Thermodynamic *vs* Supramolecular Effects in the Regiocontrol of the Formation of New Cyclotriphosphazene-Containing Chiral Ligands with 1,1′-Binaphthyl Units: Spiro *vs* Ansa Substitution at the N_3P_3 Ring

Krystyna Brandt,*,† Iwona Porwolik-Czomperlik,† Mariola Siwy,† Teobald Kupka,† Robert A. Shaw,‡ David B. Davies,‡ Michael B. Hursthouse,§ and Georgia D. Sykara§

Contribution from the Institute of Polymer Chemistry, Polish Academy of Sciences, 34 M. Curie-Sklodowska Str., 41-800 Zabrze, Poland, Department of Chemistry, Birkbeck College (University of London), Gordon House, 29 Gordon Square, London WC1H OPP, U.K., and School of Chemistry & Applied Chemistry, University of Wales, Cardiff CF1 3TB, Wales, U.K.

Received July 15, 1997[⊗]

Abstract: Synthesis of new cyclophosphazene-containing chiral ligands (**6**−**9**) with 1,1′-binaphthyl units has been achieved by stepwise dicyclosubstitution of hexachlorocyclotriphosphazene (**1**), with two sodium cation paired dinucleophiles derived from bis-β-naphthol (**2**) and tetraethylene glycol (**3**). The structures of the disubstitution products have been found to be addition order-dependent. In particular, the substitution pattern of the 1,1′-binaphthalene-2,2′-dioxy substituent in the N_3P_3 ring [spiro (**4** → **6**, **7**) or ansa (**8**, **9**)] was related to whether or not the crown substituent had been incorporated into **1** beforehand. Addition of the phase transfer catalyst reagent, tetrabutylammonium bromide, to the reaction mixture of **5** + **2-Na$_2$** led to the parallel formation of both the spiro **6** and ansa **8** isomers. Spiro *vs* ansa regioisomerism of the binaphthalenedioxy derivatives formed is discussed in terms of the contributions of the respective thermodynamic and supramolecular effects to the regiocontrol of substitution in the N_3P_3 ring. It is found that there are two main factors determining the orientation of the binaphthalenedioxy substitutent incoming to the N_3P_3 ring: the thermodynamic stability of seven-membered spirocycles at the P-atoms and the crown-related cation assistance of the ansa substitution at the macrocycle bearing P-atoms; the regiocontrol resulting from the supramolecular effects predominates, whenever possible. The structures of compounds **7**−**9** were proven by X-ray crystallography. The metal cation complexing properties of compounds **6**−**9** were compared by a simple TLC method. The results show that the complexing properties of the chiral binaphthalenedioxy-containing PNP-crown ligands **6**−**9** toward alkali metal and silver cations are either similar (spiro-ansa derivative **6**) or enhanced (bis-ansa derivatives **7**−**9**) with respect to the parent tetrachloro PNP-crown **5**.

Introduction

In the previously reported cases, metal cations were found to influence the reaction kinetics of functional crown ethers with metal-containing reagents either by the so-called "naked anion phenomenon" (enhancement of anion nucleophilicity by weakening the electrostatic interactions within the ion-paired reagent by cation complexation inside the macrocyclic cavity),[1,2] or by "cation assistance" (also known as "metal-ion catalysis") operating *via* transition state stabilization, where the complexed cation assists the departure of the leaving group.[2−4]

We have developed a new class of functional crowns, derived from hexachlorocyclophosphazene (**1**), which have the reactive substituents linked to phosphorus atoms,[5] and which combine the versatile reactivity of chlorocyclophosphazenes[6−8] with the complexing properties of crown ether ligands.[4,9,10] Some examples have already been reported of cyclophosphazene-containing PNP-crown macrocycles modified by substitution of

† Polish Academy of Sciences.

‡ Birkbeck College.

§ University of Wales.

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1997.

(1) For a definition of the *naked anion phenomenom,* see, e.g.: (a) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: 1989; pp 107−108. (b) Gokel, G. W. *Crown Ethers and Cryptands*, *Monographs in Supramolecular Chemistry*; The Royal Society of Chemistry: London, 1991; pp 141−142.

(2) (a) Lehn, J.-M. *Pure Appl. Chem.* **1980**, *52*, 2303−2319. (b) Msayib, K. J.; Watt, C. I. F. *Chem. Soc. Rev.* **1992**, 237−243 and references therein.

(3) (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) Doddi, G.; Ercolani, G.; La Pegna, P.; Mencarelli, P. *J. Chem. Soc., Chem Commun.* **1994**, 1239−1240. (d) Cacciapaglia R.; Mandolini, L.; Tomei, A. *J. Chem. Soc., Perkin. Trans.* 2, **1994**, 367−372 and references therein. (e) Cacciapaglia, R.; Mandolini, L.; Spadola, F. *Tetrahedron* **1996**, *26*, 8867−8876.

(4) (a) Gobbi, A.; Landini, D.; Maia, A.; Secci, D. *J. Org. Chem.* **1995**, *60*, 5954−5957 and references therein. (b) Gobbi A.; Landini D.; Maia A.; Penso M. *J. Chem. Soc. Perkin Trans. 2* **1996**, Nov (11), 2505−2509.

(5) (a) Brandt, K.; Kupka, T.; Drozd, J.; van de Grampel, J. C.; Meetsma, A.; Jekel, A. P. *Inorg. Chim. Acta* **1995**, *228* (2), 187−192; b) Brandt, K.; Porwolik, I.; Kupka, T.; Olejnik, A.; Shaw, R. A.; Davies, D. B. *J. Org. Chem.* **1995**, *60*, 7433−7438.

(6) Allen, Ch. W. *Chem. Rev.* **1991**, *91*, 119−135.

(7) (a) Shaw, R. A. *Phosphorus, Sulfur, Silicon* **1989**, *45*, 103−136. (b) Allcock, H. R.; Turner, M. L.; Visscher, K. B. *Inorg. Chem.* **1992**, *31*, 4354−4364. (c) Allcock, H. R.; Diefenbach, U.; Pucher, S. R. *Inorg. Chem.* **1994**, *33*, 3091−3095 and references therein. (d) Brandt, K.; Jedlinski, Z. *J. Org. Chem.* **1980**, *45*, 1672−1675. (e) Pelc, R. A.; Brandt, K.; Jedliñski, Z. *Phosphorus, Sulfur, Silicon*, **1990**, *47*, 375−382. (f) Contractor, S. R.; Hursthouse, M. B.; Parkes, H. G.; Shaw, L. S.; Shaw, R. A.; Yilmaz, H. *J. Chem. Soc., Chem. Commun*. **1984**, 675. (g) Harris, P. J.; Williams, K. B. *Inorg. Chem*. **1984**, *23*, 1495−1496. (h) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whotle, R. R. *J. Am. Chem. Soc*. **1984**, *106*, 2337−2347.

(8) (a) Austin, P. E.; Riding, G. H.; Allcock H. R. *Macromolecules* **1983**, *16*, 719−722. (b) 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.

(9) (a) Cram, D. J.; Cram, J. M. *Science* **1974**, *183*, 803−809. (b) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8−14. (c) Dietrich, B. *J. Chem. Ed.* **1985**, *62*, 954−964; (d) Weber, E.; Vögtle, E. *Top. Curr. Chem.* **1981**, *98*, 1−41 and references therein.

S0002-7863(97)02372-X CCC: $14.00

their chlorine atoms with various mononucleophiles such as phenolate, β-naphtholate,[5b] linear oligoethers, or amines.[11] In agreement with previous reports on "metal-ion catalysis",[2−4] a significant enhancement of the rate of chloride substitution by aromatic oxyanions cation paired with sodium[5b] in PNP-crowns was observed, when compared with similar Cl replacement(s) in the phenolysis of non-crown chlorocyclophosphazenes.[8,12]

Our recent studies of the reactions of the functional PNP-crown **5** with sodium bis-naphtholate have shown that both the kinetics and the regiochemistry of the substitution reaction are influenced by the presence of the macrocyclic substituent and crown-related effects (supramolecular interactions), such as cation assistance.[13] It has been found that substitution of **5** by these dinucleophiles proceeds regioselectively at the positions adjacent (geminal) to the PNP-macrocycle, preferentially yielding unusual transannular ansa-bridged derivatives, rather than the thermodynamically most favored spiro isomer,[7] in which the incoming dinucleophile should substitute the PCl_2 group more distant from the macrocycle.

The substitution pattern in classic cyclophosphazene chemistry is usually governed by steric and electronic effects (charge distribution).[6] The attachment of electron-donating substituents, such as oxyanions to the N_3P_3 ring reduces the positive charge at the P-atoms and therefore hinders further nucleophilic attack, especially at P-atoms already bearing one such substituent. Consequently, nongeminal substitution patterns are usually observed for alcoholate and phenolate anions,[6] whereas for the reactions of $N_3P_3Cl_6$ with dioxy-dinucleophiles, spirosubstitution at the P-atoms is favored because of the great thermodynamic stability of the five-, six-, or seven- membered spiro rings.[7]

The first examples of transannular derivatives, *i.e.*, ansa compounds, for the cyclotriphosphazene system were reported in 1984. These were based on short chain aliphatic diols,[7f] aliphatic amino alcohols,[7g] or metallocenes.[7h] In general, yields were low. In all of the above examples, the reagents had alternative reaction sites available within the cyclophosphazenes. Allcock *et al*.[7b] developed an alternative strategy by blocking nongeminally four of the six reactive sites of a cyclotriphosphazene, N_3P_3, and thereby forcing the difunctional reagent to react to form either an ansa or a dangling structure because no other reaction sites were accessible.

By contrast, we employed as a precursor the tetrachloro(oxy-(tetraethyleneoxy))cyclotriphosphazene **5**[5] still having the PCl_2 group available for spiro substitution, and therefore, the unusual tendency toward spontaneous transannular spanning of its two macrocycle bearing P-atoms by the binaphthalenedioxy unit (capable of forming very stable seven-membered spirocycles at the P-atoms) could not be explained in terms of the typical relationships found in cyclophosphazene chemistry.[13] The preference for substitution of the chlorine atoms adjacent to the PNP-macrocycle has been ascribed to their involvement in stabilization of the sodium cation assisted transition state **5** → **8**(**9**) of the supramolecular host−guest complex type.[13]

The hypothesis about sodium cation assistance[13] as the driving force toward ansa cyclosubstitution of **5**[5] is strengthened by providing evidence in this paper that introduction to the reaction system (**5** + disodium binaphtholate, **2**) of noncomplexable tetrabutylammonium cations partially switches the substitution pattern toward the formation of the spiro isomer, 1,3-(oxy-(tetraethyleneoxy))-5,5-(1,1′-binaphthalene-2,2′-dioxy)-1,3-dichlorocyclotriphosphazene (**6**). The spiro isomer **6** has also been prepared by an alternative synthetic route [together with its bis-crown homologue, 1,3:1,3-bis[oxy(tetraethyleneoxy)]-5,5-(1,1′-binaphthalene-2,2′-dioxy)cyclotriphosphazene (**7**)] by the introduction of the 1,3-oxy(tetraethyleneoxy) unit(s) to the monospirocylic precursor, 5,5-(1,1′-binaphthalene-2,2′-dioxy)-1,1,3,3-tetrachlorocyclotriphosphazene (**4**), prepared beforehand from hexachlorocyclotriphosphazene (**1**) and **2**, as previously described.[7d,e]

Compounds **6**−**9** represent chiral ligands with 1,1′-binaphthyl units;[14] hence their synthesis is of interest from a practical point of view. It has been previously reported that the presence of 1,1′-binaphthyl units in the macrocyclic skeleton caused a dramatic decrease in the complexing power of the parent crown ligands,[15] which was ascribed to the electron delocalization and inductive effects of the aromatic groups.[15a] The chiral crowns **6**−**9** obtained in this work contain 1,1-binaphthyl units, not as an integral part of the PNP-crown skeleton but as its side substituents, which are oriented differently with respect to the macrocyclic unit due to their different substitutions of the N_3P_3 ring. Fragments of the N_3P_3 ring play the role of a spacer group, separating the fused aromatic rings from the crown structure. Consequently, the presence of the binaphthalenedioxy side unit might affect the binding power of the parent PNP-crown in a way that is different to that found for molecules with the binaphthyl moiety incorporated directly into the crown structure. In order to estimate the structure-complexing property relationships for such ligands, it seemed sensible to compare (on the basis of a simple TLC test[16]) the cation-binding abilities of the parent (binaphthyl-free) PNP-crown **5** with the new chiral ligands **6**−**9** having binaphthalenedioxy substituents.

The purpose of this work was three-fold: (a) to elucidate the contributions of thermodynamic and supramolecular effects (in particular, cation assistance enabled by the presence of the macrocyclic substituent) in the regiocontrol of chlorine substitution in the N_3P_3 ring with sodium cation paired dinucleophiles (*i.e.*, spiro *vs* ansa cyclosubstitution); (b) to develop synthetic routes to new lariat-ether-type chiral ligands **6**−**9** with 1,1′-binaphthyl units, linked *via* suitable electron-donating spacers to the PNP-polyether macrocycle, and to investigate the potential applicability of selected chiral crown representative(s), in particular the PNP-crown **8**, for preparation of polymeric

(10) (a) See in ref 1a, pp 1−269. (b) Izatt, R. I.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D., Christensen, J. *J. Chem. Rev.* **1985**, *85*, 271−339.

(11) Brandt, K.; Porwolik, I.; Siwy, M.; Kupka, T.; Shaw, R. A.; Davies, D. B.; Hursthouse, M. *Phosphorus Res. Bull.* **1996**, *6*, 17−20.

(12) (a) Fitzimmons, B. W.; Shaw, R. A. *J. Chem. Soc*. **1964**, 1735−1741. (b) Brandt, K. *Polish J. Appl. Chem*. **1991**, *35*, 143−150.

(13) (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*, 1143−1144.

(14) (a) Izatt, R.; Zhu, Ch.Y.; Huszty, P.; Bradshaw, J. S. In *Crown Compounds - Toward Future Applications;* Cooper, S. R., Eds.; VCH Publishers Inc.: New York, Weinheim, Cambridge, 1992; Chapter 12, pp 207−233 and references therein. (b) Dietrich, B.; Lehn, J.-M.; Simon, J. *Angew. Chem., Int. Ed*. Engl. **1974**, *13*, 406. (c) Peacock, S. C.; Cram, D. J. *J. Chem. Soc. Chem. Commun.* **1976**, 282−284; (d) Cram, D. J.; Cram, J. M. *Acc. Chem. Res*. **1978**, *11*, 8−14. (e) Artz, S. P.; de Grandpre, M. P.; Cram, D. J. *J. Org. Chem.* **1985**, *50*, 1486−1496. (f) Knobler, C. B.; Gaeta, F. C. A.; Cram, D. J. *J. Chem. Soc., Chem. Commun*. **1988**, 330−333.

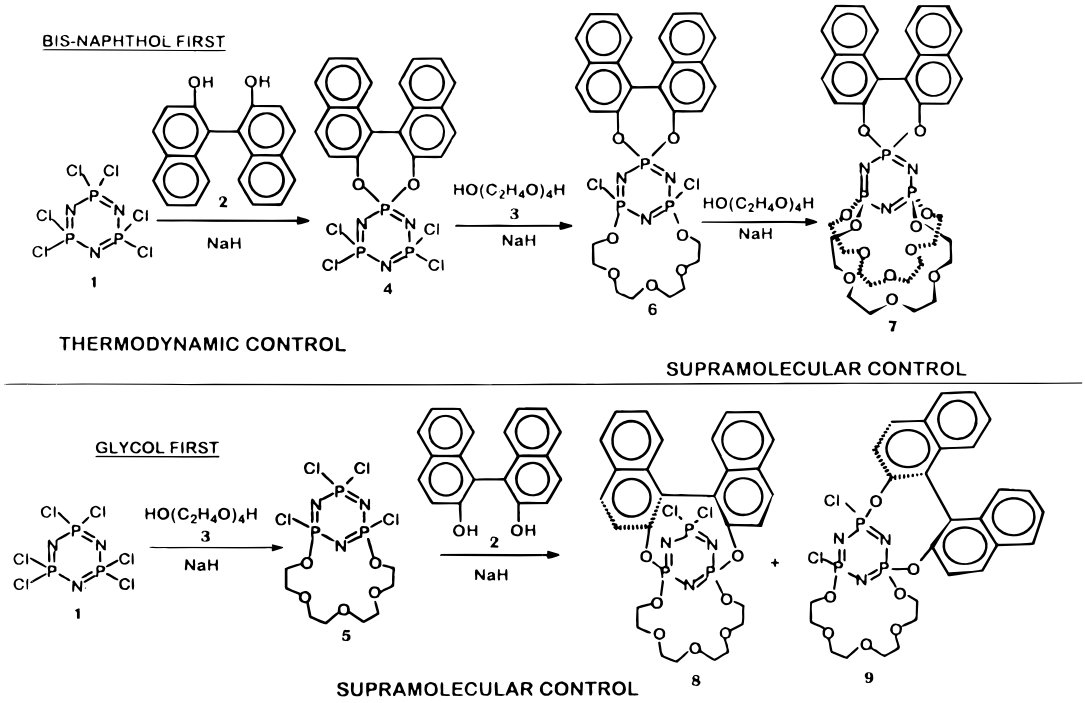
(15) (a) Timko, J. M.; Helgeson, R. C.; Newcomb, M.; Gokel, G. W.; Cram, D. J. *J. Am. Chem. Soc*. **1974**, *96*, 7097−7099. (b) Izatt, R. M.; Bradshaw, J. R.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271−339.

(16) (a) Biernat, J. F.; Wilczewski, T. *Polish J. Chem*. **1979**, *53*, 513−516; b) Kostrowicki, J.; Luboch, E.; Makuch, B.; Cygan, A.; Horbaczewski, A.; Biernat, J. *J. Chromatogr*. **1988**, *454*, 340−344.

(17) Chiral polymeric ligands are of special interest as chiral stationary phases (CSPs) for direct resolution of chiral amino acids and primary amines by high-performance liquid chromatography (HPLC).[18]

(18) For example, see: (a) Yokota, K.; Haba, O.; Satoh, T. *Makromol. Chem. Phys*. **1995**, *196*, 2383−2416. (b) Zhou, X. C.; Yan, H.; Chen, Y. Y.; Wu, C. Y.; Lu, X. R. *J. Chromatogr*. **1996**, *753*, 269−267.

Scheme 1



crowns.[17,18] (c) to establish some correlations between the structures of the new ligands **6**−**9** and their complexation properties.

Results and Discussion

Scheme 1 shows alternative pathways, differing in the order of incorporation into the N_3P_3 ring, of stepwise substitution of hexachlorocyclotriphosphazene (**1**) with two sodium cation paired dinucleophiles, derived respectively from 2,2′-dihydroxy-1,1′-binaphthyl (bis-β-naphthol) (**2**) and tetraoxyethylene glycol (**3**).

In the first case (Scheme 1, upper line), substitution started with the reaction of **1** with a stoichiometric amount of disodium bis-naphtholate (**2**) leading to quantitative formation of the tetrachloro-mono-spiro(binaphthalenedioxy)cyclotriphosphazene **4**,[7d] which was then subjected to reaction with an excess of disodium glycolate (**3**) to yield both the hitherto unreported mono- (**6**) and bis- (**7**) 1,3-ansa-(oxy(tetraethyleneoxy))-mono-spiro(binaphthalenedioxy)cyclotriphosphazenes, accompanied to some extent by a polymeric fraction having an average M_n = 4600. The first step of the reaction (**1** → **4**) is controlled by thermodynamic factors, which favor formation of the thermodynamically stable seven-membered spiro rings, in agreement with previous reports.[7] On the other hand, the next two stages, involving the formation of mono- and bis-PNP-crown derivatives [spiro-ansa (**6**) and spiro-bis-ansa, (**7**), respectively] are "template-directed" by the sodium cation, to which the polyether chain becomes coordinated by means of its oxygen atoms.[3,13] In particular, it is noteworthy that preferential formation of the bis-PNP-crown spiroderivative **7** *vs* the mono-crown derivative, **6** constitutes further evidence for sodium cation-assistance of nucleophilic substitution of the chloride functions (rate enhancement) at the positions adjacent to the PNP-macrocycles. In the formation of **7** from **6** and **3**-Na_2, the oxy(tetraethyleneoxy) dianion **3** attacks the preformed PNP-crown **6** more readily than the non-crown substrate **4,** due to the complexing ability of Na^+ with **6** and the related cation-assisted stabilization of the transition state (**6** → **7**), similar to that previously reported for formation of **8** and **9** from **5** and **2**-Na_2.[13]

In the second case (Scheme 1, lower line), the 1,3-ansa-(oxy-(tetraethyleneoxy)) substituent was first introduced into **1** by its sodium template-assisted cyclosubstitution with **3** to form the PNP-crown **5**, as described previously;[5b] the PNP-crown **5** was isolated in a pure state by column chromatography, and then allowed to react with disodium bis-naphtholate (**2**).[13]

Although for such a pair of reagents as **2** and **5** the most plausible reaction seemed to be spiro substitution at the PCl_2 group,[7d] no trace of the spiro derivative **6** was detected in the

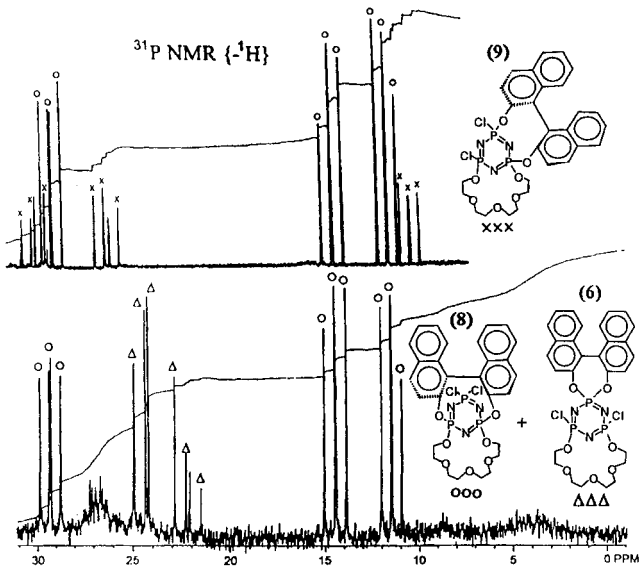


Figure 1. The ^{3} ^{1}P{−^{1}H} NMR spectra of the crude reaction mixtures (in $CDCl_3$ solutions) of the products formed by the cation-assisted substitution of the PNP-crown substrate **5** with disodium binaphtholate, **2**-Na_2, carried out in the absence [(A), upper spectrum)] and presence [(B); lower spectrum)] of tetrabutylammonium bromide (*cation participation vs anion activation*): Circles (○) denote the AMX spin system characteristic of the *gem*-bis-transannular isomer **8**; crosses (×) represent the AMX spin system of the *nongem*-bis-transannular isomer **9**; and triangles (Δ) represent the A_2B spin system of the spiro-binaphthylenedioxy isomer **6** (identical to that found for **6** synthesized by an independent route from the spiro precursor **4**).

reaction mixture. Instead, as reported in a preliminary communication,[13] its two ansa cyclosubstituted regioisomers, **8** (major) and **9** (minor), have been found as the only two products formed on complete consumption of the tetrachloro-crown precursor **5**. Figure 1 shows the proton decoupled ^{31}P NMR spectrum of the crude reaction mixture from the reaction of **5** with **2-Na$_2$** revealing the presence of two AMX spin systems belonging to **8** and **9**, respectively, as deduced by comparison with the spectra of pure **8** and **9,** separated by column chromatography.

The preference for substitution of the chlorine atoms adjacent to the macrocycle has been ascribed to their being involved in the stabilization of a sodium cation assisted transition state of the host−guest complex type,[3] where the part of the "host" is played by the macrocyclic substrate **5** and the part of the "guest" by the sodium counterion of the attacking cation-paired dinucleophile (disodium bis-arylate, **2-Na$_2$**). The undoubted increase in reactivity and the regioselectivity of the reaction may be interpreted in terms of a transition state stabilization where the complexed cation assists the departure of the leaving group (Cl^-) *via* the concerted "push-pull" mechanism, *i.e.*, the metal cation stabilizes the developing negative charge on the chlorine atom closest to the PNP-macrocycle while the nucleophile ArO^- simultaneously attacks the chlorine-bearing macrocyclic P-atom.[3b,4]

Isolation of two ansa regioisomers (**8** and **9**) provides evidence that only the first step of disubstitution with $Na^+[^-OArO^-]Na^+$ has been strictly controlled by host−guest interactions. However, as formation of the *gem*-isomer **8** has been found to predominate in all experiments (Figure 1A), some preference may also be assumed for substitution at the second macrocyclic PCl group over that at the PCl_2 site.

The presence of side arms containing donor groups has been reported to be important in the bimolecular exchange process of 18-crown-6 systems, helping to effect the removal of the bound cation, while a second one approaches the ligand from the opposite side of the molecule.[19] Similarly charge repulsion might occur between the sodium cation already complexed inside the cavity of monosubstituted open-chain intermediate, $N_3P_3Cl_3[O(CH_2CH_2O)_4][OC_{20}H_{12}O]^-Na^+$, and the second sodium cation, paired with the anionic end of this dangling-type intermediate, and approaching the PNP-macrocycle at the second step of substitution.

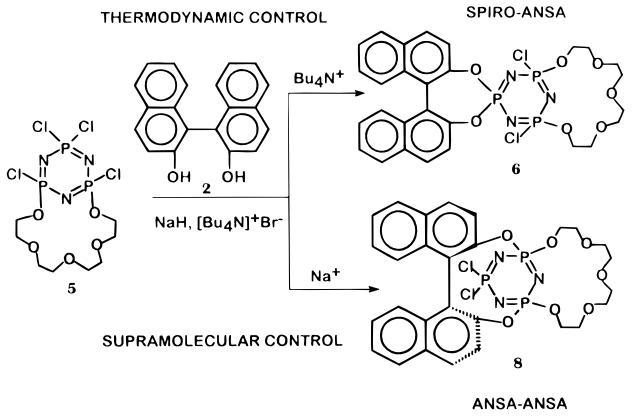
The different configuration of the crown substituent in the two regioisomers (*trans* in *nongem*-**9** and *cis* in *di-gem*-**8**), confirmed by X-ray structure determination[13] indicates an S_N2 reaction mechanism at the macrocycle-bearing P-atoms at each step of the substitution (Walden inversion), when compared with the respective *cis*-configuration of the PNP-crown precursor **5**.[5a]

This unique tendency toward geminal ansa cyclosubstitution, found in the reactions of PNP-crown **5** with dinucleophiles, has revealed that the presence of the macrocyclic substituent in the N_3P_3 ring, which involves the possibility of the host−guest complex formation provides a powerful new tool for the supramolecular regiocontrol of substitution, overriding the steric, electronic, and thermodynamic effects usually dominating the chemistry of cyclophosphazenes.

The key role of cation assistance in gem-to-macrocycle regioselectivity of nucleophilic substitution reactions of **5** has been convincingly confirmed by the formation of some of the spiro derivative **6** (as well as the expected compound **8**) in the reactions of **5** with disodium bis-naphtholate (**2-Na$_2$**) carried out in the presence of the phase transfer catalyst (PTC) cation $[N(C_4H_9)_4]^+$ (Scheme 2), which according to host−guest principles is too bulky to fit into the macrocyclic cavity of **5**.

(19) Li, Y.; Gokel, G.; Hernandez, J.; Echogoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 3087−3096.

Scheme 2



Approximately 15% of isomer **6** was observed by ^{31}P NMR spectroscopy of the reaction mixture (Figure 1B).

These findings can be explained by an equilibrium reaction (simplified as shown below) between the sodium (di)aryloxide and the tetrabutylammonium bromide:

$$Na^+[OAr]^- + Bu_4N^+Br^- \rightleftharpoons Na^+Br^- + Bu_4N^+[OAr]^-$$

The sodium diarylate reagent leads to compound **8** by the mechanism outlined above, while the tetrabutyl ammonium bisarylate, due to the lipophilic nature of the organic cation, would give rise to "naked" and, hence, very reactive, bis-arylate anions[20] which would attack the PCl2 group and lead to the thermodynamically preferred spiro isomer **6**.

Attempts to introduce the spiro-binaphthalenedioxy substituent to the PNP-crown **5** in the presence of tertiary amines failed. Only a trace amount of **6** was obtained using triethylamine as HCl scavenger (see Experimental Section). Triethylamine was succesfully employed previously as HCl acceptor for the quantitative preparation of the non-crown mono(spiro-binaphthylenedioxy)tetrachlorocyclotriphosphazene (**4**) from **1** and **2**.[7d] The reduced reactivity of the PNP-crown **5** must be due to electron transfer from the electron-donating oligoether substituent to the N_3P_3 ring, which results in a decrease of positive charge at all phosphorus atoms, although least at the PCl_2 center, which nevertheless will have been deactivated toward nucleophilic attack.

As inferred from the ^{31}P NMR spectrum of the crude reaction mixture (Figure 1B the absence of the *nongem*-isomer **9** in the products of the reaction of **5** and **2** carried out in presence of both Na and NBu_4 (PTC) cations, together with considerable amounts of unidentified P-containing byproducts, suggests that under such experimental conditions there is a competition between the thermodynamic and supramolecular effects controlling the reaction pattern leading to the further substitution of **9** with **2** at both the PCl(OR) and PCl(OAr) centers; the latter involves considerable ring strain and results in the cleavage of the N_3P_3 ring.

Structural assignments for compounds **6**−**9** have been supported by analytical, ^{1}H (Supporting Information) and ^{31}P NMR and MS data (Tables 1 and 2). All MS molecular ions are consistent with the respective calculated values; ^{31}P NMR spectra were recorded, both proton-decoupled $\{-^1H\}$ and proton-coupled $\{+^1H\}$, in order to discriminate between the $P(OCH_2)(OAr)$, $P(OCH_2)_2$, $P(OCH_2)Cl$, $P(OAr)Cl$, $P(OAr)_2$, and PCl_2 moieties.

(20) (a) Mandolini, L.; Masci, B. *J. Am. Chem. Soc.* **1984**, *106*, 168−174. (b) Landini, D.; Maia, A.; Montanari, F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 46−51. (c) Maia, A. *Pure Appl. Chem.* **1995**, *67*, 697−702 and references therein.

Table 1. Mass Spectrometric and ^{31}P NMR Spectroscopic Data of Cyclophosphazene Derivatives **6** and **7** of the General Formula $N_3P_3Cl_{4-2x}[O(CH_2CH_2O)_4]_x[O_2C_{20}H_{12}]$ (where $x = 1, 2$)

No [a]	x [b]	M^+ [c] found/ /calc.	^{31}P NMR {-^1H} (A_2B spin system) [d] P_A δ_P [ppm]	P_B δ_P [ppm]	P_B δ_P [ppm]	$\lvert J_{P-P} \rvert$ [Hz]
6	1	681/681	24.6, d[e]	-	22.3, t[g],	78.5
7	2	803/803	-	18.3, d[f]-	29.0, t[g],	86.7

[a] For structural formulae, see Scheme 1. [b] Number of ansa cyclic oxy(tetraethyleneoxy) substituents at N_3P_3 ring ($x = 1$, crown; $x = 2$, cryptand (*gem*-bis-crown). [c] Molecular ion according to mass spectrum, calculated for ^{35}Cl. [d] A_2B spin system; d, doublet of doublets, corresponds to P_A (two equally substituted P atoms); t, triplet, with the central peak split corresponds to PB; $|J_{P-P}|$ and δ_P values calculated according to ref 28. [e] Proton coupling causes collapse into a broad doublet. [f] Each peak of the doublet is split into three on proton coupling. [g] Weak proton coupling, slight broadening of resonance lines.

The proton-decoupled ^{31}P NMR spectra of both spiro-binaphthalenedioxy) derivatives, **6** and **7,** show the expected A_2B spectra, with that of **6** displaying a significant "roofing effect" due to the similarity of the $P(OAr)_2$ and P(OR)Cl chemical shifts, compared to the one for **7** (Table 1). Proton coupling was found to give distinct coupling patterns for the signals of the two P-atoms bearing transannular polyether substituent(s), but only broadens the signals of the P_{spiro} group [B part of the spin system due to $\equiv P(OAr)_2$]. Both transannular derivatives, **8** and **9,** exhibit 12-line spectra composed of three doublet of doublets, resulting from three $^2J_{P-P}$ couplings (Table 2, Figure 1), typical for AMX/ABX spin coupling systems.[21] For the *nongem*-isomer **9**, having three differently substituted P-atoms, the occurence of the AMX pattern is quite obvious, whereas for the di-*gem*-bis-ansa-cyclosubstituted regioisomer **8**, the AMX pattern results from the non-equivalency of the two P-atoms linked to the two coupled oxyarylene halves[22] caused by the twist of the biaryl rings around the linking C−C bond, introducing a chiral barrier.[23]

Electronic spectra of the spiro-binaphthalenedioxy derivatives **6** and **7** and those of the respective transannular ones **8** and **9** differ in the region of the absorption band E_2, which appears at λ 285 nm for the ansa-spanned derivatives **8** and **9** and at 305 nm for the spiro derivatives **6** and **7**. The position of the peak for **8** and **9** does not differ significantly from that of the parent bis-β-naphthol, which shows the band at 280 nm, indicating a similar, nearly perpendicular, arrangement of two coupled naphthalene rings.[23e] On the other hand, the spiro linkage of the binaphthalenedioxy substituent to the P-atom forces the coupled biaryl rings into some degree of coplanarity resulting in the bathochromic shift of the E_2 band (280 → 305 nm) as previously described for the tetrachloro spiro precursor **4**.[23e]

The molecular structures of the ligands **7**−**9** have been confirmed by X-ray structure determination. The completely resolved structures of both transannular regioisomers **8** and **9** have been reported previously.[13] The structure of the cryptand-like spiro-binaphthalenedioxy bis(ansa-crown) derivative **7** is presented in this paper (Figure 2). It shows substantial disorder by one of the two ansa-oxy(tetraethyleneoxy) substituents linked to the same two phosphorus atoms (see Experimental Section). In this figure, only one of the two configurations found for the polyether ring O8→O12 is shown. It is, however, noteworthy that the spiro moiety of the binaphthalenedioxy substituent on the N_3P_3 ring in **7** has been demonstrated unambiguosly by X-ray structure analysis (Figure 2). The same spiro-binaphthalenedioxy substituent must be present in ligand **6**, being a mono-crown precursor of **7**. The A_2B spin system of **6** found in the ^{31}P NMR of the crude reaction mixture formed from **5** and **2-Na$_2$** in the presence of the tetrabutylammonium cation (Figure 2) is the same as that for the ^{31}P NMR spectrum of pure **6** (formed according to Scheme 1) and supports the reaction course according to Scheme 2.

Approach to Chiral Polymeric Ligands. We have found that the remaining 2 chloride functions in the major di-*gem*-substituted chiral PNP-ligand **8** can be readily substituted, e.g., with ethylenediamine as shown in Scheme 3.

The relative ease and high yield (∼70%) of preparation of the spiro-ethylenediamine derivative **10**, as deduced from the ^{31}P NMR spectrum of the crude reaction mixture from the aminolysis of **8** (Figure 3, Supporting Information), suggest that **8** could potentially be coupled to amino polymers to give polymer-bound chiral phosphazene crowns.[24]

Comparison of the Metal Cation Complexation Properties of the Chiral PNP Ligands 6−9. In the chiral ligands **6**−**9**, the binaphthyl unit is not a constituent part of the macrocycles, but plays the role of side substituent, and therefore, it might be expected that its influence on binding ability would be more of the *lariat ether* type, *i.e.*, it would consist in synergistic enhancement of the complexing power[25] instead of its decrease, as found for crowns with integral aromatic subunits.

The metal cation complexing properties of the chiral ligands **6**−**9** have been investigated using a simple test, based on the different rate of migration of the free ligand and its complex in TLC experiments, the differences of the R_f values being related to the complex stability constants.[16] In several cases, complex formation has been confirmed by the mass spectrometric investigations (LSIMS), showing the presence of the molecular ions of the respective metal$^+$−ligand complexes.

Table 3 shows a comparison of the complexing properties of the chiral crown regioisomers **6**, **8**, and **9** and the cryptand-like ligand **7** [bis(1,3-ansa-crown) homologue of **6**] compared to those of the parent tetrachloro-PNP-crown **5**. The comparison revealed that in all cases the complexing properties of the ligands containing chiral units are either similar to or even better than those of the parent crown **5**, which contains only chlorine substituents.

The following structure−complexation property relationships are observed:

(a) The chiral spiro-binaphthalenedioxy PNP-crown **6** displays very similar complexing abilities with monovalent cations (alkali metals + silver) to those of the parent tetrachloro PNP-crown ligand **5**, indicating that there are no significant electronic interactions between the PNP-polyether macrocycle and the conjugated aromatic π-system *via* a -N=P−O spacer, which might contribute to the binding properties of the polyether skeleton.

(21) Kemp, W. *NMR in Chemistry−A Multinuclear Introduction*; Macmillan Education Ltd.: Houndsmille, Hampshire, London, 1986; pp 72−73.

(22) Izatt, R. M.; Bradshaw, J. R.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271−339.

(23) (a) See in ref 1b, pp 12−13 and 164−166. (b) Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999. (c) Hanazaki, I.; Akimoto, H. *J. Am. Chem. Soc.* **1972**, *94*, 4102. (d) Juskowiak, B.; Ihara, T.; Nakashima, H. Takagi, M. *Polish J. Chem.* **1995**, *69*, 1282−1297 and references therein. (e) Brandt, K.; Kasperczak, W. *Spectrochim. Acta* **1982**, *38A*, 961−964 and references therein.

(24) (a) Smid, J.; Sinta, R. Macroheterocyclic Ligands on Polymers. *Top. Curr. Sci.* **1981**, 105−157. (b) See in ref 1b, pp 156−158.

(25) (a) *Crown Ethers & Analogs*; Patai, S., Rappaport, Z., Eds.; John Wiley & Sons: Chichester, New York, Brisbane, Singapore, 1989; pp 308−319. (b) See in ref 1b, pp 6−12; (c) Gokel, G. *Chem. Soc. Rev.* **1992**, 39−47.

Table 2. $^{31}P\{-^1H\}$ NMR Spectroscopic Data of Bis-transannular 1,3-Oxy(tetraethyleneoxy) Cyclophosphazene Derivatives with 1,3-*gem*- (**8**) and 1,5-*nongem*- (**9**) 1,1′-Binaphthalene-2,2′-Bridges

			$^{31}P\{-^1H\}$ NMR						$^{31}P\{+^1H\}$ NMR		
cmpd	formula	M_w[a]	δ_{P_A} [ppm][b]	δ_{P_M} [ppm][b]	δ_{P_X} [ppm][b]	$J_{P_{A-M}}$ [Hz][b,d]	$J_{P_{A-X}}$ [Hz][b,d]	$J_{P_{M-X}}$ [Hz][b,d]	$J_{P_{A-H}}$ [Hz][b]	$J_{P_{M-H}}$ [Hz][b]	$J_{P_{X-H}}$ [Hz][b]
8	$C_{28}H_{28}O_7C_{l2}N_3P_3$	681/681	11.5, dd[c]	14.5, dd[c]	29.3, dd[c]	66.8	63.2	72.8	10.6[e]	12.9[e]	*f*
9	$C_{28}H_{28}O_7C_{l2}N_3P_3$	681/681	10.3, dd[c]	30.3, dd[c]	26.4, dd[c]	65.2	60.4	90.7	13.1[e]	*f*	15.6[e]

[a] According to mass spectrum; M calculated for ^{35}Cl. [b] For **8** (*gem*-bis-transannular derivative)**:** $P_A = P(OAr)(OCH_2^-)$, $P_M = P(OAr')(OCH_2-)$, $PX = PCl_2$. For *nongem*-transannular isomer **9**: $P_A = P(OAr)(OCH_2\text{-})$, $P_M = P(OAr')Cl$, $P_X = P(OCH_2\text{-})Cl$. Ar and Ar′ denote the respective coupled halves of the conjugated dioxyarylene substituent, which produce nonequivalence due to their twisting around the biarylene linkage bond (the structural formulas **8** and **9** are depicted in Scheme 1). [c] Doublet of doublets. [d] J_{P-P} values calculated according to ref 21 for the AMX coupling system. [e] Each peak of the doublet of doublets is split into three. [f] No proton coupling.

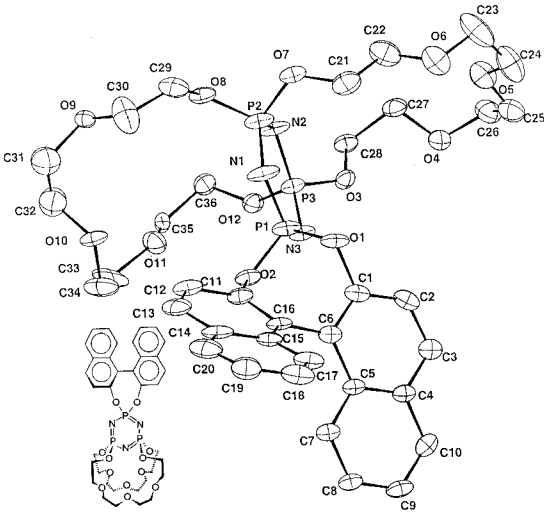
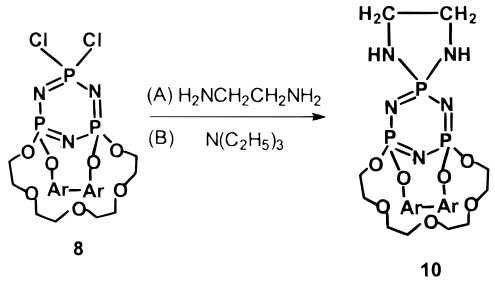


Figure 2. The X-ray crystallographic structure of 1,3:1,3-bis(oxy-(tetraethyleneoxy))-5,5-(1,1′-binaphthalene-2,2′-dioxy)cyclotriphosphazene (**7**).

Scheme 3



(b) The transannular 1,3-binaphthalenedioxy substituent, which spans the two macrocycle-bearing P-atoms, enhances the cation complexing ability of isomer **8** compared to that of compound **5,** most noticably for K^+ and Rb^+, probably as a result of $\pi-$n interactions.

(c) The asymmetric 1,5-transannular isomer **9** displays a significantly enhanced affinity for the smaller cations (particularly marked for lithium and sodium and somewhat less for silver) which might result from its different crown configuration (*trans* to the plane of N_3P_3 ring[13]) compared to the ligands **5**−**8**, which all have the macrocyclic unit *cis*-linked to the cyclophosphazene entity.[5a,13] A molecular peak at 688, observed in LSIMS spectrum when **9** was treated with LiCl, can be explained by the presence of a 1:1 complex, confirming the affinity of **9** to Li (**9**, M^+ 681; Li, M^+ 7) (see the Supporting Information).

Table 3. Comparison of Complexing Properties of Chiral PNP-Ligands **6**−**9** with Respect to the Parent Aryl-Free PNP-Crown **5**

ligand			B^h (%) $= R_F^2 - R_F^1/R_F^2$ (hexane:THF = 2:3), silica gel[i]					
cmpd[b]	*x*[c]	*n*, *m*[d]	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
5[e]	1		0	9	16	19	6	4
6[f]	1	5,5	0	4	19	9	6	11
7[g]	2	5,5	25	73	83	77	73	33
8[f]	1	1,3	0	10	39	28	11	20
9[f]	1	1,5	61	53	37	16	5	29

[a] According to TLC test.[16] [b] For structural formulae, see Scheme 1. [c] *x* = number of 1,3-oxy(tetraethyleneoxy) units in N_3P_3 ring. [d] *n*,*m* = the positions of linking 1,1′-binaphthylene-2,2′-dioxy groups to the N_3P_3 ring [1,3 (ansa), 1,5 (ansa′), 5,5 (spiro). [e] Parent reactive tetrachloro-PNP-crown. [f] Isomeric chiral [binaphthylenedioxy] PNP-crowns. [g] Bis-[oxy(tetraethyleneoxy)]-substituted cryptand-like homologue of chiral crown **6**. [h] The R_F value difference of a ligand on a silica gel and on the gel impregnated with a salt containing given metal cation. [i] Merck alumina plates.

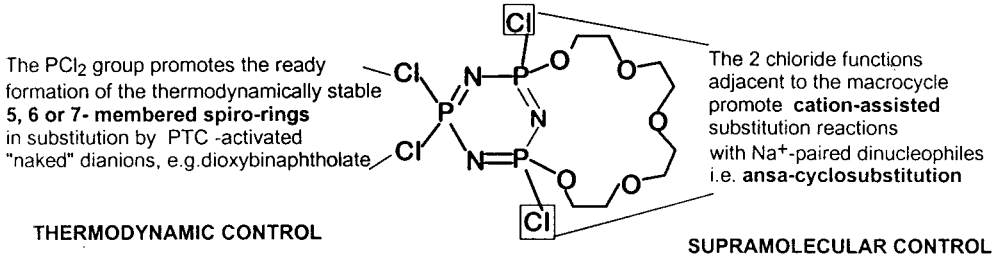
(d) The chiral PNP-cryptand **7** forms very strong complexes with all of the monovalent cations, with comparatively high affinity toward the Na, K, Rb, and Cs cations and somewhat smaller affinity toward Li^+ and Ag^+, which is probably due to the presence of the two macrocyclic rings in **7**, allowing this ligand to complex cations within one or both the macrocyclic cavities, as well as between them in a "sandwich-like" fashion.

Conclusions

The reactivity of the functional chlorocyclophosphazene-containing PNP-crowns in substitution reactions with dinucleophilic reagents, such as the sodium cation paired bis-naphtholate anions, can be explained in terms of the superposition of thermodynamic effects, which control the reactions of chlorocyclophosphazenes with dinucleophiles, and host−guest complex interactions, in particular cation assistance which are characteristic for reactions of crown ether substrates. Both these effects compete and/or cooperate during substitution processes: the thermodynamic stability of seven-membered rings is a driving force toward spiro ring formation at the PCl_2 site, whereas involvement of chloride functions at the macrocycle-bearing PCl(OR) atoms in stabilization of the cation-assisted intermediate transition state(s) favors the di-*nongem*-substitution pattern at positions adjacent to the PNP-crown structure (ansa-cyclosubstitution) (Scheme 4).

Substitution of chlorocyclophosphazene-derived crown ether substrates with cation-paired dinucleophiles has been found to be dominated by host−guest supramolecular interactions resulting in transannular ansa-spanning at the phosphorus atoms adjacent to the crown structure as the preferred substitution pattern.

Scheme 4



It is possible to switch the substitution pattern toward parallel formation of the spiro derivative by introduction of the non complexable large lipophilic tetraalkylammonium cations, resulting in ion pair separation and enhancement of the nucleophilicity of the dianion, which then acts as a "naked anion" and attacks the PCl_2 site, giving the thermodynamically preferred spiro derivative.

The complexing properties of all of the chiral crown ligands reported in this paper are either similar to (spiro derivative **6)** or better than (ligands **7**−**9**) those of the parent binaphthyl-free PNP-crown **5.** Only substituents adjacent to the macrocycle influence the binding power of a given ligand.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**1**) was obtained as a gift from the Nippon Fine Chemical Co., Ltd., and purified by fractional crystallization from hexane. Sodium hydride, 60% dispersion in mineral oil (Aldrich Chemical) was used as received. Tetraethylene glycol (**2**, Aldrich) was dried over molecular sieves 4 Å. Bis-β-naphthol (2,2′-dihydroxy-1,1′-binaphthyl, **3**) (Aldrich) was crystallized from toluene, mp 218 °C. Tetrabutylammonium bromide, 99%, (Aldrich) was used as received.

1,3-(Oxy(tetraethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazene (**5**) was synthesized and purified as previously reported.[5b] 1,1,3,3-Tetrachloro-5,5-binapthalene-2,2′-dioxycyclotriphosphazene (**4**) was prepared by interfacial condensation in the presence of NaOH according to the method reported[7e] for the synthesis of the respective monospiro-2,2′-dioxy-1,1′-biphenyl derivative from **1** and **2**.

THF (POCh Gliwice) was distilled once over CuCl, once over calcium hydride, and finally 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.

Methods. ^{1}H 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 $CDCl_3$ with 85% H_3PO_4 as an external reference. Positive shifts are 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 *m*-nitrobenzyl alcohol (NBA) matrices; the latter technique was applied to examine metal complexes. Number-average molecular masses of the polymeric components were determined by the VPO technique in $CHCl_3$, using a Knauer vapor pressure osmometer. Flash column chromatography was done with silica gel (100−200 mesh, Merck), eluted with hexane−THF. TLC analyses were performed on Merck precoated silica gel 60 plates.

TLC complexation experiments were carried out as previously described. The values of parameter *B* for the complexes of the ligands **5**−**9** with alkali metal (Li, Na, K, Rb, and Cs) and silver cations are given in Table 3.

Crystal Data. All crystallographic measurements were made using a DELFT Instruments Fast TV area diffractometer positioned at the window of a rotating anode generator with Mo Kα radiation by following previously described procedures.[26a] The θ range for data collection is $-35 \le 34$, $-14 \le 13$, $-23 \le 27$. Of 14 254 reflections collected, 5523 reflections were independent. The structure was solved by Direct methods (SHELXL86)[26b] and refined on F_2 using full-matrix least-squares (SHELXL93).[26c] The diagrams were drawn with the CAMERON program.[26d]

Synthesis of Mono- (6) and Bis- (7) 1,3-(Oxy(tetraethyleneoxy)-5,5-(1,1′-binaphthalene-2,2′-dioxy)cyclotriphosphazene Derivatives (One-Pot Method). Hexachlorocyclotriphosphazene (**1**, (1.74 g, 5 mmol) and 2,2′-dihydroxy-1,1′-binaphthyl (**2**, 1.5 g, 5.05 mmol) were dissolved in 100 mL of dry THF and placed in a 500 mL four-necked round-bottomed flask, fitted with a magnetic stirrer, reflux condenser, and argon inlet. NaH (60% oil suspension, 0.44 g, 11 mmol) was added with stirring. The reaction was carried out at 20 °C under a dry argon atmosphere for 1 h to full conversion of **1** [as deduced from TLC results (in hexane−THF = 4:1)], showing the presence of 1,1,3,3,-tetrachloro-5,5-(1,1′-binaphthalene-2,2′-dioxy)cyclotriphosphazene (**2**) as the major product formed (from ^{31}P NMR ∼95% yield) and a trace amount of the respective bis-spiro derivative.[7d]

Tetraethylene glycol (**3**, 1.94 g, 10 mmol) in 20 mL of dry THF and NaH (60% oil suspension, 0.8 g, 20 mmol) were then added, and the reaction mixture was stirred at 20 °C for 2 h, to full conversion of **4** as indicated by TLC, and filtered to remove the sodium chloride formed. THF was distilled off under reduced pressure, and the resultant yellowish oil was extracted with benzene (30 mL). The benzene solution was washed with an aqueous solution of NaOH and then with distilled H_2O to remove traces of unreacted **2** and the base. The organic layer was dried for 24 h over anhydrous Na_2SO_4 and next precipitated with 30 mL of hexane. The 1:1 hexane−benzene-soluble fraction (2.6 g, 64.7% of theoretical yield) was subjected to flash chromatography, using THF−hexane = 1:1 as an eluant. Both mono-(PNP-crown) (**6**, (yield 0.12 g, 4.6%) and bis-(PNP-crown) (**7**,(yield 0.35 g, 13.5%) were isolated as colorless oils, tending to crystallize on storage.

After **6** and **7** were separated from the chromatographed mixture of the benzene−hexane-soluble products, the low molecular oligomeric fraction $M_n = 1160$ (0.25 g, 6.7%) was also eluted with THF from the chromatographic column. The fraction precipitated with hexane (0.7 g, 16.8%) was found to consist of oligomers with $M_n = 2400$.

A similar large decrease of the chemical yield, due to the irreversible absorption on silica gel has been recently reported for other chiral PN-containing macrocyclic 1,1′-binaphthyl derivatives.[27]

Synthesis of Homologous Chiral PNP-Crown (6) and Cryptand (7): Sodium Cation Assisted Reaction of Tetrachloro(1,1′-binaphthalene-2,2′-dioxy)cyclotriphosphazene (4) with Tetraethylene Glycol (3). Tetrachloro(1,1′-binapthalene-2,2′-dioxy)cyclotriphosphazene (**4**, (5.59 g, 10 mmol) and tetraethylene glycol (**3**, 3.88 g, 20 mmol) were dissolved in 200 mL of dry THF at room temperature. Sodium hydride (60% oil dispersion, 1.6 g, 40 mmol) was added, and the reaction was carried out with stirring at room temperature for 2 h. (The course of the reaction was monitored by TLC, using hexane−THF (3:

(26) Darr, J. A.; Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A. *Inorg. Chem.* **1993**, *32*, 5204. (b) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (c) SHELXL93 program for Crystal Structure Drawing, University of Oxford, 1983; (d) Pearce, L. J.; Watkin D. J. CAMERON, Crystallography Laboratory, Oxford.

(27) Wimmer, P.; Widhalm, M. *Phosphorus, Sulfur and Silicon* **1995**, 106, 105−114.

(28) *NMR - Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1971; pp 104−105.

1) as eluant and I_2 vapor developing reagent.) The sodium chloride formed was filtered off, and the THF was removed at reduced pressure to leave a colorless oil (7.4 g), which was dissolved in benzene (50 mL) and precipitated with 50 mL of hexane. The fraction soluble in benzene−hexane (1:1) (4.6 g 57% of theoretical yield), consisting mainly of macrocyclic products **6** and **7** (from ^{31}P NMR results), was subjected to column chromatography on silica gel. Two individual fractions were isolated (eluant hexane−THF (1:2)) and identified as the respective mono- (**6**) and bis-(**7**) 1,3-(oxy(tetraethyleneoxy))-5,5-(1,1′-binapthalene-2,2′-dioxycyclotriphosphazene derivatives: **6**, yield 0.16 g (3.5%), $R_f = 0.53$ (hexane−THF (1:3), mp (after crystallization from ethanol−chloroform) 135 °C; **7**, yield 0.51 g (11.2%), $R_f = 0.25$, mp (after recrystallization from ethanol) 208−209 °C. Analytical and ^{1}H NMR data for **6** and **7** are given in Table A (Supplemenary Information) and the ^{31}P NMR and mass spectral data in Table 1.

The fraction precipitated with hexane (insoluble in benzene−hexane 1:1) was found to consist of low-molecular polymers with M_n in the range of 2000−6000. Five individual polymeric fractions were isolated by fractional precipitation with hexane [$M_n = 5200$ (34%); 4600 (21%); 3700 (11.5%); 3200 (4%); 2700 (4.5%)], the residue (25%) $M_n = 1060$ being soluble in this system. All polymeric fractions were readily soluble in chloroform and stable on storage as both solids and solutions.

Crystal Data for $C_{36}H_{44}O_{12}N_3P_3$ (7): MW = 803.65, monoclinic, space group *C*2/*c*, $a = 32.368$, $b = 23.184$, and $c = 23.184$ Å, $\beta = 128.65°$, $V = 7537.3$ Å^3, $Z = 8$, density (calculated) = 1.416 mg/m^3, $F(000) = 3376$, $\lambda = 0.710\,69$Å, $T = 293$ K, $\mu = 0.225$ mm^{-1}. All non-hydrogen atoms were refined anisotropically. One of two polyether fragments was disordered over two conformations with occupancies that agreed within experimental limits. The refinement included fixed occupancies of 0.5 for the relevant atoms and some constraints in bond lengths in the affected region. The hydrogen atoms in the structure were placed in idealized positions and included in the calculations of F_c with a U_{iso} tied to the U_{eq} of the parents. No parameters of these atoms were refined. The residual were $R_1(I>\sigma(I)) = 0.602$ and wR_2 (all data) = 0.1477. The maximum and minimum heights in final Fourier difference map were 0.365 and −0.293 Å^{-3}.

Synthesis of Isomeric Chiral Ansa-(Dioxybiarylene)-Substituted PNP-Crowns 8 and 9: Sodium Cation Assisted Reaction of 1,3-(Oxy(tetraethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazene (5) with 2,2′-Dihydroxy-1,1′-binapthyl (2). 1,3-(Oxy(tetraethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazene (**5**, 0.469 g, 1.00 mmol) and 2,2′-dihydroxy-1,1′-binapthyl (**2**, 0.286 g, 1 mmol) were dissolved in 50 mL of dry THF at room temperature. Sodium hydride (60% oil dispersion, 0.088 g, 2.2 mmol) was added, and the reaction was carried out with stirring at room temperature for 2 h. (The course of the reaction was monitored by TLC, using hexane−THF (2:3) as an eluant and I_2 vapor as developing reagent.) The sodium chloride formed was filtered off, and the THF was removed at reduced pressure to leave a colorless oil, which was dissolved in benzene (30 mL) and washed with aqueous solution of NaOH and then with distilled H_2O to remove traces of unreacted bis-naphthol, NaCl formed, some unidentified polar side products, and the base. The organic layer was dried for 24 h over anhydrous Na_2SO_4 to give 0.60 g (∼88% of theoretical yield) of a yellowish oil, consisting (as deduced from ^{31}P NMR results) of two isomeric bis-ansa-cyclosubstituted cyclophosphazene derivatives: 1,3- and 1,5-(binaphthalene-2,2′-dioxy)-1,3-(oxy(tetraethyleneoxy))cyclotriphosphazenes [(**8**, ∼70%) and (**9**, ∼30%), respectively]. The mixture of isomers was subjected to column chromatography on silica gel [(hexane−THF (1:1)]. Two individual fractions were isolated, identified as the respective 1,3- (**8**) and 1,5- (**9**) (1,1′-binaphthalene-2,2′-dioxy)-1,3-[oxy(tetraethyleneoxy))cyclotriphosphazenes: **8**, yield 0.25 g [41.7%, with respect to the amount subjected to chromatography, 36.7% of theoretical yield)], $R_f = 0.47$ (hexane−THF (2:3), mp (after crystallization from ethanol−chloroform) 192 °C; **9**, yield 0.14 g [23.3%, with respect to the amount subjected to chromatography) (20.5% of theoretical yield)], $R_f = 0.39$, mp (after recrystallization from ethanol) 270 °C (decomposition). Analytical and ^{1}H NMR data for **8** and **9** are given in Table A (Supporting Information) and the respective ^{31}P NMR and MS data are in Table 2.

Synthesis of Isomeric Chiral Ansa-(Dioxybiarylene)-Substituted PNP-Crowns 6 and 8: Sodium Cation Assisted Reaction of 1,3-(Oxy(tetraethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazene (5) with 2,2′-Dihydroxy-1,1′-binaphthyl in the Presence of Tetrabutylammonium bromide (2). 1,3-(Oxy(tetraethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazene (**5**, 0.2345 g, 0.5 mmol), 2,2′-dihydroxy-1,1′-binapthyl (**2**, 0.143 g, 0.5 mmol), and 0.322 g (1 mmol) of tetrabutylammonium bromide were dissolved in 50 mL of dry THF at room temperature. Sodium hydride (60% oil dispersion, 0.088 g, 2.2 mmol) was added to the resulting homogeneous solution, and the reaction was carried out with stirring at room temperature for 2 h and monitored by TLC as described above. The reaction mixture was freed of sodium chloride, tetrabutylammonium bromide, traces of unreacted bis-naphthol, and the base as described above, leaving 0.22 g (64.1%) of a colorless oil. The ^{31}P NMR spectrum of this crude product showed the presence of two distinctive sets of peaks (constituting altogether ∼60% of the integrated P-peak area), AMX corresponding to the 1,3-ansa-cyclosubstituted isomer **8**, and A_2B corresponding to the spiro isomer **6.** The relative ratio of their intensities AMX/A_2B was ∼2:1 (Figure 1B]. No trace of the AMX spin system characteristic for isomer **9** has been detected, and the residual components showed unidentified broad signals in the region 26−28 ppm and 2−6 ppm. Mass spectrum of the crude mixture showed intensive molecular ions at *m*/*e* 682 and 684, corresponding to the formula of both isomers **6** and **8**, $C_{28}H_{28}O_7Cl_2N_3P_3$ (MW 681) and the peak at *m*/*e* 895 that might correspond to bis-1,3:5,5-(1,1′-binaphthalene-2,2′-dioxy)-1,3-(oxy(tetraethyleneoxy))-cyclotriphosphazene, $C_{48}H_{40}O_9N_3P_3$, MW 895. Attempts to separate the above mixture by column chromatography on silica gel eluted with hexane−THF = 1:1 were unsuccessful, due to the close similarity of the respective R_f values for **6** and **8** and apparently irreversible sorption of other products on silica gel surface.

Attempted Reaction of 1,3-(Oxy(tetraethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazene (5) with 2,2′-Dihydroxy-1,1′-binaphthyl in the Presence of (i) Triethylamine or (ii) Pyridine. 1,3-(Oxy(tetraethyleneoxy))-1,3,5,5-tetrachlorocyclotriphosphazene (**5**, 0.469 g, 1 mmol) and 2,2′-dihydroxy-1,1′-binaphthyl (**2**, 0.286 g, 1 mmol) were dissolved in 100 mL of dry THF and 0.3 mL (∼2 mmol) of (i) triethylamine or (ii) pyridine were added to this solution. After the reaction was carried out with stirring (magnetic stirrer) at room temperature for 6 h, no precipitate was formed, and TLC analysis showed only the presence of unreacted substrates, as confirmed by the ^{31}P NMR spectra of the samples from reactions i and ii, showing exclusively the A_2B (AA′B) spin system characteristic for **5**.

When the reaction was continued for a an additional 5 h at the boiling point of THF with the next portion (0.3 mL) of tertiary amine (i or ii) added, the formation of a trace amount of **6** was detected [∼5% (i) or ∼3%, (ii) according to ^{31}P NMR spectra], which for thepyridine acceptor (ii) was accompanied by a significant amount of some unidentified side products, probably resulting from pyridine-catalyzed decomposition of the N3P3 ring.

Reaction of 1,3-(1,1-Binaphthalene-2,2′-dioxy)-1,3-(oxy(tetraethyleneoxy))cyclotriphosphazene (8) with Ethylenediamine To Form Spiro Derivative 10 of Compound 8. 1,3-(1,1′-Binaphthalene-2,2′-dioxy)-1,3-(oxy(tetraethyleneoxy))-5,5-dichlorocyclotriphosphazene **8**, 0.137 g, 0.2 mmol) and ethylenediamine (0.012 g, 0.4 mmol) were dissolved in 10 mL of dry benzene and stirred for 6 h at room temperature (∼20 °C). Approximately two-thirds of the stock solution was then filtered, freed of solvent *in vacuo*, and dissolved in $CDCl_3$ (→ fraction A). To the remaining reaction mixture was added a few drops of triethylamine and stirring, without heating, was continued for the next 1 hour and the resultant crude reaction mixture was subjected to the same procedure as above (→ fraction B). Both fractions were analyzed by MS and ^{31}P NMR, showing the presence of unreacted **8** and its mono-spiro ethylenediamino derivative: 1,3-(binaphthalene-2,2′-dioxy)-1,3-(oxy(tetraethyleneoxy))-5,5-(1,2-ethylenediamino)cyclotriphosphazene (**10**), $C_{30}H_{34}O_7N_5P_3$, MW 669. MS: *m*/*e* 670 (**11**), 681 (**8**). The ^{31}P NMR spectra showed two AMX spin systems: one belonging to the unreacted **8** (for δ_P and J_{P-P}, see Table 2) and one belonging to to **10** (δ_P, ppm $P_A = P[NHC_2H_4NH]$, 33.7; $P_M = P(OAr)(OCH_2-)$, 20.9; $P_X = P(OAr')(OCH_2-)$, 18.5. J_{P-P}, Hz 64.3 (A-M), 76.1 (M-X), 59.8 (A-X), with all sets of peaks being multiply split on proton coupling).

Estimated yields of **10** were ∼55% (fraction A) and 69% (fraction B) from ^{31}P NMR results by referring the intensity of AMX signals

system for **10** to the overall intensity of the 31P NMR signals in the respective spectra (Figure 3, Supporting Information).

Acknowledgment. This work has been supported by the European Commission (grant CIPA-CT93-0019), and the Polish Committee on Scientific Research (grants 3 T09A 001 13 and 886/T09/96/11), and two of us (K.B., D.B.D.) thank the Royal Society for travel grants. The authors are grateful to Nippon Fine Chemical Co., Ltd., for a generous gift of hexachlorocyclotriphosphazene.

Supporting Information Available: Analytical, ^{1}H NMR, and UV data of 1,3:1,3-bis(oxy(tetraethyleneoxy))-5,5-(1,1′-binaphthalene-2,2′-dioxy)cyclophosphazene derivatives **6**−**9** of general formula $N_3P_3Cl_{4-2x}$ {1,3-[$O(CH_2CH_2O)_4$]}$_x$[$O_2C_{20}H_{12}$], where x = 1, 2 (Table S1); Tables of crystal data and other details of the structure determination and refinement, positional and thermal parameters, and estimated standard deviations for all atoms, bond distances and angles, and anisotropic thermal parameters of the derivative **7**; ^{31}P{$^{-1}$H} NMR spectrum of the crude mixture formed by substitution of the compound **8** with ethylenediamine (Figure S1); and LSIMS spectrum of the complex of the compound **9** with LiBr (Figure S2) (15 pages). See any current masthead page for ordering and Internet access instructions.

JA972372M