99 %), PhSH (> 98.0 %), Pr^nNH_2 (≥ 99.0 %), Na_2SO_4 (≥ 99.0 %), $CHCl_3$ (99.0-99.4 %), C_4H_8NH (≥ 99.0 %), benzene (≥ 99.5%). All solvents used in this work were purified by conventional methods. THF was distilled over a sodium-potassium alloy under an atmosphere of dry argon. Solvents for NMR spectroscopy were obtained from Goss Scientific ($CDCl_3$) .

2.Methods

Elemental analyses were obtained using a Carlo Erba 1106 Instrument. Mass spectra were recorded on a VG Zab Spec GC-MS spectrometer using the fast atom bombardment (FAB) method (35 kV) with MNBA as the matrix and an AGILENT 1100 MSD LC/MS spectrometer using atmospheric pressure chemical ionization (APCI); ^{35}Cl values were used for calculated masses. Analytical Thin Layer Chromatography

(TLC) was performed on silica gel (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 70-230 mesh; for 3g. crude mixture, 100g. silica gel was used in a column of 3 cm in diameter and 60 cm in length) and. ^{1}H 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 ^{1}H NMR and 85 % H_3PO_4 as an external reference for ^{31}P.

3.Synthesis

Compound (1) was prepared as in the literature.[2a] All reactions were performed under a dry argon atmosphere.

3.1. Preparation of 6-chloro-2, 2-diphenyl-1, 3, 5, 7, 11, 16-hexaaza-4, 6-diphosphatricyclohexadeca-2, 4, 6-triene (3a): A solution of 2, 2-diphenyl-4, 4, 6, 6-tetrachlorocyclotriphosphazatriene (mp 95.5 ^{o}C) (10 g, 23.2 mmol)[8] in $CHCl_3$ (150 mL) was added dropwise to a stirred solution of spermidine (6.73 g, 46.4 mmol) in $CHCl_3$ (150 mL). The reaction mixture was stirred under an atmosphere of argon at rt for a further 3 days and then spermidine trihydrochloride was filtered off and the solvent was removed under reduced pressure at 30°C. Two compounds were detected [Rf = 0.85 (I)**(3a)** and 0.32 (II)] by thin-layer chromatography using CH_2Cl_2-THF (3:1) as mobile phase. These products were separated by column chromatography on silica gel using CH_2Cl_2-THF (8:1) as eluent. Compound **(3a)** was crystallised from THF-*n*-hexane (1:1), mp176 °C; (Yield 16 %). Anal. Calcd for $C_{19}H_{26}ClN_6P_3$: C 48.89, H 5.61, N 18.00. Found: C 48.8, H 5.10, N 18.00. MS(FAB): m/z:calcd for :466. Found: 467.1) [lit.: 176 ^{o}C , S. J. Coles et al., 2002].[3] ^{1}H NMR, δ = 3.5 (m, 2H, $NHCH_2$(spiro)), δ =3.3-3.2 (m, 4H, $NHCH_2$(bridge) and NCH_2(spiro)), δ =3.1 (m, 2H, NCH_2(bridge)), δ =2.7 (m, 2H, CH_2(bridge)) , δ = 2.1 (m, 2H CH_2(bridge)), δ =1.9 (m, 2H, CH_2(br)), δ = 1.7 (m, 2H, CH_2(spiro)) , δ = 8 (m, 2H, *p*-$CH(C_6H_5)$), δ = 7.5-7.4 (m, 8H, *o*-*m*-$CH(C_6H_5)$), δ = 4 (NH).(II), 6-ethoxy-2, 2-diphenyl 1, 3, 5, 7, 11, 16-hexaaza-4, 6-diphospha- tricyclohexadeca-2, 4, 6-triene was recrystallized from THF-*n*-hexane (1:1), mp 166-167 °C (Yield 1 %). Anal. Calcd for $C_{21}H_{31}N_6OP_3$: C 52.94, H 6.56, N 17.64. Found: C 52.97, H 6.78, N 17.89. MS(FAB): m/z:calcd for : 476. Found: 477.02. ^{1}H NMR, δ = 3.5 (m, 2H, $NHCH_2$(spiro)), δ = 3.3-3.2 (m, 4H, $NHCH_2$(bridge) and NCH_2(spiro)), δ = 3.1 (m, 2H, NCH_2(bridge)), δ = 2.7 (m, 2H, CH_2(bridge)), δ = 2.1 (m, 2H, CH_2(bridge)), δ = 1.9 (m, 2H, CH_2(br)), δ = 1.7 (m, 2H, CH_2(spiro)), δ = 8 (m, 2H, *p*-$CH(C_6H_5)$), δ =7.5-7.4 (m, 8H, *o*-*m*-$CH(C_6H_5)$), δ = 4 (m, 2H, CH_2O)), δ = 1.3 (q, 3H, CH_3 (OEt)), δ = 2.4 (NH).

3.2. Preparation of 6-chloro-2, 2-bis-thiophenoxy-1, 3, 5,7, 11, 16-hexaaza-4, 6-diphosphatricyclohexadeca-2, 4, 6-triene (3b): A solution of 2, 2-bis(thiophenoxy)-4, 4, 6, 6-tetrachlorocyclotriphosphazatriene (mp 93 ^{o}C) (8g, 16,16 mmol)[9] in $CHCl_3$ (250 mL) was stirred in a 500 mL three-necked round-bottomed flask and spermidine (4.69g, 32.32 mmol) in $CHCl_3$ (50 mL) was added dropwise. The

reaction mixture was stirred under an atmosphere of argon at rt for a further 24 h and the reaction followed on TLC silica gel plates using THF-*n*-hexane (2:3) to give a single product [Rf= 0.5] and no starting material remaining. Spermidine trihydrochloride was filtered off and the solvent was removed under reduced pressure at 30 °C. The crude product was subjected to column chromatography using THF-*n*-hexane (2:3) as eluent. Compound **(3b)** was isolated as a white powder, mp 75 °C (Yield 13.08 %). Anal. Calcd for $C_{19}H_{26}ClN_6P_3S_2$: C 42.98, H 4.94, N 15.83. Found: C 42.95, H 4.91, N 15.82. MS(FAB): m/z: calcd for: 530. Found: 531.049. ^{1}H NMR, δ = 3.5 (m, 2H, $NHCH_2$(spiro)), δ = 3.3-3.2 (m, 4H, $NHCH_2$(bridge) and NCH_2(spiro)), δ = 3.1 (m, 2H, NCH_2(bridge)), δ = 2.7 (m, 2H CH_2(bridge)), δ = 2.1 (m, 2H, CH_2(bridge)), δ = 1.9 (m, 2H, CH_2(br)), δ = 1.7 (m, 2H, CH_2(spiro)), δ = 7.7 (m, 2H, *p*-CH(C_6H_5-S)), δ =7.4-7.3 (m, 8H, *o*-*m*-CH(C_6H_5-S)), δ = 2.4 (NH).

3.3. Preparation of 6-Chloro-2, 2-di-t-butylamino-1, 3, 5, 7, 11, 16-hexaaza-4, 6-diphosphatricyclohexadeca-2, 4, 6-triene (3c): 2, 2-Bis-*t*-butylamino-4, 4, 6, 6-tetrachlorocyclotriphosphazatriene (mp 120-122 °C) (2g, 4.75 mmol) [6] was dissolved in $CHCl_3$ (30 mL) in a 100 mL three-necked round-bottomed flask and spermidine (1.38g, 9.5 mmol) in the same solvent (25 mL) was added dropwise with stirring. The reaction mixture was stirred under an atmosphere of argon at rt for a further 12 days. Spermidine trihydrochloride was filtered off and the solvent was removed under reduced pressure at 30 °C. The crude product was subjected to column chromatography using CH_2Cl_2-THF (1:1) as eluent. Compound **(3c)** was separated and recrystallized from THF-*n*-hexane (1:1), mp 186-187 °C (Yield 5.2 %). Anal. Calcd for $C_{15}H_{32}ClN_8P_3$: C 39.43, H 7.94, N 24.53. Found: C 39.50, H 8.01, N 24.22. MS(FAB): m/z:calcd for : 456. Found: 457. ^{1}H NMR, δ = 3.5 (m, 2H, $NHCH_2$(spiro)), δ =3.3-3.2 (m, 4H, $NHCH_2$(bridge) and NCH_2(spiro)), δ = 3.1 (m, 2H, NCH_2(bridge)), δ = 2.7 (m, 2H CH_2(bridge)), δ = 2.1 (m, 2H, CH_2(bridge)), δ = 1.9 (m, 2H, CH_2(br)), δ = 1.7 (m, 2H, CH_2(spiro)), δ = 1.4 (m, 18H, $CH_3(NHBu^t)$), δ = 2.4 (NH).

3.4. Preparation of 6-chloro-2, 2-(2', 2', 3', 3'-tetrafluoro-1', 4'-butanedioxy)-1, 3, 5, 7, 11, 16-hexaaza-4, 6-diphoshatricyclohexadeca-2, 4, 6-triene (3d): 2, 2-(2', 2', 3', 3'-Tetrafluoro-1', 4'-butanedioxy)-4, 4, 6, 6-tetrachlorocyclotriphosphazatriene (1 g, 1.970 mmol) (mp 95 °C) [10] was dissolved in $CHCl_3$ (20 mL) in a 100 mL three-necked round-bottomed flask and was spermidine (0.572 g, 3.94 mmol) in the same solvent (20 mL) was added dropwise with stirring. The reaction mixture was stirred under an atmosphere of argon at rt for a further 24 h. Spermidine trihydrochloride was filtered off and the solvent was removed under reduced pressure at 30 °C. The crude reaction mixture was subjected to column chromatography using EtOAc-*n*-hexane (2:1) as eluent. Compound **(3d)** was separated and recrystallized from CH_2Cl_2-*n*-hexane (1:1), mp 143 °C (Yield 9 %). Anal. Calcd for $C_{11}H_{20}ClF_4N_6O_2P_3$: C 27.95, H 4.26, N 17.78. Found: C 27.98, H 4.48, N 17.81. MS(APCI): m/z:calcd for : 472. Found:473.1. ^{1}H NMR, δ =

3.5 (m, 2H, $NHCH_2$(spiro)), δ =3.3-3.2 (m, 4H, $NHCH_2$(bridge) and NCH_2(spiro)), δ = 3.1 (m, 2H, NCH_2(bridge)), δ = 2.7 (m, 2H, CH_2(bridge)), δ = 2.1 (m, 2H, CH_2(bridge)), δ = 1.9 (m, 2H, CH_2(br)), δ = 1.7 (m, 2H, CH_2(spiro)), δ = 4.4-4.2 (m, 4H, $CH_2(OCH_2(CF_2)_2CH_2O)$), δ = 2.4 (NH).

3.5.Preparation of 6-chloro-2, 2-bisdimethylamino-1, 3, 5, 7, 11, 16-hexaaza-4, 6-diphospha-tricyclohexadeca-2, 4, 6-triene (3e): Compound **(1)** (mp 160 ^oC) (1.5 g, 3.9 mmol)[2a] and Me_2NH (5.28 g, 117 mmol) were dissolved in THF (8 mL) in a 100 mL a three-necked round-bottomed flask and the reaction mixture was stirred for 2 days at rt. The reaction was followed on TLC silicagel plates using THF-CH_2Cl_2 (1:1), which showed the formation of a single product [Rf =0.5] and the absence of starting material. Distilled water (100 mL) was added to the reaction mixture and the product was extracted using CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure at 30 °C. The crude product was subjected to column chromatography using THF-CH_2Cl_2 (1:1) as eluent Compound **(3e)** was separated and recrystallized from *n*-hexane-THF (1:1), mp 177 °C (Yield 10 %). Anal. Calcd for $C_{11}H_{28}ClN_8P_3$: C 32.97, H 7.04, N 27.96. Found: C 32.67, H 7.04, N, 27.96. MS(FAB): m/z:calcd for :400. Found: 401.045. ^1H NMR, δ = 3.5 (m, 2H, $NHCH_2$(spiro)), δ = 3.3-3.2 (m, 4H, $NHCH_2$(bridge) and NCH_2(spiro)), δ = 2.1 (m, 2H, NCH_2(bridge)), δ = 2.7 (m, 2H, CH_2(bridge)), δ = 1.9-1.7 (m, 2H, CH_2(br)), δ = 1.7-1.6 (m, 2H, CH_2(spiro)), δ = 1.5 (d, 12H, CH_3), δ = 2.4 (NH).

3.6. Preparation of 6-chloro-2, 2-bispyrrolidino-1, 3, 5, 7, 11, 16-hexaaza-4, 6-diphosphatri-cyclohexadeca-2,4,6-triene (3f): Compound **(1)** (mp 160 ^oC) (0.5g, 1.305 mmol)[2a] and C_4H_8NH (1.92g, 27.08 mmol) were dissolved in THF (8 mL) in a 100 mL three-necked round-bottomed flask and the reaction mixture was stirred for 2 days at rt. The reaction was followed on TLC silica gel plates using THF-CH_2Cl_2 (1:1). The absence of starting material and the formation of a single product [Rf:0.43] was observed. Distilled water 100 mL was added and the product extracted using CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure at 30 °C. Compound **(3f)** was recrystallized from *n*-hexane-CH_2Cl_2 (2:1), mp 173-175 °C (Yield 25 %). Anal. Calcd for $C_{15}H_{32}ClN_8P_3$: C 39.79, H 7.12, N 24.74. Found: C, 39.70; H, 7.05; N, 24.69. MS(FAB): m/z:calcd for : 452. Found: 453. ^1H NMR, δ =3.5 (m, 2H, $NHCH_2$(spiro)), δ = 3.3-3.2 (m, 4H, $NHCH_2$(bridge) and NCH_2(spiro)), δ = 3.1 (m, 2H, NCH_2(bridge)), δ =2.7 (m, 2H, CH_2(bridge)), δ = 2.1 (m, 2H, CH_2(bridge)), δ = 1.9 (m, 2H, CH_2(br)), δ = 1.7 (m, 2H, CH_2(spiro)), δ =1.8-1.6 (m, 16H, CH_2(pyr)), δ = 2.4 (NH).

3.7. Preparation of 6-chloro-2, 2-bis-*n*-propylamino-1, 3, 5, 7, 11, 16-hexaaza-4, 6-diphospha-tricyclohexadeca-2, 4, 6-triene (3g): Compound **(1)** (1.g, 2.6 mmol)[2a] was dissolved in Pr^nNH_2 (7.2 g, 121.8 mmol) in a 100 mL three-necked round-bottomed flask and the reaction mixture was refluxed in an oil

bath with stirring with magnetic stirrer for 2 h. The reaction was followed on TLC silicagel plates using THF-CH_2Cl_2 (1:1). The absence of starting material and the formation of a single product [Rf =0.26] was observed. The reaction mixture was allowed to cool to rt and then distilled water 100 mL was added and the product extracted using CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure at 30 °C. Compound **(3g)** was separated and recrystallized from *n*-hexane-THF (1:1), mp 130-131 °C (Yield 36 %). Anal. Calcd for $C_{13}H_{32}ClN_8P_3$: C 36.41, H 7.52, N 26.13. Found: C 36.74, H 7.68, N 26.55. MS(FAB): m/z:calcd for :428. Found: 428.871. ^{1}H NMR, δ = 3.5 (m, 2H, $NHCH_2$(spiro)), δ = 3.3-3.15 (m, 4H, $NHCH_2$(bridge) and NCH_2(spiro)), δ = 3.1-3.0 (m, 4H, $NHCH_2(NHPr^n)$), δ = 2.9-2.8 (m, 2H, NCH_2(bridge)), δ = 2.3-2.2 (m, 2H, CH_2(br)), δ = 2.1 (m, 2H, CH_2(br)), δ = 1.7-1.8 (m, 2H, CH_2(spiro)), δ = 0.9 (doublets of triplet , 6H, CH_3), δ = 2.4 (NH).

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