# Supramolecular Assistance to Regioselectivity in the Reactions of Chlorocyclophosphazenes with Sodium Oxyanions: Macrocyclic Effect and Anion Dependence

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Comparative studies of the naphtholysis of crown-bearing tetrachlorocyclotriphosphazene **2** and its acyclic analogue, *nongem*-diethoxytetrachlorocyclotriphosphazene **5** (*which was synthesized and isolated in the pure cis form for the purpose of this study*), reveal a significant macrocyclic effect of the substituent on both the kinetics and regiochemistry of chlorine substitution in the $N_3P_3$ ring. Whereas substitution of **5** with sodium naphthoxide provided moderate yields of the respective sterically and electronically favored *nongem*-naphthoxydiethoxy derivative as the major product, isolated as the mixture of cis and trans isomers **8** + **9**, the corresponding reaction of crown substrate **2** resulted in highly regioselective formation of the gem-to-macrocycle substituted mononaphthoxy PNP-crown derivative **11a**. The importance of the PNP-crown related effects for the regio- and stereocontrol of the substitution of chlorine atoms in the $N_3P_3$ ring is discussed in terms of supramolecular sodium cation-assisted interactions between the ring oxy substituent(s) and incoming oxyanions. To approach the problem of the anion-dependence of the regioselectivity, a comparison has been drawn between the reactions of the PNP-crown substrate **2** with sodium arylates derived from $\beta$-naphthol (**10a**) and phenol (**10b**), carried out with equimolar or 100% excess sodium oxyanion with respect to **2**, and the corresponding reactions of **2** with sodium monoenolates derived from the $\beta$-dicarbonyl compounds: acetylacetone (**10c**) and ethyl acetylacetate (**10d**). The effectiveness of supramolecularly assisted transition state stabilization is found to be dependent not only on the dimensional complementarity between the cation and the macrocycle but also on the properties of the four interacting ionic centers according to the HSAB principle and on the nature of the electronic interaction of the PNP-crown substituent with the $N_3P_3$ ring, the latter determining the extent of regiocontrol to either one or two macrocyclic chloride functions. The increase of the extent of regioselectivity of gem-substitution at the PNP-macrocycle when passing from arylate to $\beta$-dicarbonyl enolate oxy anions is related to the observed trends in the $^{31}P$ NMR chemical shifts and refers to the electronic structure of the oxy substituent.

## Introduction

Reactive crown ethers are one of the main focuses of modern supramolecular chemistry as they possess some of the attributes of enzymes. Like enzymatic processes, the reactions of functional macrocycles are considerably influenced by metal cations complexed inside the macrocyclic cavity, which take part in stabilization of supramolecularly assisted transition states leading to the regioselective and/or stereoselective formation of the specific products.[1] Cation participation (revealed as catalysis or inhibition) was previously shown to be a general phenomenon in nucleophilic displacement reactions at phosphorus, sulfur, and carbon centers.[2] Model studies revealed that alkali metal cation catalysis is particularly pronounced in the reactions of macrocyclic substrates due to the beneficial influence of additional binding energy provided by a polyether moiety proximal to the reaction zone.[1,3] Since the question of selective transition-state stabilization in small model systems is crucial to the understanding and design of more complex supramolecular systems capable of displaying enzyme-like catalytic activity, it seemed worthwhile to extend the studies of metal ion effects, hitherto focused mainly on the reactivity of functional benzocrown ethers (*nucleophilic substitution at the oxygen*[1−3] *or carbon center*[1h]) to the reactions of crown ethers bearing reactive functions at the ring phosphorus atoms derived from hexachlorocyclotriphosphazatriene ($N_3P_3Cl_6$, **1**). The latter resembles the benzene ring as far as uniformity of all bond

(1) For cation catalysis in the reactions of crown ethers, see, e.g.: (a) Cacciapaglia, R.; Mandolini, L.; Romolo, F. S. *J. Phys. Org. Chem.* **1992**, *5*, 457−460. (b) Cacciapaglia, R.; Mandolini, L. *Chem. Soc. Rev.* **1993**, 221−231 and references therein. (c) Cacciapaglia, R.; Mandolini, L.; Van Axel Castelli, V. *Recl. Trav. Chim. Pays-Bas*, **1993**, *112*, 347−350. (d) Doddi, G.; Ercolani, G.; La Pegna, P.; Mencarelli, P. *J. Chem. Soc., Chem Commun.* **1994**, 1239−1240. (e) Cacciapaglia R.; Mandolini, L.; Tomei, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 367−372 and references therein. (f) Cacciapaglia, R.; Mandolini, L.; Spadola, F. *Tetrahedron* **1996**, *26*, 8867−8876. (g) Cacciapaglia, R.; Mandolini, L.; Van Axel Castelli, V *J. Org. Chem.* **1997**, *62*, 3089−3092. (h) Schroeder, G.; Leska, B. *Supramol. Chem.* **1998**, *9*, 17−24. (i) Cacciapaglia, R.; Di Stefano, S.; Kelderman. E.; Mandolini, L. *Angew. Chem., Int. Ed.* **1999**, *38*, 348−351.

(2) (a) Pregel, M. J.; Buncel, E. *J. Org. Chem.* **1991**, *56*, 5583−5588. (b) Mentz, M.; Modro, A. M.; Modro, T. M. *J. Chem. Res., Synop.* **1994**, 46−47. (c) Pregel, M. J.; Dunn, E. J.; Nagelkerke, R.; Thatcher, G. R. J.; Buncel, E. *Chem. Soc. Rev.* **1995**, 449−455.

(3) Landini, D.; Maia, A.; Penso, M. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chairman of the Editorial Board; Gokel, G. W., Volume Ed.; Pergamon: New York, 1996; Vol. 1, pp 417−464 (anion activation).

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lengths and planarity of ring system are concerned. However, the cyclophosphazenic $\pi$ bonds are strongly polarized toward the nitrogen atoms resulting in reduced or no $\pi$-electron density at the phosphorus atoms.[4] Therefore, contrary to benzene, which requires the presence of electron-withdrawing groups ortho and/or para to the leaving group to promote nucleophilic substitution at aromatic carbon atoms,[5] nucleophilic substitution at the electropositive $N_3P_3$-ring phosphorus atoms occurs spontaneously with a wide scope of nucleophiles and is the subject of intensive studies aimed at the clarification of the factors controlling its stereo- and regiochemical pathways.[4,6]

2,4-(Oxytetraethylenoxy)-2,4,6,6-tetrachlorocyclotriphosphazatriene (**2**[7a]) and its analogues, called in general PNP-crowns,[7b] developed in our laboratory, combine the versatile reactivity of chlorocyclophosphazenes[4] with the capability of forming *host−guest* complexes typical for crown ethers.[8] Therefore, the research in this field contributes both to the supramolecular chemistry[9] and to the chemistry of phosphazenes.[4]

Reactions of the functional PNP-crown **2**[7] with sodium bis-$\beta$-naphtholate have been found to proceed regioselectively at the positions adjacent (*geminal*) to the PNP-macrocycle,[4a,b] despite steric and electronic effects, which favor the attack of the incoming dinucleophile on the cyclophosphazenic $PCl_2$ center remote from the macrocycle.[4c] This unusual substitution pattern was ascribed to cation assistance[1] of the respective transition state by the above ion-paired dinucleophile, and this phenomenon attributed to the presence of the crown substituent on the cyclophosphazene ring. However, this hypothesis lacked direct experimental evidence based on a comparison of related cation-assisted reactions of the PNP-crown substrate **2** and an appropriate acyclic analogue. Such comparative studies have been performed earlier by others to establish the important influence of macrocyclic effects on the substitution pattern and kinetics in reactions of numerous benzocrown and calixcrown substrates.[1a,b,d,h]

Another problem to be clarified is the extent of supramolecular regiocontrol in reactions of the PNP-crown substrates with sodium oxyanions**.** The question to be answered is how the nature of the oxyanion influences the substitution pattern, and, in particular, the regioselectivity of substitution of the first and second macrocyclic chloride functions. In the reaction of **2** with disodium bis-$\beta$-naphtholate, only the first step of the disubstitution was found to be controlled by *host−guest* interactions, whereas substitution at the second macrocyclic PCl-group was only slightly preferred over that at the $PCl_2$ site.[10] However, one could assume that in the case of this bulky chiral dinucleophile control of the second step in disubstitution might be influenced by steric factors, in particular, hindered rotation of the 1,1′-binaphthyl unit. To assess how well conclusions based upon reactions of **2** with the disodium bis-$\beta$-naphtholate can be extended toward mononucleophilic species we have studied now reactions of **2** with sodium $\beta$-naphthoxide carried out with 1:1 and 1:2 molar ratios of reagents.

To probe the generality of conclusions drawn from the reaction of **2** with this nucleophile, the study has been extended toward other sodium cation-paired oxyanions. It is widely recognized that the nature of the interaction of the exocyclic group with the cyclophosphazene is one of the major factors responsible for regio-and stereoselectivity in substitution reactions of cyclophosphazenes.[4c] Aryloxy groups are known to be weakly electron-donating with respect to the remaining chlorine atoms.[4c] Comparison of the $^{31}P$ chemical shifts of naphthoxy[11] and acetylacetone monoenolate[12] derivatives of $N_3P_3Cl_6$ (**1**) reveals much increased electronegativity of the $\alpha$, $\beta$-carbonyl unsaturated oxy-substituents with respect to the aryloxy ones.[6d,13c] Therefore, to approach the problem of the anion-dependence of the regioselectivity in the reactions of chlorocyclophosphazene-containing crown ethers with sodium oxyanions, we have compared the reactions of the PNP-crown substrate **2** with sodium arylates derived from phenol and $\beta$-naphthol with the corresponding reactions of **2** with sodium monoenolates derived from the $\beta$-dicarbonyl compounds—acetylacetone and ethyl acetylacetate. The recognition of anion effect seemed to be of importance to predict the efficiency of cation catalysis, which is known to be dependent on the differential affinity of the complexed cation the initial state (substrate, i.e., attacking nucleophile) and to the transition state (product, i.e., leaving group).[1] The mutual affinity of chemical species can be considered in view of the hard−soft acid−base principle (HSAB),[14] which is a concept widely used to explain the regiochemical outcome of various reactions or to predict the reaction pathway.[14e−g] To the best of our knowledge, there have been no reports

(4) For general relationships in cyclophosphazene chemistry, see, for example: (a) Allcock, H. R. *Phosphorus−Nitrogen Compounds: Cyclic, Linear and High Polymeric Systems*; Academic Press: New York, 1972; Russ. Ed. Moscow, Mir, 1976; Chapters 5, 6, 7, and 12. (b) Krishnamurthy, S. S.; Sau, A. C. *Adv. Inorg. Chem., Radiochem.* **1978**, *21*, 41−11 (c) Allen, C. W. Cyclophosphazenes and Heterocyclophosphazenes. *The Chemistry of Inorganic Homo- and Heterocycles*; Academic Press: London, 1987; Vol. 2, pp 501−661. (d) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119−135.

(5) March, J. In *Advanced Organic Chemistry. Reactions, Mechanisms and Structure*, 4th ed.; Wiley: New York, 1992; pp 641−653.

(6) For representative recent papers, see, e.g.: (a) Allcock, H. R.; Al-Shali, S.; Ngo, D. C.; Visscher, K. B.; Parvez, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3521−3532 and references therein; (b) McIntosh, M. B.; Hartle, T. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1999**, *121*, 884−885. (c) Lee, S. B.; Song, S.-Ch.; Jin J.-Il, *J. Am. Chem. Soc.* **2000**, *122*, 8315−8316. (d) Allen, Ch. W.; Brown, D. E.; Worley, S. D. *Inorg. Chem.* **2000**, *39*, 810−814 and references therein.

(7) (a) Brandt, K.; Kupka, T.; Drozd, J.; van de Grampel, J. C.; Meetsma, A.; Jekel, A. P. *Inorg. Chim. Acta* **1995**, *228*, 187−192. (b) Brandt, K.; Porwolik, I.; Kupka, T.; Olejnik, A.; Shaw, R. A.; Davies, D. B. *J. Org. Chem.* **1995**, *60*, 7433−7438.

(8) For complexation properties of crown ethers, see, e.g.: (a) *Crown Ethers & Analogues*; Patai, S., Rappaport, Z., Eds.; John Wiley & Sons: Chichester, New York, Brisbane, Singapore, 1989. (b) Gokel, G. W. *Crown Ethers & Cryptands, Monographs in Supramolecular Chemistry*; The Royal Society of Chemistry, Thomas Graham House: Science Park, Cambridge, 1991. (c) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, New York, New Rochelle, Melbourne, Sydney, 1989.

(9) For basic knowledge on supramolecular chemistry, see, e.g., review papers: (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89−112. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304−1319; Fyfe, M. C. T.; Stoddard, J. F. *Acc. Chem. Res.* **1997**, *30*, 393−401.

(10) (a) Brandt, K.; Porwolik, I.; Olejnik, A.; Shaw, R. A.; Davies, D. B.; Hursthouse M. B.; Sykara, G. D. *J. Am. Chem. Soc.* **1996**, *118*, 4496−4496. (b) Brandt, K.; Porwolik, I.; Siwy, M.; Kupka, T.; Shaw, R. A.; Davies, D. B.; Hursthouse M. B.; Sykara, G. D. *J. Am. Chem. Soc.* **1997**, *119*, 51, 12432−12440.

(11) Brandt, K. *Polish J. Appl. Chem.* **1991**, *35*, 143−150.

(12) Drozd, J.; Brandt, K.; Kupka, T. *Inorg. Chem.* **1994**, *33*, 3602−3604.

(13) (a) In ref 4a, Chapter 3, pp 94−125. (b) In ref 4c, p 508−509. (c) Allen, C. W. Applications of $^{31}P$ NMR Spectroscopy in Cyclophosphazene Chemistry. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkrade, J. G., Eds.; VCH Publishers: Weinheim, Germany, 1994; Chapter 9, pp 103−128 and references therein.

on the applicability of the HSAB principle to the nucleophilic substitution reactions for a series of chlorocyclophoshazene derivatives. Also, little attention has been given to the HSAB principle being operative in cation-assisted reactions of functional macrocycles.[1c,15]

**The purpose of this work was 3-fold:** (i) to design and prepare an appropriate acyclic model of the tetrachloro-PNP-crown **2** that mimics all of the steric and electronic features of the latter except for the macrocyclic character of its dioxy-substituent(s); (ii) to assess the macrocyclic effect on the regiochemistry of chlorine substitution in the of $N_3P_3$ ring by comparison of the regiochemical outcomes of the sodium cation-assisted naphtholysis reactions of corresponding macrocyclic and acyclic chlorocyclophosphazene substrates; and (iii) to approach the problem of the anion-dependence of supramolecular assistance to regioselectivity in reactions of the PNP-crown **2** with sodium oxyanions by comparison of the efficiency and extent of the regiocontrol of chlorine substitution in **2** with sodium arylates and sodium $\beta$-dicarbonyl enolates, representing oxyanions of different polarizability, which might be expected to display different electronic interactions with the phosphazene ring; being known to be of paramount importance in pathway selection for such chlorine substitution reactions.[4d] Additionally, we have assumed that the availability of a series of new, closely related compounds will contribute to the continuous search for systematic trends in NMR data and, in particular, $^{31}$P chemical shift correlations in cyclophosphazene series.

## Results and Discussion

**"Macrocyclic Effect" in Reactions of *cis-nongem*-Dialkoxytetrachlorocyclophosphazenes with Sodium Naphthoxide.** To assess the importance of the macrocyclic nature of dioxy substituent(s) on the reactivity of *nongem*-tetrachlorocyclophosphazenes, we decided to study the substitution reaction of tetrachloro PNP-crown **2** with sodium naphthoxide along with the similar reaction of an appropriate acyclic model compound. Sodium cation was assumed to be the best potential catalyst as it served as a template for the synthesis of **2**.[7a] Its catalytic efficiency has been previously demonstrated in the reaction of **2** with sodium bi-$\beta$-naphtholate.[10]

**Preparation of an Acyclic Analogue of the PNP-crown.** In obtaining the desired analogue of **2** we encountered the problem of cis−trans isomerism, which is still one of the less clarified issues in cyclophosphazene chemistry.[4c,d,6c−d,16] The key point was that the PNP-crown **2** to be modeled has been unambiguously established to be the cis-isomer by X-ray crystallography.[7a]

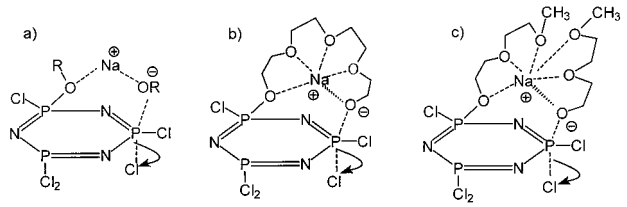



**Figure 1.** Rationalization of the cis stereoselectivity in the $S_N2$ reactions of $N_3P_3Cl_6$ with (a) sodium methoxide[4d] and sodium ethoxide (this work), (b) disodium (tetraethylenoxy) oxide,[7a] and (c) sodium 2-(2-methoxyethoxy)ethoxide[6c] in terms of the co-coordination (cooperative binding) of sodium counterion by the present and incoming oxy substituents.

Therefore, what we needed was the respective *cis-nongem*-diethoxytetrachlorocyclotriphosphazene, which would mimic all the steric and electronic features of **2** except for the macrocyclic character of its ansa dioxy substituent.

**Supramolecular Assistance to Stereoselectivity in the Reactions of $N_3P_3Cl_6$ with Sodium Oxyanions.** The cis form was the only geometrical isomer of ansa-macrocyclic nongem-derivative of formula $N_3P_3Cl_4[O(CH_2CH_2O)_4]$ (**2**) isolated from the substitution products of $N_3P_3Cl_6$ (**1**) with the disodium salt of tetraethylene glycol.[7a] Recently, complete cis stereoselectivity has been also found in the reactions of **1** with sodium methoxy diethylene glycol.[6c] Distinctive cis preference has been previously observed in the reactions of chlorocyclophosphazenes with sodium methoxide.[4d,16]

In our opinion, all these effects could be rationalized in terms of supramolecular assistance[19] to stereoselectivity, consisting of stabilization of the respective cis-alignments against the $N_3P_3$ ring by cooperative supramolecular ion−dipole interactions of sodium cation with oxygen donors of both the ring substituent and incoming nucleophile. A similar interpretation has been proposed recently for cis stereoselectivity induced by sodium salts of alkoxy poly(ethylene glycol)s.[6c] The greater the total number of oxygens (up to 6) available for coordination, the stronger is stabilization of the formed supramolecular assembly. This results from an optimum coordination number of 6 for sodium cation.

The strongest complexes are formed when the number of oxygen donors available for coordination matches, as far as possible, the coordination number of a particular cation.[20] Therefore, it might be assumed the effect of supramolecular control of cis stereoselectivity would be much stronger for the reactions of $N_3P_3Cl_6$ (**1**) with both the glycol salts,[7a,6c] which provide five and six oxygen donors, respectively, for coordinative interactions with sodium cation, than for the reaction of **1** with sodium methoxide,[4d] whose transition state offers coordination with only two oxygen atoms (Figure 1).

(14) For contemporary definition and comprehensive information on the HSAB principle, see: (a) Pearson, R. G. *Chemical Hardness, Applications from Molecules to Solids*; Wiley-VCH: Verlag GmbH, Weinheim, 1997; (monograph book). (b) Pearson, R.G. *Inorg. Chim. Acta* **1995**, *240*, 93−98 (the HSAB principle: more quantitative aspects). (c) Gazquez, J. L. *J. Phys. Chem. A* **1997**, *101*, 4657−4659. (d) Gazquez, J. L. *J. Phys. Chem.* **1997**, *101*, 9464−9469. (e) Damoun, S.; Van de Woude, G.; Mendez, F.; Geerlings, P. *J. Phys. Chem. A* **1997**, *101*, 886−893. (f) Mendez, F.; de. L. Romero, M.; De Proft, F.; Geerlings, P. *J. Org. Chem.* **1998**, *63*, 5774−5778. (g) Chandra, A. K.; Michalak, A.; Nguyen, M. T.; Nalewajski, R. F. *J. Phys. Chem.* **1998**, *102*, 10182−10188.

(15) Gobbi, A.; Landini, D.; Maia, A.; Secci, D. *J. Org. Chem.* **1995**, *60*, 5954−5957 and references therein.

(16) Kumara Swamy, K. C.; Krisnamurthy, S. S. *Inorg. Chem.* **1986**, 25, 920−928.

(17) (a) Ramachandran, K.; Allen, Ch. W. *Inorg. Chem.* **1983**, *22*, 10, 1445−1448 and references therein. (b) Brown, D. E.; Allen, C.W. *Inorg. Chem.* **1987**, *26*, 934−987.

(18) Allcock, H. R.; Schmutz, J. L. *Inorg. Chem.* **1975**, *14*, 2433−2438.

(19) The term "supramolecular assistance to molecular synthesis", which means the employment of noncovalent bonding interactions between appropriately complementary substrates to guide the formation of covalent bonds, was first introduced by Stoddart, J. F. et al. in ref 9c. See also: (a) Philip, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154−1196. (b) Gillard, R. E.; Raymo, F. M.; Stoddart, J. F. *Chem. Eur. J.* **1997**, *3*, 1933−1940.

(20) In ref 8a, Chapter 4, pp 207−304.

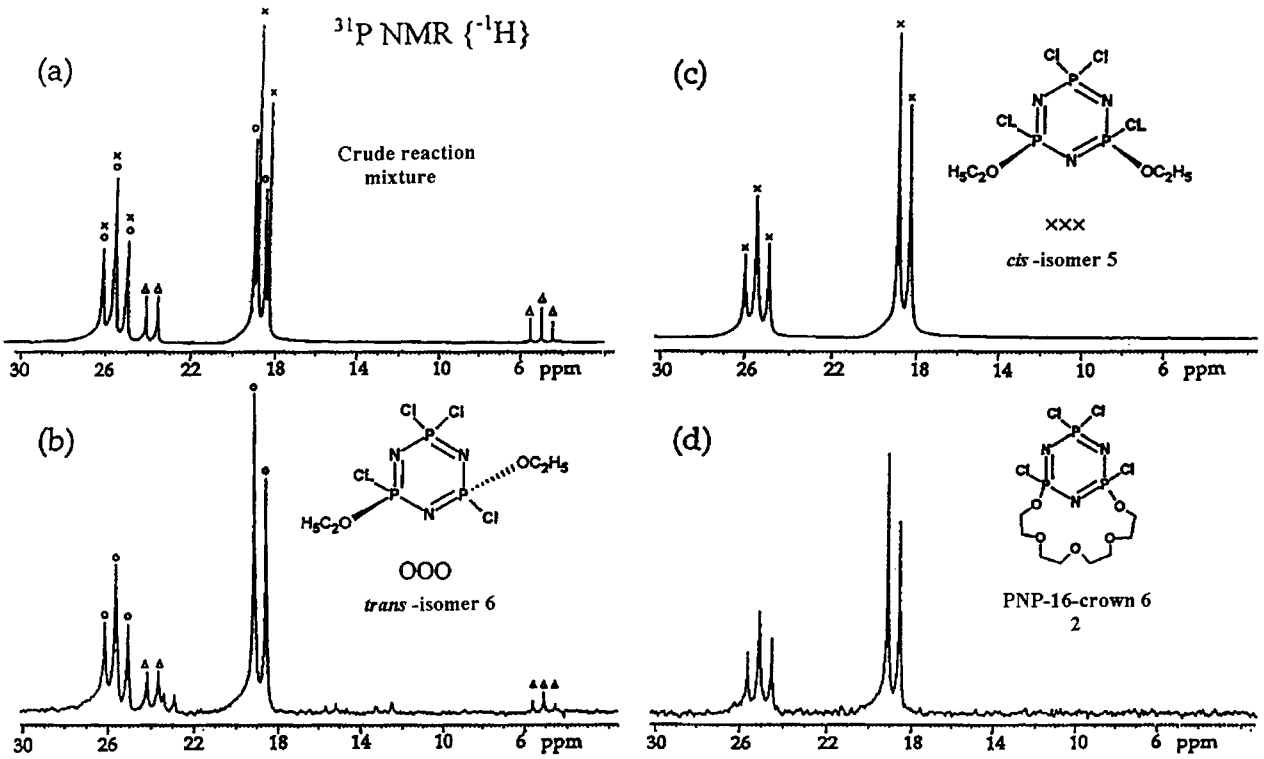
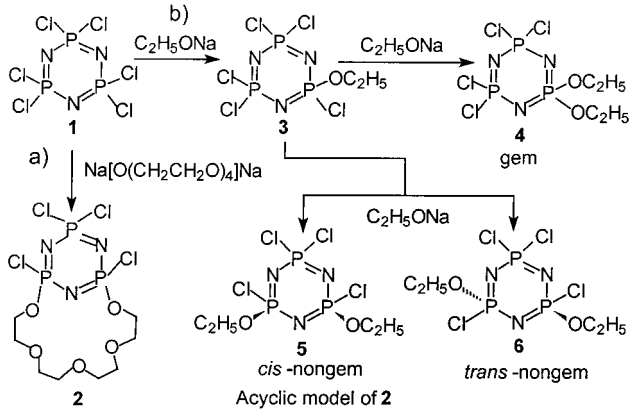



**Figure 2.** Proton-decoupled $^{31}$P NMR spectra for the products (in $CDCl_3$ solutions) of the reaction of $N_3P_3Cl_6$ (**1**) with 2 molar equiv of sodium ethoxide aimed at the synthesis of acyclic model **5** of the PNP-crown substrate **2**: (a) the spectrum of the product eluted by flash chromatography (hexane−chloroform = 5:1) from the crude reaction mixture; (b) and (c) the respective spectra of two individual fractions separated chromatographically (eluant: hexane−chloroform 15:1) from the initial mixture (a); (d) for comparison: $^{31}$P NMR spectrum of $N_3P_3Cl_4[O(CH_2CH_2O)_4]$, **2** (macrocyclic analogue of **5**). Circles (○) denote the $AB_2$ spin system with more positive chemical shift for $P_A$ center, according to the previous reports[17] assigned to the less abundant trans isomer of *nongem*-$N_3P_3Cl_4(OC_2H_5)_2$ (**6**); crosses (×) denote the $AB_2$ spin system with less positive chemical shift for $P_A$ center, assigned to the more abundant cis isomer of *nongem*-$N_3P_3Cl_4(OC_2H_5)_2$ (**5**), representing an acyclic model of the PNP-crown **2**; and triangles (△) denote the $A_2X$ spin system ascribed to *gem*-$N_3P_3Cl_4(OC_2H_5)_2$ (**4**).

Similarly, only a modest cis preference would be expected in the disubstitution of **1** with sodium ethoxide. This expectation has been confirmed by the results of our current investigation. Thus, a mixture of cis-trans isomers of *nongem*-diethoxytetrachlorocyclophosphazene, **5** and **6**, respectively, slightly contaminated with a small amount (∼5%)[21] of the third product, assumed to be gem derivative **4**, was isolated by flash chromatography of the crude product mixture obtained by the room-temperature reaction of $N_3P_3Cl_6$ with two molar equivalents of sodium ethoxide in THF (Scheme 1).

Structural assignments were based on analysis of the $^{31}$P NMR data of the crude isomeric mixture (Figure 2a), following the approach applied by Allen for the discrimination of cis-trans isomers of (vinyloxy)chlorocyclophosphazenes.[17a,21c] The nongeminal isomers **5** and **6** both exhibit $AB_2$ spectra (parts b and c of Figure 2, respectively) with identical A regions corresponding to $PCl_2$ groups. In the B region corresponding to $\equiv PCl(OC_2H_5)$, the chemical shifts are slightly different. A comparison

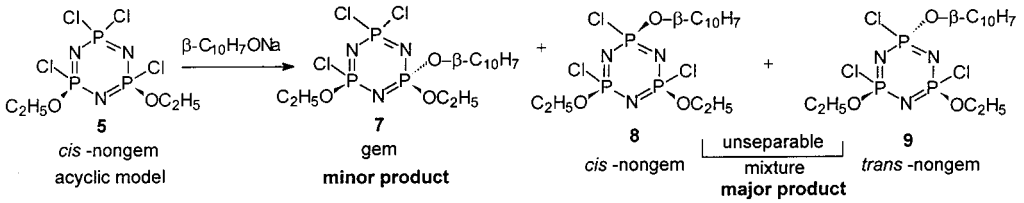
**Scheme 1. Synthesis of the PNP Crown 2 (a) and Its Acyclic Analogue 5 (b) by Cation-Assisted Disubstitution of Hexachlorocyclotriphosphazatriene 1 with the Appropriate Sodium Oxyanions**



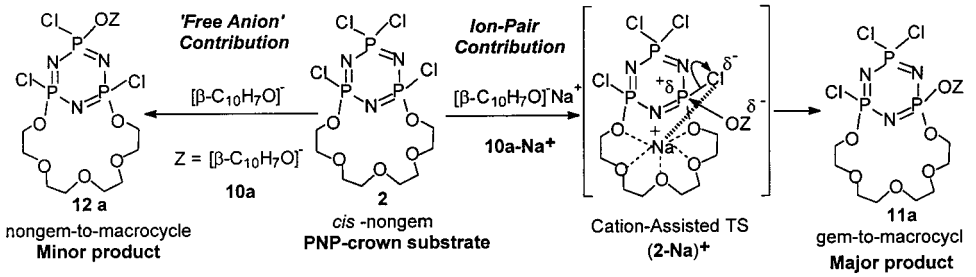

of the doublet intensities of the B portions clearly demonstrates that the isomer with a less positive chemical shift predominates in the isolated crude isomeric mixture. While the $^{31}$P NMR data allow for unambiguous identification of positional isomers, the stereochemistry of the individual components of the sets of configurational isomers cannot be made with certainty. However, on the basis of previously reported $^{31}$P NMR spectra of bis(dimethylamino) and bis(divinyloxy)chlorocyclotriphosphazenes, where more positive chemical shifts of the

(21) (a) All relative abundances have been inferred from the respective $^{31}$P NMR spectra by referring the integrated spin area corresponding to a given compound to overall peak intensity. (b) in the case of overlapping of some parts of the respective spin systems the comparison was limited to the nonoverlapping parts of the spectra, e.g., for $A_2B$ spectra of cis−trans isomers with the same B parts − to referring the respective doublet intensities. (c) To estimate the relative abundances of the isomers (cis−trans ≅ 3:2) we disregarded the computer simulation of the observed $^{31}$P spectra, used by Allen in ref 17a as the quantitative assignments of isomeric composition were beyond the scope of this study.

**Scheme 2. Substitution Pattern for Naphtholysis of Acyclic Substrate 5**




**Scheme 3. Substitution Pattern for Naphtholysis of Macrocyclic Substrate 2**




≡PCl(X) centers (X = $NMe_2$ or $OCH{=}CH_2$, respectively) have been found for the trans (compared to the cis) isomers,[17] it seems reasonable to ascribe the cis configuration to the more abundant isomer in the mixture of nongem diethoxycyclotriphosphazenes obtained by sodium-assisted disubstitution of **1** with ethoxide anion.

The minor product shows a low-intensity $A_2X$ spectrum (Figure 2a) that closely resembles that of *gem*-divinyloxycyclotriphosphazene reported by Allen.[17a] The observed $A_2X$ spin pattern seems to be consistent with the respective gem-disubstituted product 2,2-$N_3P_3Cl_4(OC_2H_5)_2$, **4**. The A part is in the $\equiv PCl_2$ chemical shift range while the X part is in the range found for $P[O(CH_2CH_2O)_4]$ $^{31}P$ chemical shift for spiro-isomer of the PNP-crown **2**, the latter resembling the *gem*-diethoxycyclotriphosphazene **4** to the same extent as the acyclic model **5** is reminiscent of **2**.[22]

The unambiguous assignment of **4** could not have been made due to its trace amounts and the resistance to the chromatographic separation. However, the detailed study on the structure of that product has been beyond the scope of our work.

In keeping with the main goal of this research, our interest has been focused on the separation of the configurational cis−trans isomers and, in particular, on isolating in a pure state the *cis*-2,4-$N_3P_3Cl_4[OCH_2CH_2\text{-}X]_2$, **5**, needed as a model compound for the studies of macrocyclic effect in the reactions of *nongem*-dioxy-substituted chlorocyclophosphazenes with cation-paired oxyanions. Using a multistep chromatographic procedure (see the Experimental Section), we have succeeded to separate the initial mixture (Figure 2a) into two fractions, the first of which contained trans isomer **6** with the small contamination of **4** (Figure 2b), whereas the second one consisted of the pure cis isomer **5** (Figure 2c). To the best of our knowledge, it is the first example of the successful preparative separation of the configurational cis−trans isomers of dialkoxycyclotriphosphazenes.[4d,6b,d,16,17]

**Naphtholysis of the PNP-crown and Its Acyclic Model.** Regarded as chlorocyclophosphazene compounds, both **2** and **5** represent the same type of derivatives: *cis-nongem*-dialkoxytetrachlorocyclophosphazenes of general formula 2,4-$N_3P_3Cl_4[OCH_2CH_2\text{-}X]_2$, where X = H for acyclic model **5** and X- - -X = $(OCH_2CH_2)_2O$ for **2**, where the oxydiethylenoxy chain makes a bridge assembling two independent ethylenoxy units into a macrocyclic polyether substituent. From the point of view of steric and electronic factors dominating the cyclophosphazene chemistry[4d] there are no remarkable differences between the compounds **2** and **5**, which is reflected in their giving almost identical $^{31}P$ NMR spectra (see Figure 2c,d). To assess the importance of additional binding energy rendered available in the cyclic substrate relative to the open chain model, in particular its effect on substitution pattern, we have compared the sodium-assisted naphtholysis reaction of the model compound, *cis*-1,2-diethoxytetrachlorocyclophosphazene (**5**) (Scheme 2) with that of the PNP-crown **2** (Scheme 3).

In keeping with the expectations, the different reactivity patterns have been found for the acyclic model (**5**) (*control*) (Scheme 2) and the PNP-crown **2** (Scheme 3), with the overall rate of substitution being distinctly higher for the macrocyclic substrate **2**.

The latter was inferred from the comparison of the $^{31}P$ NMR spectra of the respective crude reaction mixtures showing the presence of significant amount of the unreacted model substrate **5** (∼25%)[21] (Figure 3, a1, a2), with the complete consumption of the PNP-crown **2** in a similar experiment. (Figure 3, b1). In accord with the generally accepted substitution pattern for alkoxy and aryloxycyclophosphazenes[2,6a,11] the main product of naphtholysis of the acyclic model **5** is the *nongem*-5-naphthoxy-1,3-diethoxycyclotriphosphazene, isolated as the mixture of cis and trans isomers **8** and **9** (Figure 3, a3), which resisted the attempts of separation by column chromatography. The relative abundance of the respective gem-substituted acyclic derivative **7** was no more than ∼20% (Figure 3, a1), whereas the corresponding macrocyclic product **11a** definitely predominated (yield ∼90%) in the similar reaction mixture formed by the naphtholysis of the PNP-crown substrate **2** (Figure 3, b1, b2).[21]

The results obtained clearly indicate that the substitution process is strongly dependent on the ability of chlorocyclophosphazene substrate to complex alkali metal cations. The facility of complex formation increases along with a number of donor sites available for coordination of sodium cation, and therefore, it is greater for **2**, where

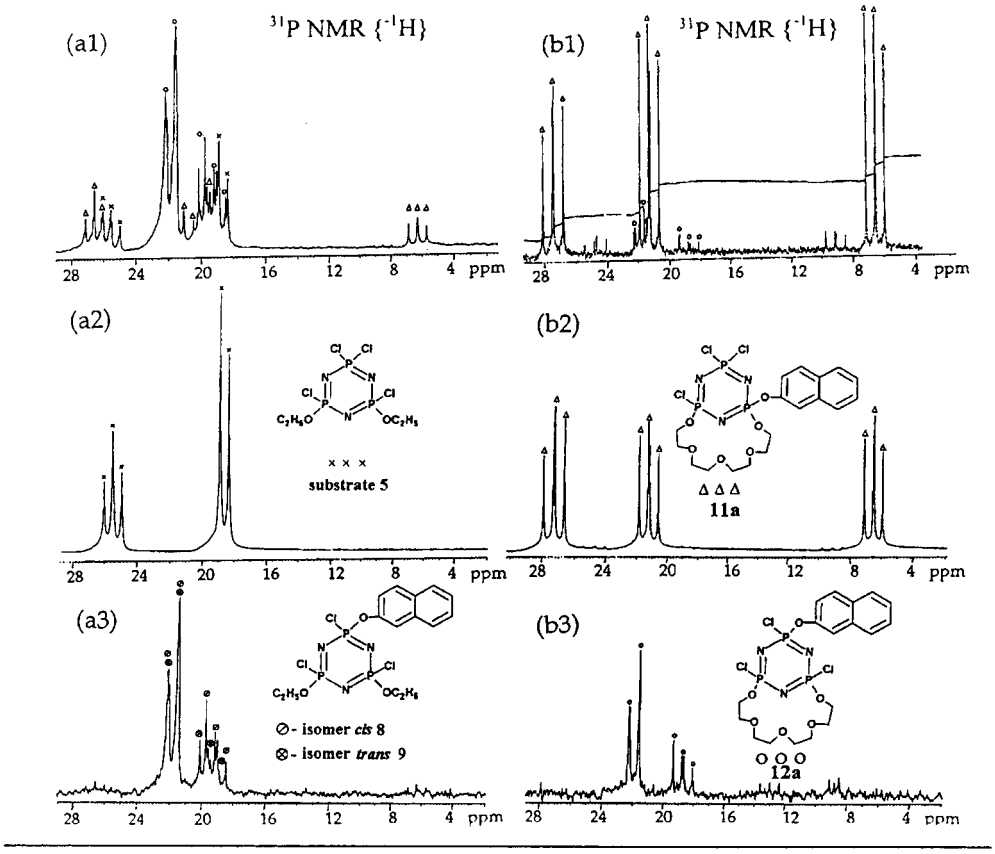



**Figure 3.** Comparison of the proton-decoupled $^{31}$P NMR spectra of the crude reaction mixtures (in $CDCl_3$ solutions) of the products formed by the equimolar (1:1) cation-assisted substitutions of (a) *cis-nongem*-$N_3P_3Cl_4(OC_2H_5)_2$, **5** (acyclic model of **2**) and (b) *cis*-nongem-$N_3P_3Cl_4[(OC_2H_4)_4O]$, **2** (macrocyclic analogue of **5**) with sodium $\beta$-naphtholate, $(\beta\text{-}C_{10}H_7O)^-Na^+$, carried out under the same experimental conditions (solvent THF; concentration of the substrates $2.5 \times 10^{-2}$ mmol/cm$^3$, $t = 20$ °C; $\tau = 2$ h): (a1) the spectrum of the crude reaction mixture from the naphtholysis of the acyclic substrate 5; (a2) and (a3) the spectra of two individual fractions separated from the crude mixture (a1) by column chromatography on silica gel (eluant hexane−chloroform = 6:1). Crosses (×) denote the $AB_2$ spin system characteristic of *cis-nongem*-$N_3P_3Cl_4(OC_2H_5)_2$ (**5**), triangles (△) denote the AMX spin system ascribed to the gem-isomer of $N_3P_3Cl_3(OC_2H_5)_2(\beta\text{-}C_{10}H_7)$ **7**; circles (○) denote the two very close to each other $A_2B$ spin systems with identical A regions, corresponding to the mixture of nongem-(**8** (cis) + **9** (trans) $\beta$-naphthoxy derivatives $N_3P_3Cl_3(OC_2H_5)_2(\beta\text{-}C_{10}H_7)$, whereas the $A_2B$ spin systems assigned to each particular isomer are marked with lined-across circles (Φ) (cis (**8**), and crossed-out circles (⊗) (trans, **9**); (b1) the spectrum of the crude reaction mixture from the supramolecularly assisted naphtholysis of the macrocyclic substrate **2**; (b2) and (b3) the spectra of two individual fractions separated from the crude mixture b1 by column chromatography on silica gel (eluant: hexane−THF = 5:1) and characterized by spectral data (Tables 2 and 3). Triangles (△) denote the AMX spin system characteristic of the gem-$N_3P_3Cl_3[(OC_2H_4)_4O]$ $(\beta\text{-}C_{10}H_7)$ (**10a**, major product) and circles (○) represent the $A_2B$ spin system of the respective nongem-isomer, **11a** (minor product). The $AB_2$ spin system of the substrate **2** (see Figure 1 d) was not detected, thus indicating its complete conversion to the substitution products.

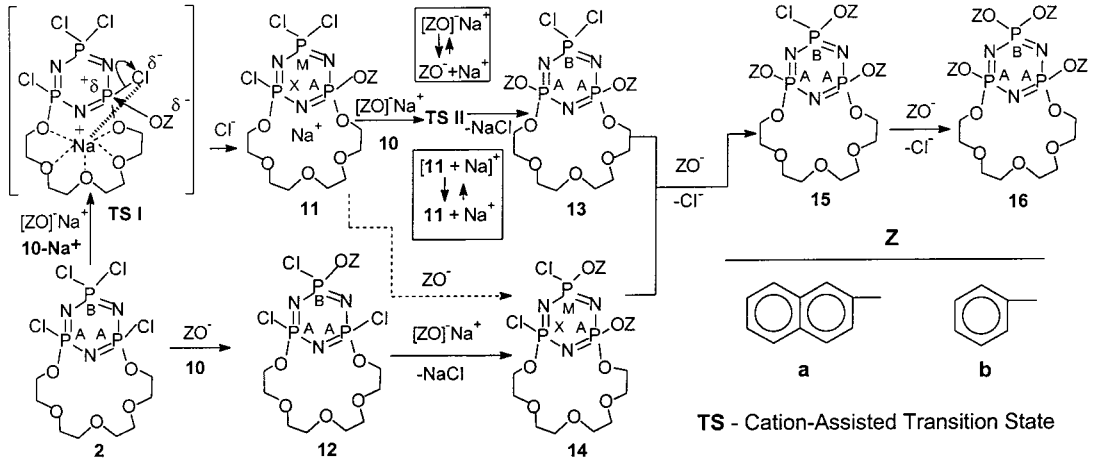
the cation is coordinated to the oxy(tetraethylenoxy) polyether chain, than for **5**, which provides for coordination only two single oxygen donors of the ethoxy substituents.

As the coordination of the cation to the polyether moiety in **2** is the initial step of the process, naphthoxide anion $(OAr)^-$ does not attack a neutral molecule **2** but the positively charged complex. $(\mathbf{2}-Na)^+$. It has been long recognized that metal catalysis in the reactions of crown substrates is due to a greater stabilization of the transition state relative to the reactants.[1,3] Considering that in the transition state the negative charge is mainly delocalized on the nucleophile and on the leaving group metal ion can interact either of them but not with both.[1b,d] The concentrations of two transition state structures depend on their relative energy; i.e., the respective affinities of $Na^+$ to $ArO^-$ (*parent nucleophile*) and $Cl^-$ (*leaving group*). Naphthoxide anion $OAr^-$ is a soft, easily polarizable nucleophile that makes it an unwelcome partner for hard sodium cation. Chemical hardness mismatch within the parent ion pair $Na^+OAr^-$ favors the exchange reaction of the $OAr^-$ for $Cl^-$, the latter making an ideal counterpart for the sodium cation as far as hardness is a criterion,[14,23] and thus seems to be a driving force for the substitution of both **2** and **5** with naphthoxide ion according to the HSAB principle.[14] Similar effect

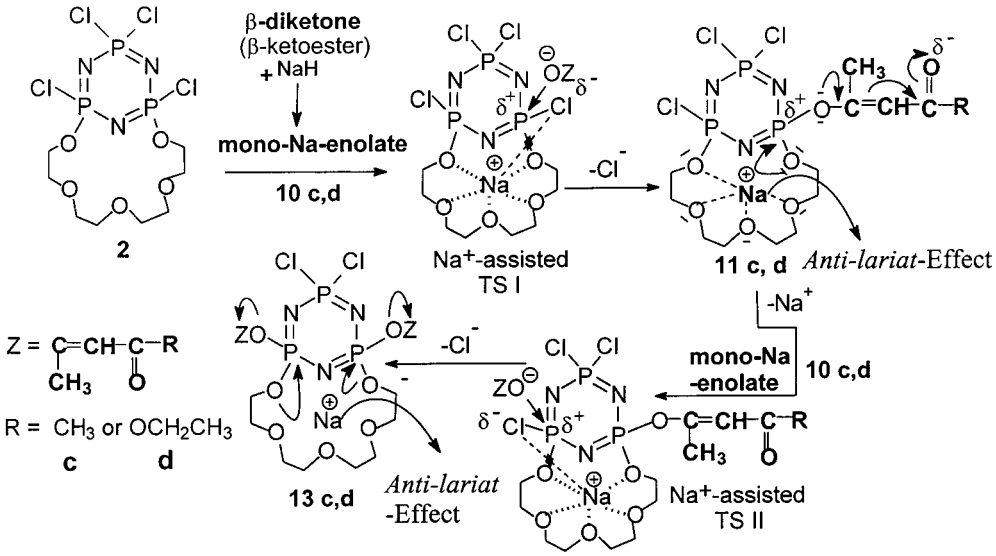
(22) We have recently reinvestigated the composition of the crude reaction mixture from the synthesis of **2**: Reinvestigated NMR-parameters for the oxytetraethylenoxy derivatives of $N_3P_3Cl_6$: for spiro-$N_3P_3Cl_4[O(CH_2CH_2O)_4]$; $\delta_A = PCl_2 = 23.5$ ppm (no proton coupling), $\delta_B$=P(spiro) = 5.3 ppm (each peak of the triplet is split into quintet on proton coupling, $J_{P-H} = 9.7$ Hz); $J_{P-P} = 66.9$ Hz, $m/z = 468$; $M_{calc}$ 467 (for $C_8H_{16}O_5Cl^{35}{}_4N_3P_3$); for bino: $N_3P_3Cl_5[O(CH_2CH_2O)_4]N_3P_3Cl_5$: $\delta_A = PCl_2 = 22.7$ ppm (no proton coupling); $\delta_B$=P(Cl)[O(CH$_2$CH$_2$O)$_4$]− = 15.9 ppm (each peak of the triplet is split into three on proton coupling, $J_{P-H} = 9.7$ Hz) $J_{P-P} = 62.8$ Hz; $m/z$ =814 ($M_{calcd}$ 812 (for $C_8H_{16}O_5Cl^{35}{}_4N_3P_3$). The detailed results of the reinvestigation of the reaction of $N_3P_3Cl_6$ with sodium tetraethylene glycolate will be published soon under separate cover after completing the structure determination of higher macrocyclic derivatives, presumably being formed by the (2 + 2) and (3 + 3) ansa-cyclocondensation of the reagents via the bino-precursor.

(23) In ref 14a, pp 24−25 (exchange reactions).

**Scheme 4. Substitution Pattern in the Reactions of the PNP-crown 2 with Sodium Arylates with a Contribution from the Ion Pair (Cation Assistance) and "Free" Anion Mechanisms to the Regioselectivity**




**Scheme 5. Substitution Pattern in the Reactions of the PNP-crown 2 with Sodium *β*-Dicarbonyl Enolates: Electronic Effects Arising from the Transmitted Across the $N_3P_3$ Ring Interaction of the Polyether Crown and α,*β*-Carbonyl Unsaturated Substituents Responsible for the Observed Antilariat Effect, Enabling the Cation Assistance to the Second Step of the Substitution at the PNP-Macrocycle**




was previously observed in the nucleophilic substitution reactions of *n*-octyl sulfonates promoted by the complexes of polyether ligands with alkali metal iodides, for which the nucleophilic activity sequence reflected the increasing interaction of the leaving group with increasing the Lewis acid character of the cation ($K^+ < Na^+ < Li^+$)[3], as well as in the cleavage of 2-methoxycarbonyl-1,3-xylylene-18-crown-5 by benzenemethanethiolate anion, which was the best assisted by hard alkali metal ions, weakly pairing with the soft benzenemethanethiolate anion.[1c]

**Comparison of the Sodium Cation-Assisted Substitution Reactions of the PNP-crown 2 with Oxyanions Derived from Hydroxyaromatic and *β*-Dicarbonyl Compounds.** To evaluate the influence of anionic member of the ion-paired nucleophile on the extent of cation assistance to the substitution proximal to the crown structure (*anion dependence*), we have investigated reactions of **2** with sodium oxyanions differing in electronegativity and polarizability derived from 2-naphthol (**10a**), phenol (**10b**) (Scheme 4), or α,*β*-dicarbonyl compounds: acetylacetone (**10c**) and ethyl acetylacetate (**10d**) (Scheme 5).

Reactions of **2** with equimolar or 100% excess sodium oxyanion in THF were conducted at 20 °C for 2 h in THF solution at the concentration of **2** equal to $2.5 \times 10^{-2}$ mmol/cm$^3$. Product proportions in the crude product mixtures were estimated from the $^{31}$P NMR spectra. Results are recorded in Table 1. The $^{31}$P NMR coupling system was AMX[24] for products **11** and **14** and $A_2B$[25] for products **12**, **13**, **15**, and **16**. In separate experiments, all of the products listed in Table 1 were isolated and characterized. Their mass spectrometric and $^{31}$P NMR spectroscopic data are given in Table 2 and in the Supporting Information (Table S1).

Figure 4 shows the comparison of the $^{31}$P NMR spectra of crude mixtures from the room-temperature reactions of **2** with sodium cation-paired phenolate **10b** and acetyl

(24) The NMR parameters of the AMX system were calculated according to: Kemp, W. In *NMR in Chemistry − A Multinuclear Introduction*; Macmillian Education Ltd.: Houndsmille, Basingstoke, Hampshire, and London,1986; pp 72−73.

(25) The NMR parameters of the $A_2X$ spin system were calculated according to Hoffman, R. A.; Forsen, S.; Gestblom, B. In *NMR − Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin−Heidelberg−New York, 1971; Vol 5, pp 104−105.

**Table 1. Composition of the Crude Product Mixtures from Substitution Reactions of Tetrachloro-PNP-crown (2) with Various Sodium Cation Paired Oxyanions, $ZO^-Na^+$ (10a−d), Estimated from the Proton-decoupled $^{31}P$ NMR Spectra (Reaction Conditions: Molar Ratio of 2/ZOH/NaH =1:1:1 or 1:2:2 in THF at 20 °C for 2 h; Concentration of 2 = $2.5 \times 10^{-2}$ mmol/cm³)**

| | components of the reaction mixture (%)[a,b] at the molar ratio of 2:10 (a−d) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1:1 | | | | | 1:2 | | | | |
| base | **2** | **11** | **12** | **13** | **14** | **11** | **13** | **14** | **15** | **16** |
| **10a**[c] | | 90 | 5 | | 5 | 60 | 5 | | 20 | 15 |
| **10b**[d] | | 80 | 10 | | 10 | 40 | | 20 | 30 | 10 |
| **10c** | 15 | 60 | | 15 | | | 95 | | 5[e] | |
| **10d**[d] | 10 | 85 | | 5 | | 60 | 40 | | | |

[a] For structures, see Scheme 4. [b] In parentheses is the approximate content of a given compound as estimated from integration of absorptions in the $^{31}P$ NMR spectra. [c] See Figure 3b. [d] See Figure 4. [e] Not being unambiguously identified due to the trace amounts.

acetate monoenolate **10d** at a molar ratio of **2**:**10** (**b**,**d**) equal to 1:1 (I) and 1:2 (II), respectively. For the reactions (I), in the crude reactions mixtures dominate the respective mono-gem-substituted derivatives **11b** and **11d**, whereas minor products result either from the competitive attack of the oxyanion at the nongeminal $PCl_2$ center (→ **12g**, **14g**) or at the second macrocycle-bearing P-atom (→ **13d**). For the reactions (II), in the crude mixture from the reaction of **2** with sodium phenolate (**10b**) there is a collection of all possible substitution degrees (**11**, **14**, **15**, **16**)**b**, except for the product **13b** of the assumed *gem*-di-PNP-crown substitution. On the other hand, for the base **10d** the respective $^{31}P$ NMR spectrum indicates only the presence of gem-to-macrocycle disubstituted derivative: (**13d**, $A_2B$ spin system) and trace amounts (<5%) of the assumed tri-gem-substituted derivative substituted **15d** ($A_2B$ spin system), not fully identified due to its trace amounts. Thus, Figure 4 illustrates differences in the substitution patterns in which cation assistance extends only to the substitution of the first one (a) or of the both macrocyclic chlorides (b).

From the data presented in Table 1, it is evident that the compositions of 1:1 and 1:2 reaction products of the naphtholysis of **2** (**2** + **10a**) resemble those from the respective phenolysis reactions (**2** + **10b**) with some preference toward gem-to-the-macrocycle substitution in the case of the naphtholate anion (**2a**). The latter is revealed by the increased content of gem derivatives in the mixtures of the naphtholysis products when compared to the respective mixtures derived from similar phenolysis reactions. On the other hand, the regiochemical outcomes of the reactions of **2** with sodium acetylacetone enolate (**10c**) are reminiscent of those of the corresponding reactions of **2** with ethyl acetylacetate enolate (**10d**) (Figure 4) with only gem-to-the-macrocycle mono- (**11**) and disubstituted (**13**) products being formed.

The results have shown that whereas the first step of the substitution with sodium arylate is strictly regiocontrolled and the reaction of **2** with 1 equiv of sodium phenoxide or β-naphthoxide gave a preponderance (∼80−90%) of the gem-to-macrocycle product **11a**(**b**), with only a minor amount of its sterically and electronically favored nongem regioisomer **12a**(**b**), there is a lack of noticeable preference for substitution at the second macrocyclic PCl group over that at the $PCl_2$ site. That may be explained in terms of so-called "lariat effect",[26] which means the cooperation of oxygen donors in the respective aryloxy substituents with oxygen lone pair electrons of the PNP-crown unit in binding sodium cation entrapped into the macrocyclic cavity, which hinders the dissociation of the **11**-$Na^+$ complex, necessary to enable the cation assistance to the substitution of the second macrocyclic chloride function (Scheme 4).

It can be concluded that cation catalysis leading to regiospecific gem-to-macrocycle substitution in reactions of crown-bearing chlorocyclotriphosphazatriene with sodium oxyanions takes place when the sodium ion forms a better matched ion pair in terms of hardness with the leaving group than with the oxyanion. (The chemical hardness mismatch is known to be a driving force for exchange reactions according to the HSAB principle.[14]) It is just a case for sodium arylates where there is a mismatch in hardness between the hard sodium cation and soft arylate anion in the attacking ion pair (*initial state of the reaction*). The soft nature of arylate oxygens, which is due to their resonance interaction with aromatic π-electrons, allows transition states such as that depicted as cation-assisted TS in Scheme 4 to play an important role in the reactions. The supramolecular assistance in such transition states also explains the regioselectivity since gem-to-macrocycle substitution allows for interaction of the sodium cation with the crown ether ring, the oxyanion and the leaving group in the transition state, as reported for other crown ether substrates.[1,15]

Similarly, the delocalized oxyanion centers in **10c** and **10d** promote initial gem-to-macrocycle monosubstitution. However, in the reactions of **2** with **10c** and **10d**, regioselective substitution occurred at both macrocyclic P-atoms (Scheme 5, Figure 4b).

This can be explained in terms of a conjugative interaction of α,β-unsaturated carbonyl oxy-substituent[27] in **11c** and **11d** with lone pair electrons of the polyether oxygens, lowering their coordinative ability so the sodium ion which was entrapped in the crown cavity during the first step of the substitution can be liberated. This allows complexation of a $Na^+$-counterion from a second attacking monoenolate molecule **10c**(**d**) and the cation-assisted formation of the disubstituted product **13c**(**d**).

The quantitative relationships involving transmission of electronic effects arising from the interaction of the different co-substituents across the cyclophosphazene ring system have been demonstrated recently by Allen who has proposed a simple model for rationalization of the spectroscopic observations for the vinyloxyorgano-(-or halogeno)cyclophosphazene series from the a consideration of the relative donor−acceptor properties of the different exocyclic groups in question.[6d] Similar model seems to be operative also in the above case (Scheme 5), assuming that when the co-substituent to the macrocycle is an electron-withdrawing entity such as α,β-carbonyl unsaturated OZ group (**c**, **d**), electron density is removed from the phosphorus center, and this increased electropositive nature of phosphorus results in a strong polarization of electron density in the P-bound ethylenoxy group away from polyether chain, thus lowering its fraction available for coordination of the metal cation.

(26) For definition of *lariat* ethers, see: (a) ref 8b, pp 141−142. (b) Gokel, G. W. *Chem. Soc. Rev.* **1992**, 39−47.

(27) For electronic interactions within conjugated α,β-unsaturated carbonyl systems see: Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon Inc.: 1987; Chapter 31, pp 1079−1089.

**Table 2. Mass Spectrometric and $^{31}$P NMR Spectroscopic Data of Monoorganoxy-Substituted Derivatives 11a−d of Tetrachloro-PNP-crown 2 of General Formula $N_3P_3[O(CH_2CH_2O)_4](OZ)Cl_3$, Obtained by Substitution of 2 with Sodium Cation Paired Oxy Anions 10a−d**

| | | | $^{31}$P{$-^1$H} NMR, AMX spin system[d] | | | | | | $^{31}$P {$+^1$H }NMR | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $\delta_P$, ppm | | | $J_{P-P}$, Hz[g] | | | $J_{P-H}$, Hz | | |
| N$^0$ [a] | formula[a] | MW calcd/found[b] | $P^{e,f}$ | $P_M{}^{e,f}$ | $P_X{}^{e,f}$ | A−M | A−X | M−X | $P_A$−H | $P_M$−H | $P_X$−H |
| **11a** | $C_{18}H_{23}O_6N_3P_3Cl_3$ | 576.5/576 | 6.5 | 27.3 | 21.2 | 74.6 | 68.6 | 80.5 | 12.8[i] | *j* | 17.7[i] |
| **11b** | $C_{14}H_{21}O_6N_3P_3Cl_3$ | 525.5/526 | 6.3 | 27.3 | 21.2 | 74.0 | 69.0 | 81.1 | 12.8[i] | *j* | 17.5[i] |
| **11c** | $C_{13}H_{23}O_7N_3P_3Cl_3$ | 532.5/532 | 4.3 | 27.3 | 20.5 | 75.2 | 73.2 | 83.7 | 12.1[i] | *j* | 18.6[i] |
| **11d** | $C_{14}H_{25}O_8N_3P_3Cl_3$ | 562.5/562 | 4.2 | 27.1 | 21.0 | 74.5 | 72.4 | 81.5 | 12.4[i] | *j* | 18.3[i] |
| **14b**[l] | $C_{20}H_{26}O_7N_3P_3Cl_2$ | 584/585 | 8.9 | 21.0 | 24.6 | 84.5 | 72.9 | 88.3 | *m* | *m* | *m* |

[a] For structures and identification of Z in **11a**,**b** and **14g**, see Scheme 4; for **11c**,**d**, see Scheme 5. [b] According to the mass spectrum: LSIMS (**11a**,**b**,**d**, **14b**); ESI-MS (**11c**); (for **11a**, **d**, also CI-MS: free ligand *m*/*z* 575.9). [c] AMX spin system denoted according to ref 24. [d] ($M^+ + Na^+$) with the absence of a peak for the free ligand. [e] For **11a**−**d**: $P_A = P(OCH_2CH_2-)(OZ)$, $P_M = PCl_2$; $P_X = P(OCH_2CH_2\sim)Cl$; for **14b**: $P_A = P(OCH_2CH_2-)(OZ)$, $P_M = PCl_2$; $P_X = P(OCH_2CH_2-)Cl$. [f] Doublet of doublets. [i] $J_{P-P}$ values calculated according to ref 24 for the AMX coupling system. [j] For each peak of the double doublet split into quintets. [i] For each peak of the double doublet split into triplets. [j] No proton coupling was evident. [k] Broadening was evident. [l] The only isolated *gem-nongem*-disubstitued derivative of **2**, showing also AMX coupling system. [m] Due to the small quantity of **14b** (∼5% in the reaction mixture) and the resultant low intensity of the respective resonance signals it was not possible to calculate reliably the $J_{P-H}$ values.

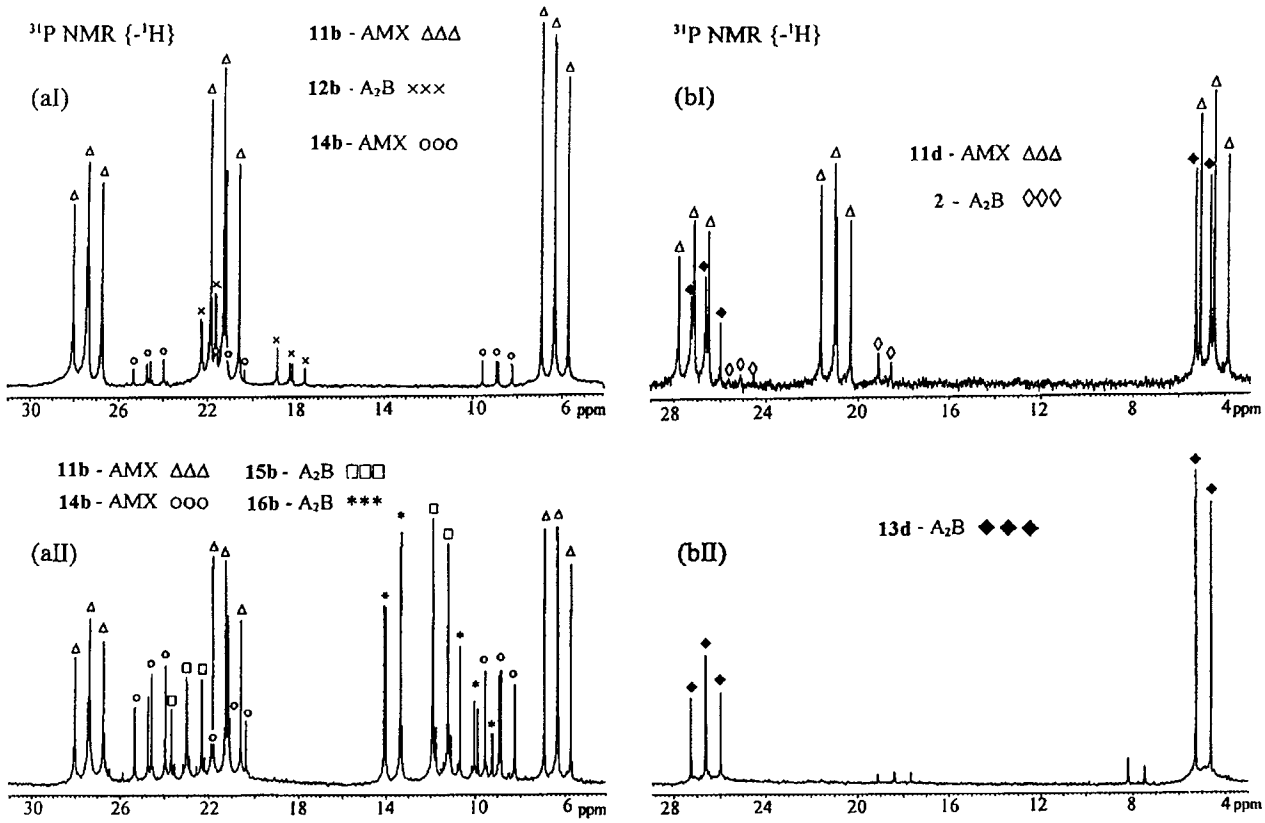



**Figure 4.** Comparison of the proton-decoupled $^{31}$P NMR spectra of the crude reaction mixtures (in $CDCl_3$ solutions) of the products formed by the substitution of **2** with (a) sodium phenolate **10b**, and (b) sodium ethyl acetylacetate enolate **10d**, at a molar ratio of **2:10** (**b**, **d**) =1:1 (i) or 1:2 (ii), carried out under the same experimental conditions (solvent THF, concentration of the substrates $2.5 \times 10^{-2}$ mmol/cm$^3$, $t = 20$°c, $\tau = 2$ h). (aI) Triangles (△) denote the AMX spin system characteristic of the *gem*-monophenoxy derivative **11b**; crosses (×) denote the $AB_2$ spin system of the *nongem*-monophenoxy isomer **12b**; circles (*o*) denote the AMX spin system of the mixed *gem-nongem*-diphenoxy-PNP-crown derivative **14b**. (aII) Triangles (△) and circles (○) as above; squares (□) and stars (*) represent the $A_2B$ spin systems of *gem-nongem*-triphenoxy (**15b**) and tetraphenoxy derivative (**16b**), respectively. (bI, bII) Triangles (△) denote the AMX spin system characteristic of the *gem*-mono-α,*β*-unsaturated carbonyl derivative **11d**; diamonds (◆) represent the $A_2B$ spin system of the respective *gem*-di-PNP-crown substituted derivative **13d**, whereas rhombs (◇) correspond to the trace amounts of the $A_2B$ spin system of unreacted substrate **2**. In separate experiments, all of the products identified in the respective spectra were isolated and characterized.

That weakens the respective binding energy and facilitates the dissociation of the complex [**11**(**c**, **d**)]-**Na**$^+$. The liberated free ligand **11**(**c**, **d**)] is capable of getting involved into the cation-assisted transition state **TS II** with the second attacking monoenolate ion-pair $Na^+$ ($OZ_{c,d}$) to form **13**(**c**, **d**).

**Substituent Dependence of the $^{31}$P Chemical Shifts in the Series of Organoxy-Substituted Crown-Bearing Cyclophosphazenes.** Chemical softness is a parameter characterizing electronic polarizability.[14a,b] For the series of the OZ substituents **a**−**d** (Scheme 4, Table 2) the latter can be considered in terms of the electron-

accepting character of the substituent OZ with respect to the $N_3P_3$ ring, which is reflected in the respective $^{31}P$ NMR spectra. Observations for organophosphazenes include downfield shifts with increasing electron-donating effect of the organo substituent.[13] Thus, the remarkable upfield shift of the $\delta P_A$ values when passing from aryloxy derivatives **11a**,**b** to oxy-α,β-carbonyl-unsaturated derivatives **11c**,**d** (Table 2) is consistent with enhancement of the electron-withdrawing power of substituents **OZ**(**c**,**d**) when compared to **OZ**(**a**,**b**)[6d,13c] and may be correlated with the unique tendency toward gem-disubstitution of **2** with sodium β-dicarbonylenolates **10c**,**d** (Scheme 5) discussed above.

## Conclusions

Supramolecular interactions between the ring oxy substituent(s) and incoming oxyanions have been found to be of primary importance for the regio- and stereocontrol of the substitution of chlorine atoms in the $N_3P_3$ ring. A definitive cis-preference found in the disubstitution of $N_3P_3Cl_6$, **1**, with sodium ethoxide and disodium oxy(tetraethylenoxy)oxide was rationalized in terms of substituent stabilization[4d,6c] with the emphasis given to the supramolecular assistance to stereoselectivity.

The different substitution patterns revealed in the similar reactions of the PNP-crown **2** and its acyclic model **5** with sodium naphtholate, the first yielding predominantly the unique, sterically hindered and electronically inconvenient gem-to-macrocycle substituted derivative **11a**, whereas the second one, the mixture of the respective sterically and electronically favored nongem **8** (cis) and **9** (trans) isomers, indicates the importance of the macrocyclic nature of the substituent on the regiochemical outcome of cation-assisted oxy substitution of chlorine atoms in $N_3P_3$ ring.

Our results demonstrate that the effectiveness of supramolecularly assisted transition-state stabilization is due not only to the dimensional complementarity between the cation and the macrocycle, as previously disclosed[1,10] but also to the properties of the four interacting ionic centers according to the HSAB principle[14] and to the nature of the electronic interaction of the PNP-crown substituent with the $N_3P_3$ ring, the latter being found to determine the extent of regiocontrol to either one or two macrocyclic chloride functions.

Consequently, the developed method represents a general strategy that provides access to a wide range of oxyanion-derivatized PNP-crowns, which may be regarded as mono- and diarmed P-pivot lariat ethers.[26] In particular, the remarkable regioselectivity in formation of mono-PNP-lariat ethers **11a**−**d** and diarmed PNP-lariat ethers **13c**,**d** may be of practical importance. The increase of the extent of regioselectivity of gem substitution at the PNP-macrocycle when passing from arylate to β-dicarbonyl enolate oxy anions has been related to the observed trends in the $^{31}P$ NMR chemical shifts and referred to the electronic structure of the oxy substituent.

## Experimental Section

**Materials.** Hexachlorocyclotriphosphazatriene, **1,** was obtained from Otsuka Chemical Co., Ltd., and purified by fractional crystallization from hexane. Sodium hydride, 60% dispersion in mineral oil (Aldrich-Chemie) was used as received. Ethanol (absolute, POCh, Gliwice Poland) was refluxed over magnesium strips activated with iodine, according to standard procedure. Phenol and β-naphthol (2-naphthol) (POCh, Gliwice, Poland) were crystallized from toluene. Acetyloacetone (Veb Labor Chemie Lapolda, Germany) and ethyl acetoacetate (Aldrich Chemie) were used as received. 2,4-(Oxytetraethylenoxy)-2,4,6,6-tetrachlorocyclotriphosphazatriene, **2**, was synthesized and purified as previously reported.[7b] THF (POCh Gliwice) was distilled over CuCl, then over calcium hydride, and finally twice over a sodium−potassium alloy under an atmosphere of dry argon. *n*-Hexane (Merck) was used without purification. All reactions were performed under a dry argon atmosphere.

**Methods.** $^1H$ NMR spectra were recorded on a Varian VXR 300 spectrometer using solutions in $CDCl_3$ with TMS as 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 on Finnigan Mat SSQ 700 spectrometer by chemical ionization (positive and negative) with an isobutane matrix and/or liquid secondary ion mass spectrometry (LSIMS) on an AMD 604 two-sector mass spectrometer made by Intectra (Germany) using glycerol and meta-nitrobenzyl alcohol (NBA) matrixes, and/or electrospray mass spectrometry (ESI-MS). ESI-MS analysis was performed with a Finnigan LCQ ion trap spectrometer (Finnigan, San Jose, CA). The ESI-source was operated at 4.25 kV and the capillary heater was set to 200 °C. The experiments were performed in positive ion-mode.

Flash column chromatography was done with silica gel (100−200 mesh), product of Merck, eluted with hexane−THF = 5:1. TLC analyses were performed on Merck precoated silica gel 60 plates.

**Preparation of *cis-nongem*-Diethoxytetrachlorocyclotriphosphazatriene, *cis*-2,4-$N_3P_3Cl_4(OC_2H_5)_2$, 5 (Acyclic Model of the Tetrachloro-PNP-crown 2).** A solution of 6,96 g (20 mmol) of $N_3P_3Cl_6$, **1**, in 250 mL of dry THF was treated with 40 mmol of $NaOC_2H_5$ (40 mL of 1 M solution). The alkoxide was prepared from sodium hydride, 60% oil suspension (4 g, 0.1 mol), and anhydrous ethanol (46 g, 1 mol) and next diluted to 100 mL with THF. The mixture was stirred at room temperature for 3 h and filtered, and the solvent was removed in vacuo to obtain a colorless oil (7.21 g, 98.2% of theory) that was subjected to column chromatography on silica gel (eluant: hexane−chloroform = 5:1) to give $N_3P_3Cl_5(OC_2H_5)$, **3** (1.81 g, 25.15% of theory), and the mixture of cis−trans isomers of *nongem*-$N_3P_3Cl_4(OC_2H_5)_2$, **5** and **6,** respectively (2.23 g, 31.0% of theory) with relative abundances of 5:6 ≅ 3:2,[21] with the small impurity, **4** (about 10% of total amount of **5** + **6**),[21] assumed to be *gem*-$N_3P_3Cl_4(OC_2H_5)_2$. The structural assignments were based on the $^{31}P$ NMR spectra of the eluted mixed fraction (Figure 2a) with consideration of the reported trends in chemical shifts $\delta_P$ for cyclophosphazene compounds,[13,28] particularly for the respective geometrical isomers.[13,16,17]

This three-component mixture (2.23 g) was rechromatographed on silica gel using less polar eluant (hexane−chloroform 15:1) to yield **6** (isomer trans) slightly contaminated with **4** (0.13 g, molar ratio *(relative abundances*) **6**:**4** ≅ 8:1[21]), the mixed fractions containing **4**, **5**, and **6** with continuously increasing ratio of **5** (cis) to **6** (trans) isomers (Σ 1.31 g), and finally pure **5** (isomer cis) (0.73 g), the latter representing the acyclic model of **2**.

**Analytical Data. 3**. MW: calcd for $C_2H_5Cl_5N_3OP_3$ 357.5, found 358 (mass spectrum). $^1H$ NMR (chemical shifts in ppm and coupling constants in Hz): δ (≡ $POCH_2CH_3$), 1.48 (triplet, 3H); δ (≡ $POCH_2CH_3$), 4.25 (quartet, 2H). $^{31}P$ NMR $A_2B$; δ (≡ $PCl_2$) = 23.1; δ (≡ $P(OCH_2CH_3)Cl$ = 15.1, $J_{P-P}$ = 62.3. **4**, 2,2-$N_3P_3Cl_4(OCH_2CH_3)_2$. $^1H$ NMR (chemical shifts in ppm and coupling constants in Hz) δ (=$POCH_2CH_3$), 1.35 (triplet, 3H); δ (≡ $POCH_2CH_3$), 4.05 (multiplet, 2H); $^{31}P$ NMR: $A_2X$; δ (≡

(28) Krishnamurthy, S. S.; Woods, M. *Ann. Rep. NMR Spectrosc.* **1987**, *19*, 176−319.

$PCl_2$) = 23.84; $\delta$ ($P(OC_2H_5)_2$ =5.04, $J_{P-P}$ = 64.25. **5**, *cis*-2,4-$N_3P_3Cl_4(OCH_2CH_3)_2$. MW: calcd for $C_4H_{10}Cl_4N_3O_2P_3$ 367, found 367 (mass spectrum). $^1$H NMR (chemical shifts in ppm and coupling constants in Hz): $\delta$ (≡ $POCH_2CH_3$), 1.39 (triplet, 6H); $\delta$ (≡ $POCH_2CH_3$), 4,23 (multiplet, 4H). $^{31}$P NMR: $AB_2$; $\delta$ (≡ $PCl_2$) = 25.44; $\delta$ (≡ $P(OCH_2CH_3)Cl$ = 18.53, $J_{P-P}$ = 66.0. **6**, *trans*-2,4-$N_3P_3Cl_4(OCH_2CH_3)_2$. MW: calcd for $C_4H_{10}Cl_4N_3O_2P_3$ 367, found 367 (mass spectrum). $^1$H NMR (chemical shifts in ppm and coupling constants in Hz): $\delta$ (≡ $POCH_2CH_3$), 1.41 (triplet, 6H); $\delta$ (≡ $POCH_2CH_3$), 4.25 (multiplet, 4H). $^{31}$P NMR: $AB_2$; $\delta$ (≡ $PCl_2$) = 25.42; $\delta$ (≡ $P(OCH_2CH_3)Cl$ = 18.70, $J_{P-P}$ = 65.37.

**Model Reaction of *cis-nongem*-Diethoxytetrachlorocyclotriphosphazatriene (5) with Sodium *β*-Naphthoxide.** *cis*-2,4-Ethoxy-2,4,6,6-tetrachlorocyclotriphosphazatriene **5** (0.367 g, 1 mmol) and the *β*-naphthol (0.144 g, 1 mmol) were dissolved in 40 mL of dry THF and placed in a 100 mL four-necked round-bottomed flask, supplied with a magnetic stirrer, reflux condenser, and argon inlet. NaH (60% oil suspension, 0.04 g, 1 mmol (**1**) was added and the reaction carried out with stirring at room temperature for 2 h. The course of the reaction was monitored by TLC, using hexane−THF (3:1) as eluant and pyridine−*m*-toluidine (1:1) (all chlorine-containing cyclophosphazene- derivatives) and $I_2$ vapor (multiple bond containing organic derivatives) developing reagents. The sodium chloride formed was filtered off and THF removed at reduced pressure to leave colorless oil, which was extracted with benzene (50 mL).

The crude reaction mixture (0.49 g,) consisting of the respective substitution products **7**−**9** and of unreacted substrate **5** (as inferred from $^{31}$P NMR results, Figure 3, a1) was subjected to column chromatography on silica gel using hexane−chloroform (6:1) as an eluant to yield the following: (a) **5**, (0.092 g; 25.1% of starting amount) ($R_f$ = 0.44 (hexane−THF = 1:1) (Figure 3, a2); (b) the mixed fraction containing **5** and the isomers **7**−**9** (0.088 g); and (c) the *nongem*-2,4-ethoxy-6-(*β*-naphthoxy)-2,4,6-trichlorocyclotriphosphazatriene (0.31 g, 65.3% of theory, $R_f$ = 0.0.39 (hexane-THF = 1:1)), apparently consisting of the mixture of cis (**8**) and trans (**9**) isomers in approximate ratio cis/trans ≅ 1:2, as inferred from the $^{31}$P NMR data[20] (see Figure 3, a3).

**Analytical Data. 2,4-Diethoxy-2-(*β*-naphthoxy)-4,6,6-trichlorocyclotriphosphazatriene (7).** MW: calcd for $C_{14}H_{17}Cl_3N_3O_3P_3$ 474.5, found 474 (mass spectrum). $^1$H NMR: peaks indiscernible from those for nongem isomers (**8** + **9**). $^{31}$P NMR (chemical shifts in ppm and coupling constants in Hz): AMX; $P_A$ = (≡ P $(OCH_2CH_3)(O-C_{10}H_7)$; $P_M$ = (≡ $PCl_2$); $P_X$ = (≡ $P(OCH_2CH_3)Cl$); $\delta P_A$ = 6.26; $\delta P_M$ = 26.59; $\delta P_X$ = 19.65; $J_{A-M}$ = 70.72, $J_{A-X}$ = 68.72; $J_{A-M}$= 73.57.

***cis*/*trans*-2,4-Diethoxy-6-(*β*-naphthoxy)-2,4,6-trichlorocyclotriphosphazatriene (8 + 9).** MW: calcd for $C_{14}H_{17}Cl_3N_3O_3P_3$ 474.5, found 474 (mass spectrum). $^1$H NMR (chemical shifts in ppm and coupling constants in Hz): $\delta$ (≡ $POCH_2CH_3$), 1.24−1.42 (complex multiplet, 6H); $\delta$ (≡ $POCH_2CH_3$), 4.10−4.25 (complex multiplet, 4H); $\delta$ (≡ $POC_{10}H_7$), 7.35−7.53, 7.67−7.90 (two complex multiplets, 7H). $^{31}$P NMR: $A_2B$; $\delta$ (≡ P−$(OCH_2CH_3)Cl$: two overlapping double doublets: 21.80 ($P_A$-trans); 21.75 ($P_A$-cis); $\delta$ (≡ $P(OC_{10}H_7)Cl$: 2 overlapping triplets, 19.50 ($P_B$-trans); 19.12 ($P_B$-cis), $^2J_{PP}$ =73.57 (trans), 75.80 (cis). The separation of geometrical cis/trans isomers could not be achieved.

**Reaction of 2,4-(Oxytetraethylenoxy)-1,3,5,5-tetrachlorocyclotriphosphazatriene (2) with Sodium *β*-Naphthoxide.** The naphtholysis of PNP-macrocyclic substrate **2** was carried out under the same reaction conditions as the described above naphtholysis of the acyclic model **5** (molar ratio of the tetrachlorocyclotriphosphazene substrate−$\beta$-$C_{10}H_7OH$−NaH = 1:1:1, solvent THF, $t$ ∼20 °C (room temperature), $\tau$ 2 h, concentration in THF: 2.5 × $10^{-2}$ mmol/cm$^3$), starting from 2,4-(oxytetraethylenoxy)-1,3,5,5-tetrachlorocyclotriphosphazatriene (**2**) (0.469 g, 1 mmol) instead of *cis*-2,4-ethoxy-2,4,6,6-tetrachlorocyclotriphosphazatriene **5**. The sodium chloride formed was filtered off and THF removed at reduced pressure to leave colorless oil, which was extracted with benzene (50 mL). The fraction soluble in benzene (∼0.45 g) consisting of the respective substitution products **11a** and **12a** (as inferred from $^{31}$P NMR results) was subjected to column chromatography on silicagel. The products **11a** and **12a** were separated and individually characterized, that enabled the estimation of the composition of the crude reaction mixture from $^{31}$P NMR results by referring the intensities of AMX signals system for **11a** and of $A_2B$ signals for **12b** to the overall intensity of the $^{31}$P NMR signals in the spectrum of the crude reaction system.

**Analytical Data. 2,4-[Oxytetraethylenoxy]-2-(*β*-naphthoxy)-4,6,6-trichlorocyclotriphosphazatriene (11a).** MW: calcd for $C_{18}H_{23}O_6N_3P_3Cl_3$ 576.5, found 576 ($M^+$), 596 ($M^+ + Na^+$) (mass spectrum). $^1$H NMR (chemical shifts in ppm and coupling constants in Hz) $\delta$ ($OCH_2CH_2O$), 3.48−3.56, 3.60−3.76, 3.80−3.88 (three complex multiplets, 12 H); $\delta$ (≡ $POCH_2CH_2$), 4.04−4.30, 4.36−4.49 (two complex multiplets, 4H); $\delta$ (≡ $POC_{10}H_7$), 7.30−7.53, 7.72−7.87 (two complex multiplets, 7H). $^{31}$P NMR (chemical shifts in ppm and coupling constants in Hz) (Figure 3, b2): AMX; $P_A$ = (≡ $P(OCH_2CH_2-)(OC_{10}H_7)$; $P_M$ = (≡ $PCl_2$); $P_X$ = (≡ $P(OCH_2CH_3)Cl$); $\delta P_A$ = 6.50; $\delta P_M$ = 27.30; $\delta P_X$ = 21.20; $J_{A-M}$ = 74.60, $J_{A-X}$ = 68.60; $J_{A-M}$= 80.5

**2,4-Oxytetraethylenoxy-6-(*β*-naphthoxy)-2,4,6-trichlorocyclotriphosphazatriene, 12a.** MW: calcd for $C_{18}H_{23}O_6N_3P_3Cl_3$ 576.5, found 576 ($M^+$), 596 ($M^+ + Na^+$) (mass spectrum). $^1$H NMR (chemical shifts in ppm and coupling constants in Hz): $\delta$ ($OCH_2CH_2O$), 3.38−3.48, 3.50−3.56, 3.60−3.78 (3 complex multiplets, 12 H); $\delta$ (≡ $POCH_2CH_2$), 4.14−4.37, complex multiplet, 4H); $\delta$ (≡ $POC_{10}H_7$), 7.40−7.54, 7.68−7.88 (two complex multiplets, 7H). $^{31}$P NMR: $A_2B$; $\delta$ (≡ $P(OCH_2CH_3)Cl$:: 21.90 (double doublet, 2P); $\delta$ (≡ $P(OC_{10}H_7)Cl$, 18.83 (triplet, 1P), $^2J_{PP}$ = 77.6 (Figure 3, b3). Product seems to be rather unique, presumably of cis-form, as deduced from the geometry of the precursor **2**, and the possibility of some stabilization of the cis-alignment by cooperative interaction of sodium cation with naphthoxide ion and oxygen donors of the crown substituent. However, the presence of trace amounts of the trans-isomer cannot be excluded as some unidentified low intensity peaks alternating with those the $P_B$ triplet might be noticed (Figure 3, b3) The separation of the assumed geometrical cis/trans isomers could not be achieved.

**Reactions of 2,4-(Oxytetraethylenoxy)-2,4,6,6-tetrachlorocyclotriphosphazatriene (2) with Sodium Cation Paired Oxyanions $ZO^-Na^+$ (10a−d), Derived from Hydroxyaromatics (*β*-Naphthol (a); Phenol (b)) and *β*-Dicarbonyl Compounds: Acetylacetone (c); Ethyl Acetoacetate (d).** Considering the important influence of the concentration of reagents and the polarity of reaction medium on the *supramolecular versus thermodynamic effects* all the substitution experiments (**2** + **10a**−**d**) were carried under the same reaction conditions (*found optimum in preliminary investigations*), such as: molar ratio of **2**−ZOH−NaH =1:1:1 (**1**) or 1:2:2 (**2**); solvent THF, $t$ ∼20 °C (room temperature), $\tau$ 2 h, concentration of **2** in THF: 2.5 × $10^{-2}$ mmol/cm$^3$.

**2,4-(Oxytetraethylenoxy)-2,4,6,6-tetrachlorocyclotriphosphazatriene (1)** (0.469 g, 1 mmol) and the respective hydroxy compound **10a**−**d** (1 (**1**) or 2 (**2**) mmol) were dissolved in 40 mL of dry THF and placed in a 100 mL four-necked round-bottomed flask, supplied with a magnetic stirrer, reflux condenser and argon inlet. NaH (60% oil suspension, 0.04 g, 1 mmol (**1**) or 0.08 g, 2 mmol (**2**)) was added and the reaction carried out with stirring at room temperature for 2 h. The course of the reaction was monitored by TLC, using hexane−THF (3:1) as eluant and pyridine−*m*-toluidine (1:1) (all chlorine-containing cyclophosphazene derivatives) and $I_2$ vapor (multiple bond- containing organic derivatives) developing reagents. The sodium chloride formed was filtered off and THF removed at reduced pressure to leave a colorless oil which was extracted with benzene (50 mL). The fraction soluble in benzene (from ∼0.45 g (**i**, **j**) to ∼0.50 g (**a**, **b**) consisting of the respective substitution products **11**−**16**(**a**−**d**) and in some cases − of unreacted substrate **2** as inferred from $^{31}$P NMR results), was subjected to column chromatography on silicagel. All the products depicted on the Scheme 1 (except for **14b**, due to its trace amounts) and listed in the Table 1 (**11a**−**d**, **12a**,**b**, **13a**,**c**,**d**, **15a**,**b**, **16a**,**b**), were separated and individually

characterized, which enabled the estimation of the composition of the particular crude reaction mixtures from $^{31}$P NMR results by referring the intensities of AMX signals system for **11(a**−**d**) and of $A_2B$ signals for **2**, **12**(**a**,**b**), **13**(**a**,**c**,**d**), **15**(**a**,**b**), and **16**(**a**,**b**) to the overall intensity of the $^{31}$P NMR signals in the respective spectra. (Table 1, Figure 4). In the case of overlapping of some parts of the respective spin systems the comparison was limited to the nonoverlapping parts of the spectra. Quantitative assignments of the composition of the crude reaction mixtures were beyond the scope of this study, as the regiochemical trends of interest could be satisfactorily deduced from the approximate contents of the respective substitution products.

To enable the comparison of spectral properties of the analogous organoxy-PNP-crown compounds, and in particular, following the systematic trends in the chemical shifts in the series of mono-gem-to the macrocycle substituted derivatives (**3a**−**d**), the respective $^{31}$P and $^{1}$H NMR data, together with confirming their identify mass spectral data are presented in tabular form. Analytical and $^{1}$H NMR data for **11**−**16** are given in Table S2 (Supporting Information) and the $^{31}$P NMR and mass spectral data in Tables 2 and S1.

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**Supporting Information Available:** Mass spectrometric and $^{31}$P NMR spectroscopic data of organoxy-substituted derivatives of tetrachloro-PNP-crown **2** of general formula $N_3P_3[O(CH_2CH_2O)_4](OZ)_nCl_{4-n}$, showing $A_2B$ coupling systems in $^{31}$P NMR spectra (Table S1); $^{1}$H NMR of PNP-lariat ether organoxy derivatives **11**−**16** of general formula: $N_3P_3[O(CH_2CH_2O)_4](OZ)_nCl_{4-n,}$ where $n = 1-4$ (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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