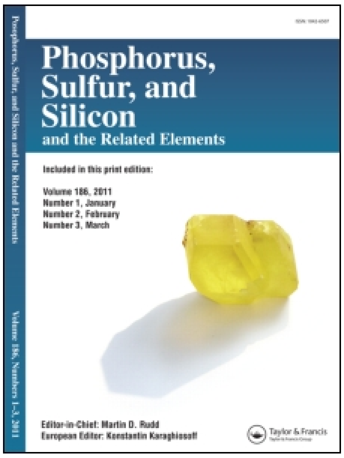

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ON THE SCENT OF DANDELION DENDRIMERS. PART II.* CYCLOPHOSPHAZENIC DECAPODANES AS NEW CORES

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Aminolysis of two-ring bridged-assembly cyclophosphazenes (coded as bino moieties) by long-chain diamines, $H_2N—(CH_2)_n—NH_2$ ($n \geq 6$), leads regiospecifically to decadangling (or decapodanes or decapus) monomeric species provided it was achieved on alumina impregnated with a suitable amount of potassium hydroxide. These reactions run very fast at room temperature. Such decapodanes constitute starting materials (spherical bi-cores) for future design of cyclophosphazenic dandelion dendrimers.

Key words: Cyclophosphazene; regiospecific aminolysis; dry media; alumina supported reaction; dendrimers; dandelion flower.

INTRODUCTION

We recently reported[1] on the neat obtention of pure cyclophosphazenic hexapodanes (coded as sexapus by reference to an octopus with only six tentacles) through a regiospecific aminolysis of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, by long-chain diamines, $H_2N—(CH_1)_n—NH_2$ ($n \geq 6$), on alumina impregnated with a certain amount of potassium hydroxide. These sexapus are 3-dimensional 6-functional cores suitable for generating cyclophosphazenic spherical (i.e. aesthetically similar to the structure of a dry dandelion flower and not of a Tomalia's cauliflower[2]) dendrimers.

On the other hand, aminolysis of $N_3P_3Cl_6$ by long-chain diamines in homogeneous conditions (i.e. with ethyl ether as the solvant and Et_3N for scavenging hydrogen chloride) yields serendipitous two-ring bridged-assembly structures (coded as bino moieties) in which the diamino ligand bridges two different N_3P_3 rings.[3] X-Ray structure of one of these chemicals, namely bino $\underline{4}$, $N_3P_3Cl_5[HN—(CH_2)_4—NH]Cl_5P_3N_3$, revealed[4] an helical architecture with the two N_3P_3 rings as the steps of a spiral staircase centered on the diamino linkage (Figure 1), the relative twist of the two steps being about 60°.

Then, a concerted use of the two processes, that is of the one in homogeneous conditions and of the dry media one in sequence, would allow to synthesize new bi-cores with helical structure for further design of exotic cyclophosphazenic dandelion dendrimers.[1]

The present contribution reports on the two-step pathway which allows to reach such bi-cores which will be coded as decapus cores thanks to the number of their tentacles (see below).

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*For Part I, see Reference 1.

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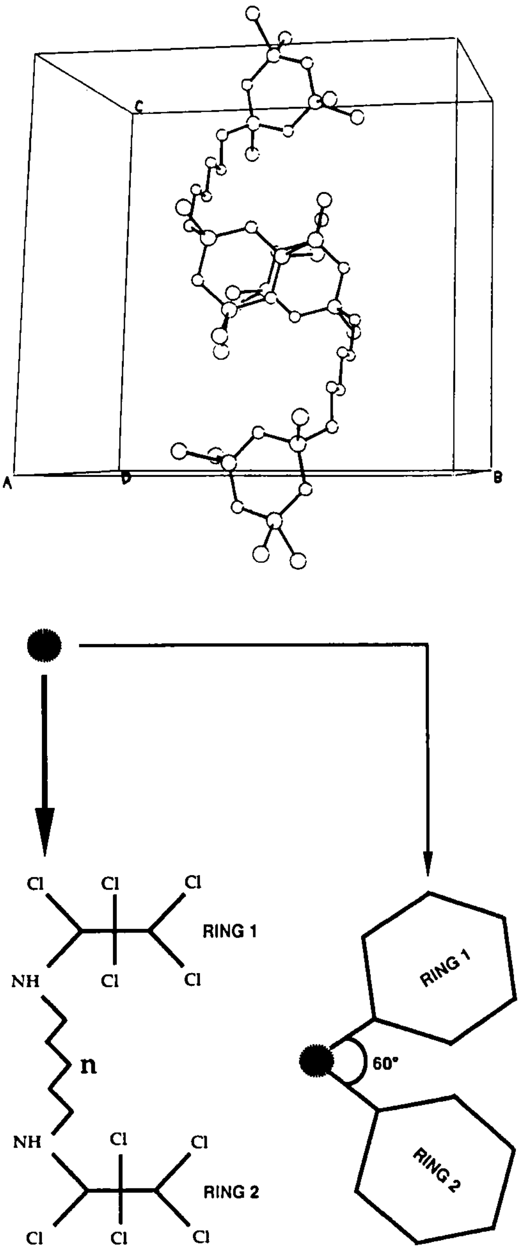

FIGURE 1 Perspective view of the unit cell (from Reference 4) and molecular pattern of a two-ring bridged-assembly cyclophosphazene (bino 4 architecture).

SYNTHESIS OF PURE BINO ENTITIES

The reactions

$$2\ N_3P_3Cl_6 + 1\ H_2N\text{—}(CH_2)_n\text{—}NH_2$$
$$+ 2\ Et_3N \rightarrow N_3P_3Cl_5[HN\text{—}(CH_2)_n\text{—}NH]Cl_5P_3N_3 + 2\ HCl \cdot Et_3N$$

were then achieved in ethyl ether with Et_3N for scavenging hydrogen chloride. Final products are characterized by their 81.015 MHz ^{31}P NMR A_2B systems. A single SiO_2 column chromatography leads pure bino n derivatives as identified by DCI/NH_3 mass spectra. Incidentally, it must be noticed that the DCI/NH_3 negative ions technique is a powerful tool for revealing molecular ions of bino n with a high accuracy: indeed, the molecular ion of any bino n in such conditions is the parent peak (I = 100%) when the intensity of the molecular ion in common conditions is only 4.8%. Moreover, the negative ions technique gives the M^+ molecular ion itself (without the $M \cdot NH_4^+$ sidepeak) conversely to common DCI/NH_3 which gave the MH^+ ion.

FAST SYNTHESIS OF PURE DECAPUS CORES

We recently demonstrated that aminolysis of chlorinated cyclophosphazenes can be promoted regiospecifically in heterogeneous media thanks to the basic sites located on the surface of alumina-supported potassium hydroxide.[1] The most significant advantages of such a "solid support" reaction, relatively to the corresponding homogeneous reaction with Et_3N for scavenging hydrogen chloride, are the milder conditions, the more specific transformations, the extremely high rate of reaction and the easier isolation of final pure products.

The alumina-supported potassium hydroxide we used [coded as ALPOT (50:11)] was prepared according to.[5] Then, a typical experiment of aminolysis of bino **10** by 1,6-Diaminohexane was achieved as detailed on Figure 2 and in the Experimental Part of this contribution (see below). It yields instantaneously the pure decapus **10,6** (**10** and **6** being the number of methylenic groups into the chain and into the tentacles, respectively) as an hygroscopic micro-cristalline (mica folia-like) white product. Incidentally, the same reaction in homogeneous conditions leads regioselectively (and not regiospecifically) after 48 h at room temperature (and not in few minutes) to a medley of partially substituted (from tetra to deca) derivatives.

The same synthesis may be repeated with homologues of bino n and with higher parents of 1,6-Diaminohexane (till 1,12-Diaminododecane). Several decapus **n,p** (with both n and p varying from 6 to 12) were prepared through the same pathway with the aim of disposing of many cores with various morphologies about the length of their tentacles.

Then, decapus **n,p** (with n and p ≥ 6) (Figure 3) may be synthesized fast in a pure state on ALPOT (50:11). These amazing architectures constitute bi-cores for further design of dendrimers according to their 10 tentacles ended by free amino functions pointed isotropically in space. These decapus **n,p** (like sexapus n) are then capable of generating cyclophosphazenic dandelion dendrimers through the chain of reactions we shall evoke briefly now.

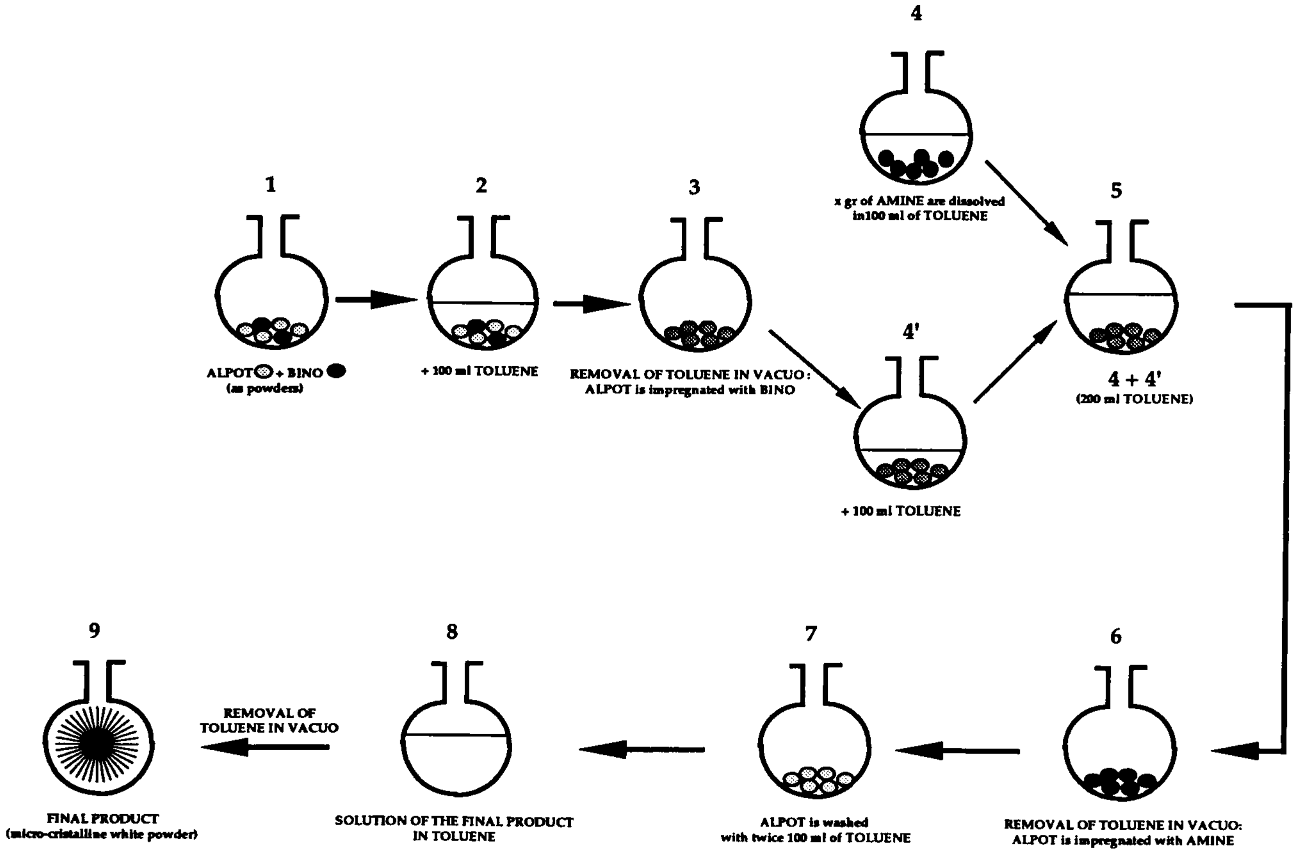

FIGURE 2 A typical experiment of aminolysis on ALPOT (50:11).

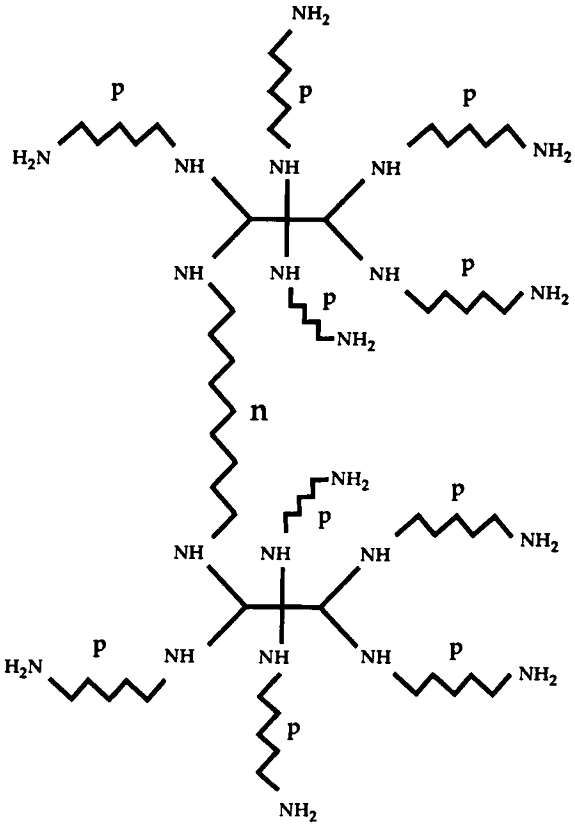

FIGURE 3 Molecular pattern of a decapus n,p bi-core.

THE FIRST STEP OF THE SYNTHESIS OF CYCLOPHOSPHAZENIC DENDRIMERS FROM DECAPUS n,p AS NEW BI-CORES (Figure 4)

What happens indeed when a decapus is allowed to react with 10 new molecules of $N_3P_3Cl_6$? According to our previous results about the synthesis of polybino derivatives,[3] polar solvents are required for linking $N_3P_3Cl_5$ to each tentacle, leading so to architectures of the so-called 1st generation. In other words, toluene is no more the right solvent for such syntheses and ethyl ether has to be used here. Reactions were then achieved in ethyl ether with Et_3N for scavenging hydrogen chloride (they do not work at all on ALPOT (50:11) whatever the solvent is, final products remaining definitely glued on the solid support whatever the eluent is) and they yield the expected 1st generation steps of dandelion dendrimers. Final products are characterized by a 81.015 MHz ^{31}P NMR A_2B system and by FAB mass spectrometry. The final products correspond actually to the expected polybino structures.

Now, we are in the position to go on, the next step of the dendrimers design

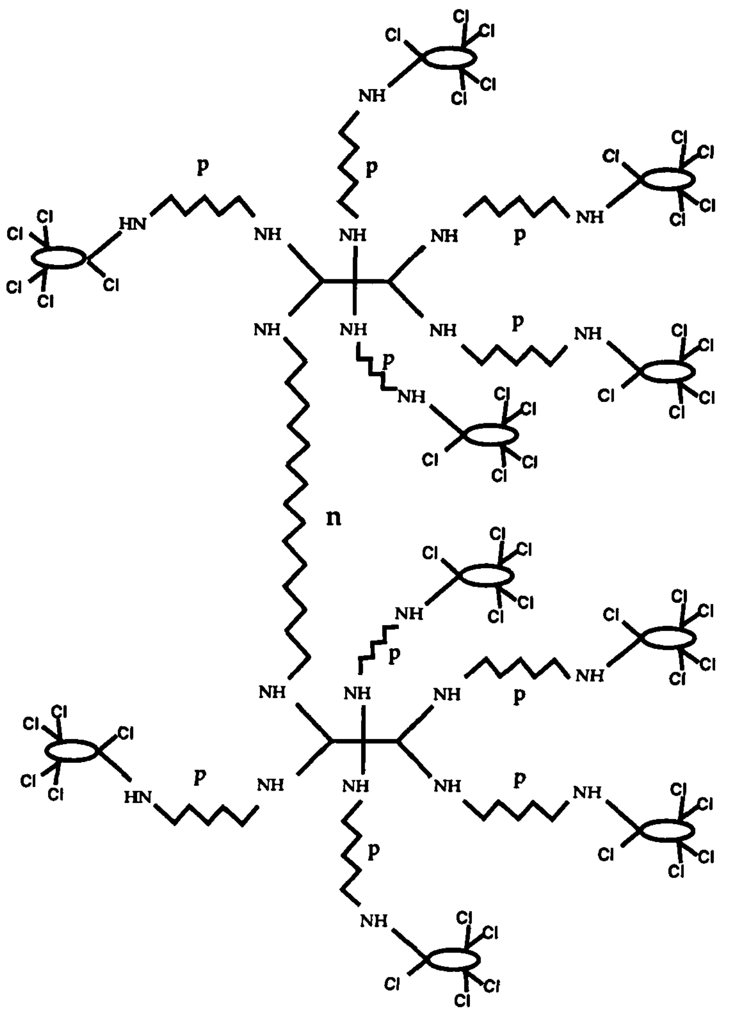

FIGURE 4 Architecture of 1st generation dendrimers from a decapus n,p bi-core.

(2nd generation chemicals) being the further linkage of 50 diamino ligands as dangling tentacles on the 50 chlorine atoms of the 1st generation chemicals.

THE SECOND STEP OF THE SYNTHESIS OF DANDELION DENDRIMERS FROM DECAPUS n,p AS NEW BI-CORES (Figure 5)

These chemicals were prepared through peraminolysis of the polybino configurations of the 1st generation chemicals. Reactions were achieved once more in ethyl ether as the solvent with Et_3N for scavenging hydrogen chloride. 2nd generation chemicals were identified by ^{31}P NMR spectroscopy, a pattern with 3 singlets

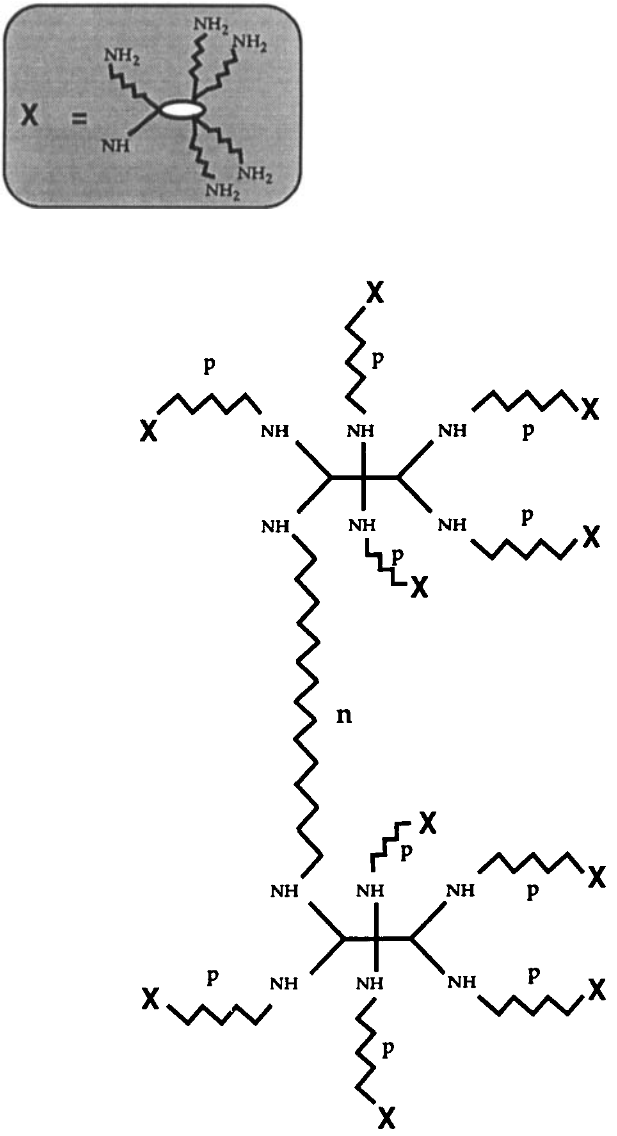

FIGURE 5 Architecture of 2nd generation dendrimers from a decapus **n,p** bi-core.

between 21 and 22 ppm (in $CDCl_3$) being revealed which characterizes the various $\underline{P}(NH)_2$ external atoms of the expected "2nd generation" architectures.

CONCLUSIVE REMARKS

Synthesis of decadangling dicyclophosphazenic architectures (coded as decapus) runs regiospecifically when achieved on a peculiar solid support [ALPOT (50:11)] constituted from alumina impregnated with potassium hydroxide. These decapus are exotic bi-cores for the design of dandelion dendrimers through alternate additions of $N_3P_3Cl_5$' flagstones ("1st generation" architectures) and of diamino tentacles as linkers ("2nd generation" architectures). Identification of architectures obtained in the further steps will require not only FAB and/or Electrospray mass spectrometry and ^{31}P NMR spectroscopy at 202.46 and even 242.95 MHz but also non-conventional physicochemical techniques such as LALLS (Low-Angle Laser Light Scattering) and the capability of these approaches to reach the actual molecular weights of the chemicals in a plus or minus accurate manner will probably constitute the unique limitation for the design of large cyclophosphazenic dendrimers.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker AC 200 spectrometer with H_3PO_4 85% as the external reference.

The DCI mass spectra were recorded on a Ribermag R1010-H Quadrupole Mass Spectrometer.

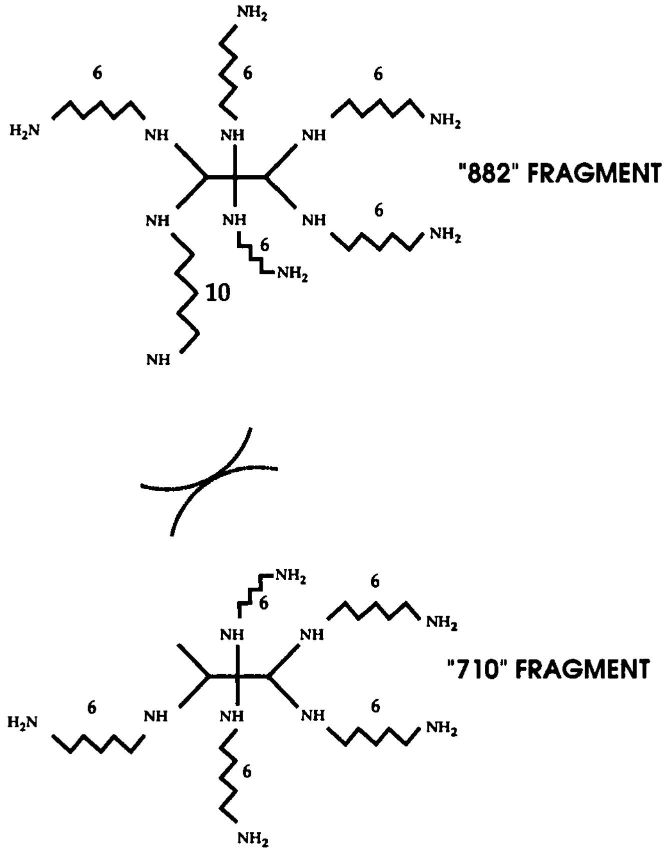

FIGURE 6 Nature of the "882" and "710" fragments observed in the mass spectrum of decapus <u>10,6</u>.

Molecular modelings were achieved by using functionalities of the MAD (Molecular Advanced Design) software developed by Lahana (Oxford Molecular SA, X-Pole, Ecole Polytechnique, 91128 Palaiseau Cedex, France).

Hexachlorocyclotriphosphazene was generously provided to us (degree of purity ≥ 99.8%) by SHIN NISSO KAKO Co., subsidiary company of NIPPON SODA Co. FLUKA supplied us with the primary diamines (degree of purity ≥ 98%).

Alumina-supported potassium hydroxide: Potassium hydroxide (Prolabo Rectapur, 11g) in H_2O (250 ml) was mixed with neutral chromatographic alumina (Fluka, type 207 C, 90–110 μ, 50 g). After stirring for 5 min, the water was removed under reduced pressure. The resulting powder was further dried at 70°C for 24 h in oven. This reagent [coded as ALPOT (50:11)] may be kept in a dessicator without loss of activity during several months.

General pattern for the synthesis of bino $\underline{n}$: The reactions

$$2\ N_3P_3Cl_6 + 1\ H_2N\text{—}(CH_2)_{\underline{n}}\text{—}NH_2$$
$$+\ 2\ Et_3N \rightarrow N_3P_3Cl_5[HN\text{—}(CH_2)_{\underline{n}}\text{—}NH]Cl_5P_3\ N_3 + 2\ HCl\cdot Et_3N$$

were achieved in ethyl ether with Et_3N for scavenging hydrogen chloride. As an example, let us describe here the synthesis of bino $\underline{10}$. A solution of 10 g of 1,10-Diaminodecane in 600 ml of Et_2O was added dropwise at room temperature to a mixture of 40,32 g of $N_3P_3Cl_6$ and of 11.7 g of Et_3N in 1300 ml of Et_2O. The reaction takes 48 h and is considered as complete when the ^{31}P NMR singlet of $N_3P_3Cl_6$ at 20.1 ppm remains unchanged in time. Final product (which appeared to be soluble in $CDCl_3$) is characterized by a 81.015 MHz ^{31}P NMR A_2B system (triplet $\underline{P}ClNH$ centered at 18.7 ppm, doublet $\underline{P}Cl_2$ centered at 21.5 ppm). A single SiO_2 column chromatography (150 g of SiO_2 for 11 g of bulk) was achieved firstly with 1000 ml of n-hexane as the eluant, yielding 2.6 g of pure unreacted $N_3P_3Cl_6$. Then, a direct washing of the column with 800 ml of Et_2O leads 6 g of pure bino $\underline{10}$. The DCI/NH_3 mass spectrum of the final product reveals the MH^+ molecular peak at m/z 795 with a satellite distribution

TABLE I

Micro-analytical data of some chemicals described in the present study

CODE	FORMULA	M.W.	MICRO-ANALYTICAL DATA (%) [Theor. (first line) *versus* exp. (second line)]				
BINO 6	$N_3P_3Cl_5[HN\text{-}(CH_2)_6\text{-}NH]Cl_5P_3N_3$ $C_6H_{14}N_8P_6Cl_{10}$	738	C 9.8 9.5	H 1.9 2.0	N 15.2 14.8	P 25.2 25.4	Cl 48.0 47.6
DECAPUS 6.6	(BINO 6 - 10Cl) + 10[HN-$(CH_2)_6$-NH_2] $C_{66}H_{164}N_{28}P_6$	1536	C 51.6 51.0	H 10.8 10.5	N 25.5 25.0	P 12.1 12.3	
BINO 10	$N_3P_3Cl_5[HN\text{-}(CH_2)_{10}\text{-}NH]Cl_5P_3N_3$ $C_{10}H_{22}N_8P_6Cl_{10}$	795	C 15.1 14.8	H 2.8 3.0	N 14.1 13.8	P 23.4 23.8	Cl 44.6 44.0
DECAPUS 10.6	(BINO 10 - 10Cl) + 10[HN-$(CH_2)_6$-NH_2] $C_{70}H_{172}N_{28}P_6$	1592	C 52.8 51.9	H 10.9 10.7	N 24.6 24.8	P. 11.7 11.5	
1st GENERATION from DECAPUS 6.6	(DECAPUS 6.6 - 10H) + 10($N_3P_3Cl_5$) $C_{66}H_{154}N_{58}P_{36}Cl_{50}$	4648	C 17.1 17.0	H 3.3 3.5	N 17.5 16.9	P 24.0 23.9	Cl 38.1 38.6
1st GENERATION from DECAPUS 10.6	(DECAPUS 10.6 - 10H) + 10($N_3P_3Cl_5$) $C_{70}H_{162}N_{58}P_{36}Cl_{50}$	4704	C 17.9 17.5	H 3.5 3.0	N 17.3 18.0	P 23.7 24.0	Cl 37.7 38.2

TABLE II

Physico-chemical data of some chemicals described in the present study

CODE	FORMULA	m.p. °C	Sol.	$\delta\underline{P}Cl_2$ (ppm)	$\delta\underline{P}ClNH$ (ppm)	$\delta\underline{P}NHNH$ (ppm)	ν (P-Cl) (cm^{-1})
BINO 6	$N_3P_3Cl_5[HN\text{-}(CH_2)_6\text{-}NH]Cl_5P_3N_3$ $C_6H_{14}N_8P_6Cl_{10}$	98	in any organic solvent	21.9	19.4	-	520 585
DECAPUS 6.6	(BINO 6 - 10Cl) + $10[HN\text{-}(CH_2)_6\text{-}NH_2]$ $C_{66}H_{164}N_{28}P_6$	42	in any organic solvent	-	-	17.9	-
BINO 10	$N_3P_3Cl_5[HN\text{-}(CH_2)_{10}\text{-}NH]Cl_5P_3N_3$ $C_{10}H_{22}N_8P_6Cl_{10}$	74	in any organic solvent	21.5	18.7	-	520 580
DECAPUS 10.6	(BINO 10 - 10Cl) + $10[HN\text{-}(CH_2)_6\text{-}NH_2]$ $C_{70}H_{172}N_{28}P_6$	35	in any organic solvent	-	-	18.3	-
1st GENERATION from DECAPUS 6.6	(DECAPUS 6.6 - 10H) + $10(N_3P_3Cl_5)$ $C_{66}H_{154}N_{58}P_{36}Cl_{50}$	liq.	in any organic solvent	21.3	18.7	21.5	530 575
1st GENERATION from DECAPUS 10.6	(DECAPUS 10.6 - 10H) + $10(N_3P_3Cl_5)$ $C_{70}H_{162}N_{58}P_{36}Cl_{50}$	liq.	in any organic solvent	21.3	18.7	21.5	530 575

indicating the presence of 10 chlorine atoms in the molecule. The $M \cdot NH_4^+$ peak was also observed at m/z 812, the magnitude of MH^+ and of $M \cdot NH_4^+$ peaks being 4.8 and 3.0%, respectively. Incidentally, if the "negative ions" technique is introduced into the DCI/NH_3 experiment, the M^+ peak itself is revealed at m/z 794 as the parent peak (I = 100%) of the mass pattern and the $M \cdot NH_4^+$ mass is no more observed.

General pattern for the synthesis of a decapus: 40 g of ALPOT (50:11) were firstly impregnated with a toluene solution of bino 10 (3.37 g in 150 ml) and the solvent was immediately removed in vacuo at 25°C, throwing so bino 10 down to the alumina surface. Then, (i) 100 ml of toluene and (ii) a toluene (100 ml) solution of the 1,6 Diaminohexane (10 diamines, i.e. 4.92 g, for 1 $N_3P_3Cl_6$) were added and the solvent was immediately removed in vacuo as previously. A simple washing of the solid support with twice 100 ml of toluene as the eluent leads to the final product (2.61 g, 40% yield) which is the pure $\{N_3P_3[HN—(CH_2)_6—NH_2]_5\}_2[HN—(CH_2)_{10}—NH]$ ({coded as decapus **10,6**) chemical. Indeed, (i) the ^{31}P NMR spectrum at 81.015 MHz reveals a singlet at 18.3 ppm and (ii) the DCI/NH_3 mass spectrum reveals two complementary ions MH^+ at m/z 882 and 710 (together with a major side-peak at m/z 766 which corresponds to the "882" fragment minus one $[HN—(CH_2)_6—NH_2]$ tentacle). The "882" fragment corresponds to the $N_3P_3[HN—(CH_2)_6—NH_2]_5[HN—(CH_2)_{10}—NH]$ moiety whereas the "710" one corresponds to the complementary fragment $N_3P_3[HN—(CH_2)_6—NH_2]_5$ (Figure 6). Thus, aminolysis of bino **10** by 1,6-Diaminohexane on ALPOT (50:11) yields instantaneously the pure decadangling (or decapodane or decapus **10,6**) entity (m.p. = 35°C). Incidentally, the molecular ion at m/z 1590 was not observed owing to the limiting upper threshold of our detector.

Micro-analytical and physico-chemical data: Micro-analytical data are reported in Table I for some of the chemicals described here. Notice the huge variations of C% to Cl% when passing from each step to the next one, making identification of each step unambiguous. Physico-chemical data of the related derivatives are gathered in Table II.

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