New Lariat Ether-Type Macrocycles with Cyclophosphazene Subunits

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New side-armed ligands of lariat ether type **6-13** have been synthesized by the respective phenolysis and naphtholysis reactions of the parent isomeric ansa (**2, 4**) and spiro (**3, 5**) macrocyclosubstituted cyclophosphazenes of general formula $N_3P_3Cl_4[O(CH_2CH_2O)_n]$ (where $n = 4, 5$), separated by column chromatograhy, and characterized by mass spectrometry and ^1H and ^{31}P NMR spectroscopies. The synthesized side-armed ligands **6–13**, as well as their respective functional chlorine-containing precursors **2–5**, represent crown ethers with cyclophosphazene subunits and may thus be considered as diphosphaza[16]crown-6 or PNP16C6 (**2, 6, 10**), diphosphaza[19]crown-7 or PNP19C7 (**4, 8, 12**), phospha[14]crown-5 or P14C5 (**3, 7, 11**), and phospha[17]crown-6 or P17C6 (**5, 9, 13**). The one-pot method of synthesis developed for (aryloxy)-crowns **6–13**, with the phenolysis (or naphtholysis) performed *in situ* immediately after completing the formation of the respective chlorine-containing macrocycles **2–5**, made it possible to obtain high yields of the corresponding 16- and 19-membered ansa-PNP-cyclosubstituted side-armed diphosphaza-crowns PNP16C6 and PNP19C7 (**6, 8, 10, 12**) and to isolate the stable 14- and 17-membered spiro-P derivatives P14C5 and P17C6 (**7, 9, 11, 13**), inaccessible by other synthetic routes. The diphosphaza-crowns thus obtained with β-naphthoxy substituents (**10, 12**) offer promising prospects as new ligands of the P-*pivot* lariat ether type, capable of complexing both alkali and transition metal cations and of potential catalytic activity in phase and electron-transfer processes.

Introduction

Since the discovery of [18]crown-6 and other cyclic polyethers[1] efforts have continued to modify the widely useful properties of such crowns by variations of all possible structural parameters in order to make accessible new *tailor-made* ligand systems. In particular variable parameters include the number of ether oxygen atoms, ring size, substitution by other heteroatoms (N, S), and introduction of aromatic (benzene, biphenyl, naphthalene) and heteraromatic systems (pyridine, furan, thiophene) in the ring.[2]

Recently some of us have reported the synthesis of new reactive crown ethers **2** and **3** (Scheme 1), obtained by the sodium cation-assisted reaction of hexachlorocyclotriphosphazatriene (**1**) with tetraethylene glycol.[3] Both of these macrocycles contain fragments of the N_3P_3 ring system incorporated into the crown structure (**2**, PNP; **3**, P) and, therefore, considering the crown nomenclature rules, can be regarded as diphosphaza[16]-crown-6 (**2**) and phospha[14]-crown-5 (**3**), respectively.[4] Consequently they might be expected to exhibit interesting complexing properties with alkali and—in the case of lone electron pair nitrogen-containing macrocycle **2**—also to transition metal cations.[5] However, the presence of four reactive chloride functions in the molecules of **2** and **3** could lead to some disadvantageous side reactions accompanying complexation processes, similar to those previously described.[6] To avoid these problems we decided to convert the reactive crowns **2** and **3**, as well as their hitherto unknown oxypenta(ethyleneoxy) homologues **4** and **5**, into their chemically and thermally stable aryloxy derivatives. In this paper we describe the synthesis of new side-armed ligands of the lariat ether type[7] (**6–13**) by the respective phenolysis and naphtholysis reactions of the parent macrocycles **2, 3** or **4, 5**.

Of particular interest are the respective tetranaphthoxy-crowns **10–13**. Some naphthoxycyclophosphazene derivatives were previously reported to form stable radical anions.[8] Our ESR studies on β-naphthoxycyclophosphazenes $N_3P_3Cl_n(\beta\text{-}OC_{10}H_7)_{6-n}$[9] were consistent with those findings.[10] Binding both naphthalene and crown moieties to the N_3P_3 ring may thus be expected to result in favoring not only radical anion formation but also an anion activation processes ("naked anion" phenomenon[11]), both playing an important part in anionic polymeriza-

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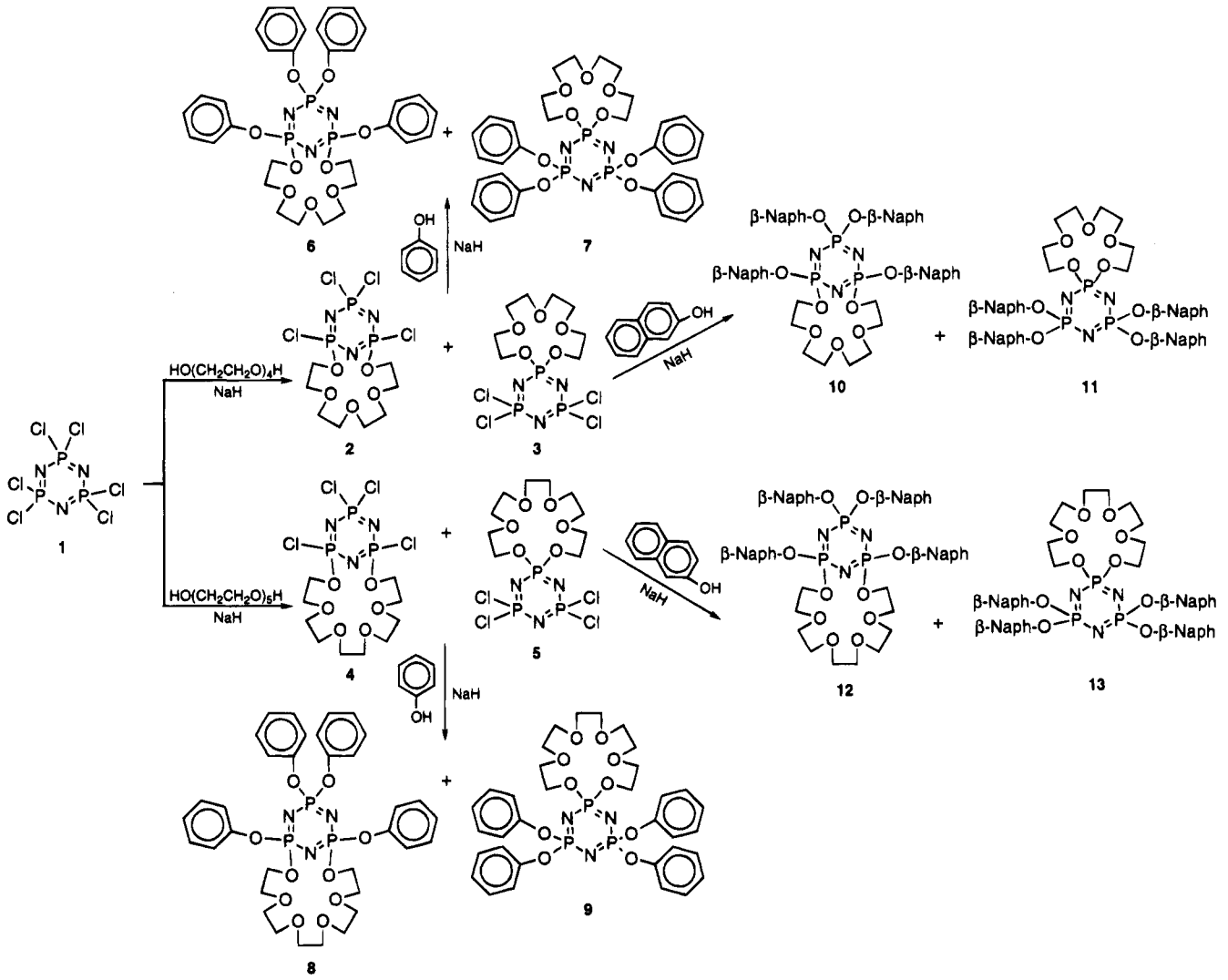
Scheme 1. Synthetic Route to Side-Armed Spiro and Ansa Cyclophosphazene Crowns[a]



[a] **2, 6, 10**; PNP[ANSA(4)]; diphosphaza[16]-crowns-6; PNP 16C6. **4, 8, 12**; PNP[ANSA(5)]; diphosphaza[19]-crowns-7; PNP19C7. **3, 7, 11**; P[SPIRO(4)]; phospha[14]-crowns-5; P14C5. **5, 9, 13**; P[SPIRO(5)]; phospha[17]-crowns-6; P17C6.

tion reactions.[12] It is worth pointing out that the complexes of naphthoxy-crowns **10–13** with potassium cations would combine structural features of potassium naphthalenide as well as classic crown ethers, a combination which has been recently found to act as a very efficient initiator in the processes of anionic polymerization of β-lactones.[13] On the other hand β-naphthoxycyclophosphazenes are known to be effective excitation energy quenchers, acting thus as photostabilizers of some light-sensitive structures.[14] All these advantages make the naphthoxycyclophosphazene crowns described in this paper promising candidates to act as cation complexing ligands and possible phase-transfer and electron-transfer catalysts in various processes proceeding in hydrolytic and photooxidative conditions.

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Results and Discussion

The synthesis and derivatization of reactive chlorine-containing macrocycles of the crown ether type containing cyclophosphazene subunits have been studied. The parent functional macrocycles were obtained by the *template-type* reactions of hexachlorocyclotriphosphazatriene (**1**) with tetra- and pentaethylene glycols, respectively, in the presence of sodium hydride by the slightly modified method described recently for the synthesis of oxytetra(ethyleneoxy) cyclophosphazene derivatives[3] (Scheme 1).

Two pairs of the respective isomeric ansa (**2, 4**) and spiro (**3, 5**) macrocyclosubstituted cyclophosphazenes of general formula $N_3P_3Cl_4[O(CH_2CH_2O)_n]$, where $n = 4, 5$, have been synthesized, separated by column chromatography, and characterized by mass spectrometry and ^1H and ^{31}P NMR spectroscopies (Tables 1 and 2). The synthesized new ligands **2–5** represent functional crown ethers with cyclophosphazene subunits and may thus be considered as the analogues of classic crown ethers: 15-crown-5 and 18-crown-6, respectively, in which one ethylene group has been replaced either by a P atom (spiro isomers **3, 5**) or by a three-membered fragment =P—N=P— of chlorocyclophosphazene ring (ansa isomers **2, 4**). Using the crown nomenclature rules[4] these parent

Table 1. Analytical and ^1H NMR Data of Isomeric Ansa and Spiro Oligo(oxy(ethyleneoxy)) Cyclosubstituted Chlorocyclophosphazene Crowns and Their Side-Armed Phenoxy and β-Naphthoxy Derivatives of General Formula $N_3P_3X_4[O(CH_2CH_2O)_n]$, $n = 4, 5$

				Anal.[b]			^1H NMR, δ_H, ppm[c]		
no.	X	n[a]	formula	C	H	N	CH_2–OC	CH_2–OP	CH_{Ar}
2	Cl	4 (A)	$C_8H_{16}O_5N_3P_3Cl_4$	20.49	3.44	8.96	3.80–3.66	4.42–4.24	
				20.72	3.22	8.62	(2m, 12H)	(m, 4H)	
3	Cl	4 (S)	$C_8H_{16}O_5N_3P_3Cl_4$	20.49	3.44	8.96	3.82–3.68	4.36–4.30	
				20.11	3.05	8.52	(2m, 12H)	(m, 4H)	
4	Cl	5 (A)	$C_{10}H_{20}O_6N_3P_3Cl_4$	23.41	3.93	8.19	3.77–3.62	4.44–4.21	
				23.67	4.01	8.03	(2m, 16H)	(m, 4H)	
5	Cl	5 (S)	$C_{10}H_{20}O_6N_3P_3Cl_4$	23.41	3.93	8.19	3.79–3.67	4.22–4.18	
				23.55	3.76	8.40	(2m, 16H)	(m, 4H)	
6	OPh	4 (A)	$C_{32}H_{36}O_9N_3P_3$	54.94	5.19	6.01	3.79–3.59	4.14–4.04	7.18–6.88
				54.85	5.27	5.88	(2m, 12H)	(m, 4H)	(2m, 20H)
7	OPh	4 (S)	$C_{32}H_{36}O_9N_3P_3$	54.94	5.19	6.01	3.83–3.70	4.31–4.27	7.34–7.16
				54.57	5.01	6.11	(2m, 12H)	(m, 4H)	(2m, 20H)
8	OPh	5(A)	$C_{34}H_{40}O_{10}N_3P_3$	54.92	5.42	5.65	3.70–3.64	4.03–4.00	7.34–6.87
				55.24	5.60	5.90	(2m, 12H)	(m, 4H)	(3m, 20H)
9	OPh	5 (S)	$C_{34}H_{40}O_{10}N_3P_3$	54.92	5.42	5.65	3.58–3.47	3.82–3.79	7.36–7.13
				54.73	5.75	5.50	(2m, 4H)	(m, 4H)	(2m, 20H)
10	O-β-Naph	4 (A)	$C_{48}H_{44}O_9N_3P_3$	64.07	4.93	4.67	3.63–3.38	4.12–4.09	7.87–6.85
				64.33	5.12	4.52	(m, 12H)	(m, 4H)	(m, 28H)
11	O-β-Naph	4 (S)	$C_{48}H_{44}O_9N_3P_3$	64.07	4.93	4.67	3.60–3.42	4.14–4.10	6.79–7.95
				63.69	4.71	4.90	(m, 12H)	(m, 4H)	(m, 28H)
12	O-β-Naph	5 (A)	$C_{50}H_{48}O_{10}N_3P_3$	63.63	5.13	4.45	3.55–3.26	3.82–3.78	7.75–7.24
				63.27	5.61	4.22	(m, 16H)	(m, 4H)	(m, 28H)
13	O-β-Naph	5 (S)	$C_{50}H_{48}O_{10}N_3P_3$	63.63	5.13	4.45	3.74–3.49	4.08–4.01	7.80–6.88
				64.02	5.25	4.19	(m, 16H)	(m, 4H)	(m, 28H)

[a] Number of CH_2 groups in polymethylene chain: (A) isomers ansa, (S) isomers spiro. [b] Calcd/found. [c] In $CDCl_3$.

Table 2. Mass Spectrometric and ^{31}P NMR Spectroscopic Data of Two Pairs of Isomeric Homologous Ansa (A) and Spiro (S) Oligo(oxy(ethyleneoxy))-Cyclosubstituted Chlorocyclophosphazene Crowns and Their Side-Armed Phenoxy and β-Naphthoxy Derivatives of General Formula $N_3P_3X_4[O(CH_2CH_2O)_n]$, $n = 4, 5$

				^{31}P NMR {^1H} (A_2B spin system)[c]			
							
no.	X	n[a]	M^+[b] calcd/found	[ppm]	[ppm]	[ppm]	J_{P-P} (Hz)
2	Cl	4 (A)	467/469		18.7, d,[d,e] P_α	25.0, t,[f] P_β	67.4
3	Cl	4 (S)	467/469	15.9, t,[g] P_β		23.2, d,[d,f] P_α	−62.6
4	Cl	5 (A)	511/512		19.3, d,[e] P_α	25.5, t,[f] P_β	67.2
5	Cl	5 (S)	511/513	5.8, t,[g] P_β		24.0, d,[f] P_α	−66.4
6	OPh	4 (A)	699/699		13.7, d,[d,e] P_α	10.1, t,[h] P_β	87.2
7	OPh	4 (S)	699/699	22.9, t,[t] P_β		11.5, d,[h] P_α	−80.5
8	OPh	5 (A)	743/743		11.0, d[d,e] P_α	7.2, t,[h] P_β	88.3
9	OPh	5 (S)	743/743	14.1, t,[g] P_β		7.6, d,[d,h] P_α	−86.2
10	O-β-Naph	4 (A)	899/901		14.2, d,[d,e] P_α	10.9, t,[h] P_β	87.6
11	O-β-Naph	4 (S)	899/901	17.5, t,[g] P_β		14.6, d,[d,h] P_α	−83.8
12	O-β-Naph	5 (A)	943/942		14.3, d,[d,e] P_α	10.8, t,[h] P_β	87.5
13	O-β-Naph	5 (S)	943/942	16.9, t,[g] P_β		11.1, d,[d,h] P_α	−85.5

[a] A, isomer Ansa; S, isomer Spiro. [b] Molecular ion according to mass spectrum, calculated for ^{35}Cl. [c] A_2B spin system; d, doublet, corresponds to P_α (two equally substituted P atoms); t, triplet, corresponds to $P_\beta \neq P_\alpha$; J_{P-P} and δ_P values calculated according to ref 18. [d] Each peak of the doublet split in two on proton coupling. [e] Proton coupling causes collapse into a broad doublet. [f] Lack of proton coupling. [g] Each peak of the triplet split into quintet on proton coupling. [h] Proton coupling causes weak broadening.

macrocyclic structures can be denoted as diphosphaza-[16]crown-6 or PNP16C6 (**2**), diphosphaza[19]crown-7 or PNP19C7 (**4**), phospha[14]crown-5 or P14C5 (**3**), and phospha[17]crown-6 or P17C6 (**5**). Ansa derivatives **2** and **4** in addition to the oxygen *hard donor* sites (A-type) contain in their crown skeleton also one nitrogen atom, representing *soft* B-type donor and therefore may be expected to interact favorably with B-type cations, like Ag^+ and Cu^{2+}.[5,15]

All the new ligands **2-5** contain four reactive chloride functions capable of undergoing various nucleophilic substitution reactions, typical for halogenophosphazenes.[16] In this work we have substituted the chlorine atoms by selected aryloxides, in particular by phenoxy and β-naphthoxy groups. Scheme 1 shows the synthetic routes leading to formation of the respective side-armed phosphazene-crowns, sodium hydride being used in all cases as hydrogen chloride acceptor. An efficient and simple *one pot* reaction method has been developed, achieving the initial substitution of **1** with the tetra- or pentaoxyethylene glycol (yielding **2**, **3** or **4**, **5**, respectively), followed by that with the given aryloxide anion (yielding **6**, **7** and **8**, **9** or **10**, **11** and **12**, **13**, respectively) without the need to isolate the unstable chloro precursors **3–5** formed in the first stage of the substitution.

This method made it possible to obtain the respective (aryloxy)-substituted spiro [oxyoligo(ethyleneoxy)]cyclophosphazenes **7**, **9**, **11**, and **13**, which were unattainable

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by the *two-step method* (involving the chromatographic separation of the mixture of **2** and **3** or **4** and **5**, respectively) due to the rapid decomposition of their respective spirocyclic chloro precursors **3** and **5** during the separation procedure (trace amounts of **3** and **5** have been isolated and stored under anhydrous conditions to get analytical data). The one-pot method afforded also higher yields of the respective ansa (aryloxy)-substituted derivatives (**6**, **8** or **10**, **12**, respectively) than those obtained by the two-step method (involving initial separation followed by phenolysis or naphtholysis of the respective chlorine-containing ansa macrocycles **2** and **4**). The latter can be explained in terms of the heterofunctionality (Cl and OH groups) of some open-chain products of substitution of **1** with oxyethylene glycols present in the crude reaction mixture, capable of interaction with ansa (**2**, **4**) and spiro (**3**, **5**) macrocycles, thus lowering the final yield of these products. Quenching the reactive chloride functions in **2** and **3**, or **4** and **5**, respectively, with inert aryloxy groups provides chemically and hydrolytically stable derivatives, which can be worked up without any special precautions.

The high rate of substitution and the ease of complete replacement of the chloride functions with bulky aryloxy groups (the full conversion of all four chlorides in **2**–**5** was reached in about 1 h at room temperature, whereas e.g., β-naphtholysis of **1** required at least 6 h of stirring on heating[17]) suggest that these reactions are sodium cation-assisted, i.e. they proceed *via* complexation of Na^+ inside/or between the respective macrocyclic cavities, weakening the electrostatic interactions within the ion paired reagents ArO^-/Na^+, and thus resulting in increased nucleophilicity of the *quasi-naked* aryloxide anions, favoring their respective interactions with electrophilic P atoms.

The respective phenoxy (**6**–**9**) and naphthoxy (**10**–**13**) derivatives, displaying high thermal and hydrolytic stability, have been synthesized, separated chromatographically, and characterized by MS and NMR methods (Tables 1 and 2). All the analytical data are consistent with the proposed structures **2**–**13**. The experimentally obtained molecular ions agree with the respective calculated values for ^{35}Cl isotopes; all the ^{31}P NMR spectra represent well-resolved A_2B systems[18] with the chemical shifts δ_P, coupling constants J_{P-P}, and respective intensity ratios[A]/[B] corresponding to the presence of the given two types of substituents in each molecule **2**–**13** and the ^1H NMR spectra show all the protons characteristic for the assumed structures.

Owing to the presence in the substituents (phenoxy or naphthoxy groups) of coordinatively-active oxygen atoms, as well as π-electrons from aromatic rings, the synthesized (aryloxy)cyclophosphazene-crowns, and in particular the respective ansa derivatives **6**, **8**, **10**, and **12**, represent interesting *P-pivot lariat ether-type* modifications of the basic macrocyclic ligands. Lariat ethers are side-armed macrocycles, in which pendant groups—attached to the so-called *pivot* atoms (C, N, P)—contain atoms with lone-paired electrons, able to cooperate with the *n*-electrons of the polyether macrocyclic skeleton.[7]

Preliminary comparative studies of the complexing abilities of the corresponding chloro- (**2**) and naphthoxy-substituted (**10**) macrocycles toward various alkali and alkali earth cations have shown that the presence of aryloxy substituents significantly alters the binding capacity of the naphthoxy derivative **10** when compared to its chloro precursor **2**. In particular, **2** displays the highest affinity toward Na cations, whereas **10** favors the potassium ones, both **2** and **10** forming avidly complexes with Ag^+, significantly more stable in the case of chlorine-free lariat ether **10**. These studies are currently under way in order to establish the relationship between the ligand structure and its affinity for given types of cations. We have also started to investigate the catalytic efficiency of naphthoxy crowns **10** and **12** in anion-promoted polymerization reactions in order to evaluate the applicability of these new ligands to such types of processes in comparison with those hitherto employed for this purpose, i.e. the complex of classic crown ether 18C6 with potassium naphthalenide.[13]

Conclusions

The one-pot method of synthesis of (aryloxy)-crowns **6**–**13** with phenolysis (or naphtholysis) performed *in situ* immediately after completing the formation of the respective chlorine-containing macrocycles **2**–**5** made it possible to reach high yields of the corresponding 16- and 19-membered ansa-PNP-macrocycles **6**, **8**, **10**, and **12** (side-armed diphosphaza-crowns PNP16C6 and PNP19C7) and to isolate the stable 14- and 17-membered spiro-P derivatives (side-armed phospha-crowns P14C5 and P17C6) inaccessible by other synthetic routes. The obtained diphosphaza-crowns with β-naphthoxy substituents (**10**, **12**) offer promising prospects as new ligands of the P-*pivot* lariat ether type, capable of complexing both alkali and transition metal cations, and of potential catalytic activity in phase-transfer and electron-transfer processes.

Experimental Section

Materials. Hexachlorocyclotriphosphazatriene was obtained from Nippon Fine Chemical Co. Ltd. and purified by fractional crystallization from hexane. Sodium hydride, 60% dispersion in mineral oil (Aldrich-Chemie), was used as received. Tetraethylene glycol (Aldrich Chemie) and 99% pentaethylene glycol (Aldrich-Chemie, 98%) were dried over 4 Å molecular sieves.

Phenol (POCh, Gliwice) was distilled in a dry argon atmosphere, mp 41 °C. β-Naphthol (2-naphthol, 2-hydroxynaphthalene) (Aldrich) was crystallized from heptane–chloroform (1:1), mp 123 °C. THF (POCh Gliwice) was distilled over a CuCl, next over a calcium hydride, and then twice over a sodium–potassium alloy under an atmosphere of dry argon. *n*-Hexane (Merck) was used without purification. For column chromatography silica gel 60 (230–400 mesh, Merck) was used. All reactions were performed under a dry argon atmosphere.

Equipment. ^1H NMR spectra were recorded at 300 MHz using solutions in $CDCl_3$ with TMS as an internal reference. ^{31}P NMR spectra were recorded on the same spectrometer operating at 121 MHz using solutions in $CDCl_3$, and 85% H_3PO_4 as an external reference, with positive shifts recorded downfield from the reference. In most cases both proton-coupled and proton-decoupled ^{31}P NMR spectra were obtained. Mass spectra were recorded by electron ionization and/or chemical ionization (positive and negative) with an isobutane matrix. TLC experiments were performed on Meck precoated silica gel 60 plates. Flash column chromatography was done

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with silica gel (100–200 mesh), product of Merck, eluted with hexane–THF.

Synthesis of the mixture of isomeric ansa (2) and spiro (3) (oxytetra(ethyleneoxy))tetrachlorocyclotriphosphazatrienes was performed as previously reported[3] from hexachlorocyclotriphosphazatriene (**1**) (3.48 g 10 mmol), tetraethylene glycol, and sodium hydride (1:2:4)—with the modification that cooling the reaction mixture at the initial stage was dispensed and the whole synthesis was carried out at 20 °C (increase of temperature favors macrocyclization over polycondensation; however some side reactions involving chlorocyclophosphazenes are also accelerated; hence the room temperature reaction was a compromise allowing the highest yields of monocyclosubstituted derivatives **2** and **3**). The crude reaction product (4.4 g) was dissolved in 50 mL of benzene and precipitated with 50 mL of hexane to remove the polymeric fraction (1.2 g). The benzene–hexane (1:1) fraction consisted (according to ^{31}P NMR) of ~60% of **2** and ~10% of **3**, the remaining ~30% consisted of bis-cyclo(oligo(ethyleneoxy)) substituted cyclophosphazenes[3] was separated by column chromatography on silica gel, eluted with hexane–THF = 2:1, yielding **2** (1.1 g, 23.5%; R_f = 0.30 in hexane–THF = 1:1) and **3** (0.15 g, 3.2%). The ansa isomer **2** was recrystallized from hexane–chloroform (1:1) to give colorless crystals, mp 92 °C. The spiro isomer **3** decomposed on storage in air in a few days, whereas the ansa isomer **2** when pure was found to be air and hydrolytically stable for at least 1 year.

A similar procedure was used for the **preparation of the ansa (4) and spiro (5) isomeric (oxypenta(ethyleneoxy))-tetrachlorocyclotriphosphazatrienes** starting from **1**, pentaethylene glycol, and sodium hydride (1:2:4).

The crude product (4.6 g) (90% according to ^{31}P NMR) contained ~33% of **4** (ansa) and ~60% of **5** (spiro) isomers, the remainder being unidentified P-containing byproducts.

Column separation (in hexane–THF = 1:1) yielded **4**, 0.40 g (8%), R_f = 0.33 (in THF–$CHCl_3$ = 1:2), and **5**, 0.65 g (12%), as colorless oils. Attempts to crystallize **4** and **5** from $CHCl_3$–hexane and THF-hexane were unsuccessful. Both isomers **4** and **5** were found to lose solubility on storage in air (decomposition) within 1 week.

Synthesis of Naphtholyzed Ansa and Spiro Oxytetra(ethyleneoxy) Crown-cyclophosphazene Derivatives (One-Pot Method). Hexachlorocyclotriphosphazatriene (**1**, 3.38 g, 10 mmol) and tetraethylene glycol (2.16 g, 20 mmol) were dissolved in 200 mL of dry THF and placed in a 500 mL 4-necked round-bottomed flask supplied with a mechanical stirrer, reflux condenser, and argon inlet. NaH (60% oil suspension, 1.6 g, 40 mmol) was added with stirring. The reaction was carried out at 20 °C for 1 h to full conversion of **1** (as deduced from TLC results, showing the presence of ansa (**2**) and spiro (**3**) oxytetra(ethyleneoxy) derivatives together with some polymeric products). Then argon was passed through the reaction system, and β-naphthol (5.76 g, 40 mmol) in 50 mL of dry THF and NaH (60% oil suspension, 1.6 g, 40 mmol) were added. The reaction mixture was stirred at 20 °C for 1.5–2 h, to full conversion of all chloride functions as indicated by TLC, and then was filtered to remove the sodium chloride formed. The THF was distilled off under reduced pressure, and the resultant colorless oil was extracted with benzene (50 mL). The benzene solution was washed with an aqueous solution of KOH and then with distilled H_2O to remove traces of unreacted naphthol and the base. The organic layer was dried for 24 h over anhydrous Na_2SO_4 to give 5.1 g (55.6%) of yellowish oil consisting (as deduced from ^{31}P NMR results) of ansa, **10** (~88%), spiro, **11** (~10%), and trace amounts of polymeric products. The crude reaction mixture was subjected to flash chromatography, using THF–hexane = 1:1 as an eluant. Both ansa, **10** (yield 1.9 g, 37%; R_f = 0.275 in hexane–THF = 2:3), and spiro, **11** (yield 0.15 g, 3%; R_f = 0.14), tetranaphthoxy-substituted isomers were isolated as colorless oils. Recrystallization of **10** from hexane–chloroform yielded white crystals, mp = 124 °C, whereas attempts to crystallize **11** failed.

Direct Synthesis of 1,3-(Oxytetra(ethyleneoxy))-1,3,5,5-tetra(β-naphthoxy)-cyclotriphosphazatriene (10) by Naphtholysis of 1,3-(Oxytetra(ethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazatriene (2). In a 250 mL 4-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and argon inlet was placed 1,3-(oxytetra(ethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazatriene (**2**) (0.938 g, 2 mmol), β-naphthol (1.352 g, 8 mmol), 60% NaH (0.32 g, 8 mmol), and 200 mL of dry THF. The reaction was carried out with stirring at 20 °C for 1 h until full substitution of chlorine atoms with naphthoxy groups was achieved. The sodium chloride formed was filtered off and the filtrate freed of solvent under reduced pressure. The resultant colorless oil (1.72 g) according to TLC and ^{31}P NMR data consisted almost entirely of **1,3-(oxytetra(ethyleneoxy))-1,3,5,5-tetra(β-naphthoxy)cyclotriphosphazatriene (10).** The traces of unreacted naphthol were removed from the crude reaction product by subsequent extraction of its benzene solution with aqueous KOH and then with distilled water. The benzene solution was dried over anhydrous Na_2SO_4. Pure 1,3-(oxytetra(ethyleneoxy))-1,3,5,5-tetra(β-naphthoxy)cyclotriphosphazene (**10**) was obtained by crystallization from benzene–hexane (1:1) and then hexane–$CHCl_3$ (1:1): yield 1.30 g (72%), mp 124 °C.

Synthesis of Phenolyzed Ansa and Spiro Oxytetra(ethyleneoxy) Crown-cyclophosphazene Derivatives 6 and 7 (One-Pot Method). The reaction was carried out in a manner similar to that of naphtholyzed ansa, **10**, and spiro, **11**, crown derivatives, starting from hexachlorocyclotriphosphazatriene (**1**, 3.38 g, 10 mmol), tetraethylene glycol (2.16 g, 20 mmol), and 60% NaH (1.6 g (I step) + 1.6 g (II step), 8 mmol) in 200 mL of dry THF, the β-naphthol being replaced with phenol (3.76 g, 4 mmol). Full conversion of the chloride functions was achieved in ~1 h after addition of phenol and the second portion of NaH to the reaction mixture. The crude reaction product (3.8 g, 54%) consisting (according to ^{31}P NMR) of the respective ansa (~80%), spiro (~15%) **(oxytetra(ethyleneoxy))tetraphenoxycyclotriphosphazenes)**, and ~5% of some other P-containing products, probably polymers, was purified and separated as shown above for the corresponding naphthoxy derivatives.

Both ansa **6** (yield 0.8 g, 21%; R_f = 0.475 in hexane–THF = 2:3) and spiro **7** (yield 0.1 g, 2.5%; R_f = 0.25) tetraphenoxy-substituted isomers were isolated as colorless oils. Recrystallization of **6** from hexane–$CHCl_3$ yielded white crystals, mp = 72 °C; attempts to obtain crystals of **7** were unsuccessful.

Direct Synthesis of 1,3-(Oxytetra(ethyleneoxy))-1,3,5,5-tetraphenoxycyclotriphosphazatriene (6) by Phenolysis of 1,3-(Oxytetra(ethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazatriene (2). In a 250 mL 4-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser and argon inlet were placed 1,3-(oxytetra(ethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazatriene (**2**, 0.0.938 g , 2 mmol), phenol (0.752 g, 8 mmol), 60% NaH (0.32 g, 8 mmol), and 200 mL of dry THF. The reaction was carried out with stirring at room temperature for 1 h and pure **1,3-(oxytetra(ethyleneoxy))-1,3,5,5-tetraphenoxycyclotriphosphazatriene (6)** was isolated as described for the respective naphthoxy analogue **10**. Yield: 0.42 g, mp 72 °C.

Synthesis of Naphtholized Ansa and Spiro Oxypenta(ethyleneoxy) Crown-cyclophosphazene Derivatives 12 and 13 (One-Pot Method). Hexachlorocyclotriphosphazene (**1**, 3.38 g, 10 mmol) and pentaethylene glycol (2.60, 20 mmol) were dissolved in 200 mL of dry THF and placed in a 500 mL 4-necked round-bottomed flask supplied with a mechanical stirrer, reflux condenser, and argon inlet. NaH (60% oil suspension, 1.6 g, 40 mmol) was added, and after 1 h of stirring at 20 °C, β-naphthol (5.76 g, 40 mmol) in 50 mL of dry THF and NaH (60% oil suspension, 1.6 g, 40 mmol) were introduced to the mixture of chlorocyclophosphazene crowns **4** and **5**, having been formed. The naphtholysis reaction was carried out as described for the synthesis of the respective naphthoxy-(oxytetra(ethyleneoxy)) derivatives **10** and **11**. Full conversion of all chloride functions was achieved in ~1.5 h. The crude reaction mixture, 5.6 g (59.4%) (after removal of unreacted phenol and glycol by washing), according to ^{31}P NMR consisted of a mixture of the respective tetranaphthoxy-substituted ansa (**12**) and spiro (**13**) isomers (jointly ~87%; estimation of the

content of individual isomers was difficult due to overlap of the respective A_2B spin systems).

The crude reaction mixture was subjected to flash chromatography, using THF–hexane = 1:1 as eluant. Both ansa, **12** (yield 1.2 g, 21%; $R_f = 0.42$ in hexane–THF = 2:3), and **spiro, 13** (yield 0.56 g, 10%; $R_f = 0.0.28$), tetranaphthoxy-substituted isomers were isolated as colorless oils. Recrystallization from hexane–$CHCl_3$ afforded both **12** and **13** in the form of white crystals, mp = 102 °C (**12**); 74 °C (**13**).

Synthesis of Phenolized Ansa and Spiro Oxypenta(ethyleneoxy) Crown-cyclophosphazene Derivatives 8 and 9 (One-Pot Method). The reaction was carried out in manner similar to that for the naphtholized ansa, **12**, and spiro, **13**, crown derivatives, starting from hexachlorocyclotriphosphazatriene (**1**, 3.38 g, 10 mmol), pentaethylene glycol (2.60 g, 20 mmol), and 60% NaH (1.6 g (I step) + 1.6 g (II step), 8 mmol) in 200 mL of dry THF, the β-naphthol being replaced with phenol (3.76 g, 4 mmol). The reaction mixture was stirred at 20 °C for 2 h after the addition of phenol and the second portion of NaH. The crude reaction product (3.6 g, 48.4% of theoretical yield) consisting (according to ^{31}P NMR) mainly of the respective ansa (~50%) and spiro (~40%) **(oxypenta(ethyleneoxy))tetraphenoxycyclotriphosphazatrienes** was purified and separated as shown above for the corresponding naphthoxy derivatives.

Both ansa, **8** (yield 0.72 g, 20%; $R_f = 0.375$ in hexane–THF =1:1), and spiro, **9** (yield 0.43 g, 12.0%; $R_f = 0.25$), tetraphenoxy-substituted isomers were isolated as colorless oils. Attempts to obtain them in crystalline forms failed.

A significant drop in the yield[19] of the respective crown derivatives **2-13** during column chromatography can be explained in terms of their complex formation with the silica gel sorbent. (Attempts to achieve separation by the use of Al_2O_3 failed—as the sorption of cyclophosphazene crowns on the alumina was almost complete.)

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(19) Yields of pure chromatographically separated individuals are based on the amounts of the respective mixtures subjected to column chromatography.