A Regioselective Route to New Polytopic Receptors by Diaminolysis of Chlorocyclotriphosphazatriene-Containing Crown Ethers

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

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

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A general strategy is reported for the facile preparation of diamino-derivatized PNP-crowns, giving access to a large range of new host molecules of different sizes, shapes, and topology. Reactions of the tetrachloro-PNP-crown precursor **1** with polymethylene-diamines **2a**−**h** ($n = 2-6, 8, 10, 12$) proceed rapidly and regioselectively via substitution reactions of Cl at the PNP-crown-forming P-atoms; the reaction is assisted by the macrocyclic 1,3-oxy(tetraethylenoxy) substituent at the N_3P_3 ring which provides a site for the hydrogen-bond-driven assembly of reagents **1** and **2**. The products belong to three different classes of polytopic receptors: lateral macrobicycles (ansa, **5a**−**h**), bola-amphiphilic tritopic bis-crowns (bino, **6a**−**h**), and tetratopic cylindrical macrotricycles (bis-bino, **8a**−**h**). The structures of **5**, **6**, **8**, and **10b** were established by MS and ^{31}P NMR spectroscopy, and an X-ray crystal structure was obtained for the bis-bino 1,3-diaminopropane PNP-crown derivative **8b**. Preliminary screening by a simple TLC test of the metal−cation complexing properties of the series of compounds **5**, **6**, and **8** revealed their capacity to bind both harder (alkali and alkaline earth) and softer (transition) metal cations, with significant affinity being displayed toward potassium and silver cations by many of the ligands studied.

Introduction

We have developed a new class of functional crowns, derived from hexachlorocyclotriphosphazatriene, which combine the versatile reactivity of chlorocyclophosphazenes with the complexing properties of crown ether ligands.[1] The presence of the polyether crown substituent in **1** enables its supramolecular interactions with the attacking nucleophile that results in a new powerful type of regiocontrol, giving ready access to species which would be very difficult to form according to the rules of classic cyclophosphazene chemistry, substitution pathways of which are dominated by steric, electronic,[2] and thermodynamic effects.[3,4]

Previously we reported the reactions of PNP-crown **1** with sodium bis-β-naphtholate,[5] which yielded unusual *gem*- and *nongem* bis-*trans*-annular derivatives, as a result of sodium cation-assisted[6] regioselectivity, instead of their thermodynamically favored spiro-isomers.[5] Our preliminary studies on the aminolysis of PNP-crown **1** with both 1,2-diaminoethane and 1,3-diaminopropane (**2a**,**b**) have shown that it also proceeds regioselectively at the macrocycle-bearing P-atoms,[7] ascribed to supramolecular assistance[8] based on hydrogen-bonding interactions between host (**1**) and guest (**2**).

These results are in contrast to those for reactions of short chain diamines (**2a**−**c**) with nonmacrocyclic cyclophosphazenes which, for thermodynamic reasons, usually yield spirocyclic structures,[4,9−11] except for reactions with a ”blocked precursor” having no sites available for spirocyclosubstitution.[12]

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* Corresponding author. Tel: 48-32-271-60-77. Fax: 48-32-271-29-69. e-mail: polymer@uranos.cto.edu.pl.

[†] Polish Academy of Sciences.

[‡] Birkbeck College.

[§] University of Wales.-

[‖] Present address: Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BG, U.K.

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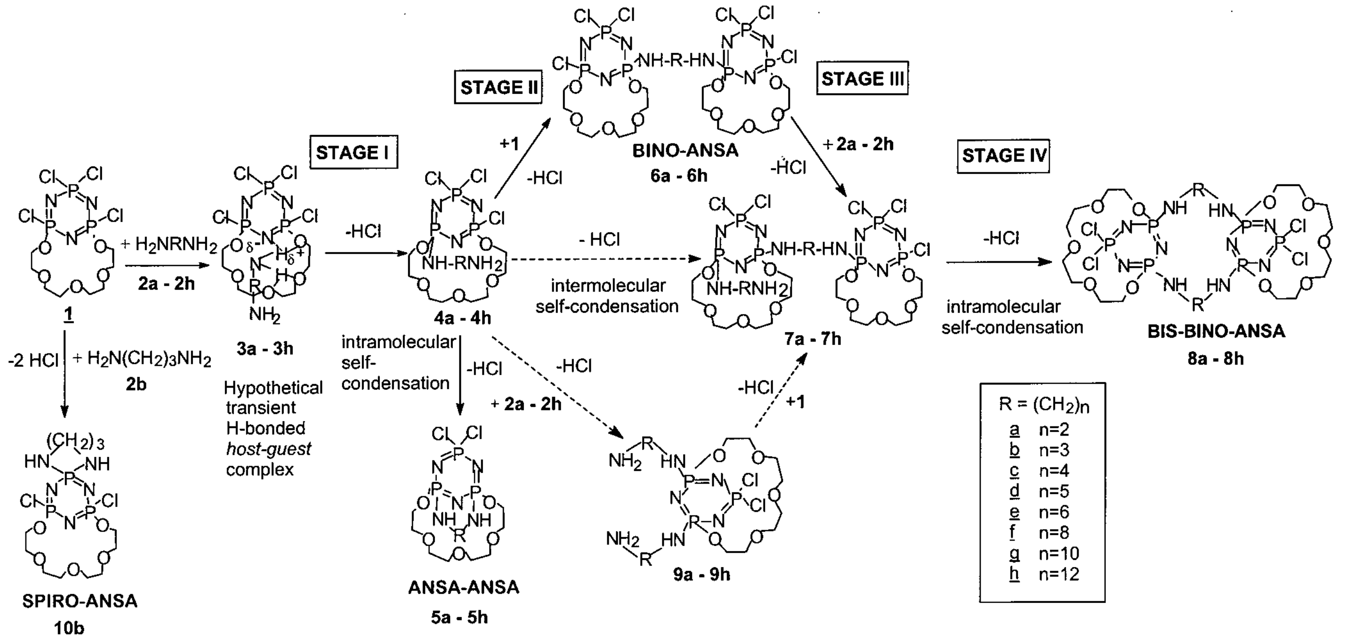
Scheme 1



For the reactions of higher members of the linear aliphatic diamine series with crown-free chlorocyclophosphazenes, only intermolecularly coupled derivatives, the singly, doubly, or triply bridged polyazaheterophanes (sic), have been reported.[13] As an extension of our work on short chain diamines ($n = 2, 3$; **2a**, **b**),[7] we demonstrate that when using **1** as a substrate, the general outcome of the diaminolysis reaction is the same for both lower and higher members of polymethylenediamine series and the same three types of the *gem*-to-macrocycle substituted diamine (**a**−**h**) derivatives **5**, **6**, and **8** are readily formed regardless the length of the methylene chain ($n = 2$−12, **2a**−**h**). Consequently the method represents a general strategy providing access to a large range of diamino-derivatized PNP-crowns, which may be regarded as lateral macrobicycles[15] (ansa, **5**), bola-amphiphilic[14] bis-crowns (bino, **6**), and cylindrical macrotricycles[15] (bis-bino, **8**). Extension of this work toward cyclic, heterocyclic, and aromatic diamines is currently under way.

Results and Discussion

Synthesis. Recently we reported the ready formation of *trans*-annular 1,2-diaminoethane- (**5a**) and 1,3-diaminopropane- (**5b**) derivatives of the [oxy(tetraethylenoxy)]-tetrachlorocyclo-triphosphazatriene, PNP-crown **1**, in which the diaminoalkylene groups span the macrocycle-bearing P atoms.[7] Both intramolecularly (**5a**,**b**) and intermolecularly, singly (**6a**,**b**) and doubly diamino-bridged (**8a**,**b**), PNP crowns were formed (Scheme 1).

The driving force for encapsulation of the diamines **2a**,**b** within the macrocyclic cavity of **1** was assumed to be “host−guest” interactions due to molecular size-fit and assembly via hydrogen bonding.[7] Hydrogen bonding-driven self-assembly is of key importance in supramolecular chemistry,[15] and plays a significant role in biological systems.[8a,16]

In the present study we report that the three homologous series of derivatives **5**, **6**, **8** are readily formed for all the polymethylenediamines (**a**−**h**) for n ranging from 2 to 12 at the molar ratio of **1** to **2** equal to 1:2 (Table 1S), which indicates that the proposed reaction is general and is likely to have a similar type of supramolecular control. A spirocyclic isomer (**10b**) is observed only for the reaction of PNP-crown 1 with 1,3-diamino-propane, **2b**, probably as a result of the particular thermodynamic stability of the six-membered P-spiro ring.[17] The formation of **10b** (15%) apparently occurred at the expense of bis-bino **8b**, whose yield (20%) was the smallest for all the reactions studied; on the other hand the reaction of **1** with **2b** also yielded the highest proportion of the respective ansa derivative **5b** (50%). The yield of the bis-bino derivative was at its maximum for $n = 2$ (65%) and minimum for $n = 3$, varying slightly in the range 40−48% for all remaining n values.

Detailed studies on the influence of the chain length of the diamine **2** (**a**−**h**; $n = 2$−12) on the distribution of reaction products indicated that for smaller values of n in the series, the composition of the reaction mixture depends on n with some preference toward intramolecular cyclization (ansa and spiro for **2b** and ansa for **2c** and **2d**), whereas, for larger n values, the composition of the reaction mixture depends only slightly on increasing n-value, exhibiting a decreasing proportion of the ansa derivative **5** and an increasing proportion of the bino

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Table 1. MS and ^{31}P NMR Data of Ansa Diamino-Substituted 1,3-Oxy(tetraethylenoxy) PNP-crown Derivatives (5a−h), $N_3P_3Cl_2[O(CH_2CH_2O)_4][NH(CH_2)_nNH]$, and the Respective Bis-Bino Cyclam-Like Compounds $\{N_3P_3Cl_2[O(CH_2CH_2O)_4][NH(CH_2)_nNH]\}_2$ (8a−h); n = 2-12

compound			^{31}P NMR,[d] A_2X spin system[e]		
type[a]	n[b]	M m/z[c]	$\delta_A(OCH_2-)NH$ [ppm]	$\delta_X(PCl_2)$ [ppm]	$\lvert ^2J_{P-P}\rvert$ [Hz]
5a	2	455/455	23.0 d[f]	30.5 t[g]	60.7
5b[h]	3	469/469	21.7 d[f]	30.6 t[g]	54.4
5c	4	484/483	19.1 d[f]	27.0 t[g]	56.3
5d	5	498/497	18.8 d[f]	26.5 t[g]	56.6
5e	6	512/511	16.6 d[f]	27.5 t[g]	55.2
5f	8	540/539	16.4 d[f]	26.3 t[g]	55.3
5g	10	568/567	16.7 d[f]	25.5 t[g]	55.1
5h	12	596/595	16.2 d[f]	24.6 t[g]	55.0
8a	2	912/910	16.4 d[f]	26.6 t[g]	56.6
8b	3	940/938	17.0 d[f]	25.1 t[g]	54.8
8c	4	968/966	16.8 d[f]	26.2 t[g]	54.6
8d	5	996/994	16.9 d[f]	25.8 t[g]	56.1
8e	6	1024/1022	16.8 d[f]	26.0 t[g]	55.7
8f	8	1080/1078	16.3 d[f]	25.1 t[g]	54.7
8g	10	1136/1134	16.7 d[f]	25.5 t[g]	55.7
8h	12	1192/1190	16.8 d[f]	26.0 t[g]	55.6

[a] For the respective formula see Scheme 1. [b] n = number of methylene groups in the polymethylene chain of the diamine unit. [c] Found/calcd relative molecular mass M with respect to ^{35}Cl; determined by LSI-MS. [d] ^{31}P NMR spectra obtained at 121 MHz in $CDCl_3$ solution at ambient temperature, referenced to external H_3PO_4. [e] A_2X spin system, d = doublet, corresponds to P_A (two equally substituted P atoms), t = triplet, corresponds to P_X; J_{P-P} and δ_P values calculated according to ref 20. [f] Doublet, broadened on proton coupling. [g] Triplet, unaffected by proton coupling. [h] The spiro compound **10b** shows a different ^{31}P NMR A_2X spin pattern (compared to its isomer **5b**): For **10b**: $P_A = P(OCH_2-)Cl$, δP_A = 23.4 ppm (doublet, slightly broadened by small proton coupling); $P_X = P(NHCH_2-)_2$, δP_X = 13.5 ppm (triplet, each peak split into a quintet on proton coupling, J_{P-H} = 15.4 Hz); $\lvert J_{P-P}\rvert$ = 56.2 Hz.

derivative **6** (Table S1). After substitution by the first electron-donating amino substituent to one of the macrocyclic P-pivot atoms (to form the intermediate, **4**), the nucleophilic susceptibility of the second P−Cl group adjacent to the PNP-macrocycle is expected to decrease,[18] and so one might not expect significant formation of the ansa compounds **5a**−**h** compared to formation of other compounds such as **6a**−**h**, which result from reactions of only one of the two >P(OR)Cl groups in the molecule. It can be seen from Table S1, however, that there is appreciable formation of the ansa compound **5** for all diamines in the series (n = 2−12), with a maximum tendency (40−50%) for n = 3−5, which may be ascribed to the energy gain accompanying ring closure with such diamines.

Structure Elucidation. Structural assignments of the products have been mainly based on the respective mass spectrometric (MS) and ^{31}P NMR spectra (Tables 1, 2); auxiliary ^{1}H NMR and elemental analysis data (Tables S2, S3) are consistent with the proposed structures. For the 1,2-diaminoethane ansa-derivative **5a** unambiguous X-ray crystallographic evidence has been published,[7] which was fully consistent with the MS and ^{31}P NMR based assignments. In this paper we present the crystal structure of the bis-bino derivative **8b** (Figure 1); the molecule has a face-to-face arrangement of the bridged cyclophosphazene rings and is *meso* due to a plane of symmetry.

On the basis of a comprehensive study of ^{31}P NMR shifts versus X-ray crystallographic data, it has been found that ^{31}P NMR spectroscopy is a reliable tool for determining molecular structures in cyclophosphazenes;[19] therefore, the molecular structures of the series of compounds **5a**−**h**, **6a**−**h**, and **8a**−**h** have been deduced by comparison of the proton-coupled and proton-decoupled ^{31}P NMR spectra, which enable assignment of P nuclei carrying aliphatic substituents. All the ^{31}P NMR data for the respective series (**a**−**h**) of derivatives **5**, **6**, **8** (Tables 1, 2) were consistent with the proposed structures, a remarkable similarity of the spectra within the particular series being observed.

Mechanistic Considerations. The same series of compounds (**5**, **6**, **8**) are formed for reaction of **1** with each of the diamines **2a**−**h** (Table S1), indicating a similar reaction mechanism for all the polymethylenediamines. The regioselectivity of *gem*-substitution in the reactions of PNP-crown **1** with short chain diamines (n = 2, 3) was ascribed by us to formation of a “host−guest” complex through hydrogen bonding between the NH_2 groups of the encapsulated guest diamine **2** (**a** or **b**) and the lone pairs of electrons of the oxygen and/or nitrogen atoms of the host PNP-macrocycle **1**.[7] A great variety of macrocyclic polyethers and azaethers have been previously shown to bind ammonium ions and neutral aminocompounds by anchoring the ammonium (amino) group into their circular cavity via N−H···O hydrogen bonds.[15]

Although the complex **3** remained hypothetical as it could not be detected due to the fast reaction of the heterogenic functions N−H (**2**) and P−Cl (**1**), we have now obtained LSIMS evidence for the formation of analogous complexes between **1** and hydrochloride-blocked amines: *n*-propylamine·HCl (m/z 527), phenylethylamine·HCl (m/z 589), and glycine ethyl ester·HCl (m/z 571).[22] It has also been observed that the corresponding aliphatic monoamines (*n*-propylamine, phenylethylamine, and glycine ethyl ester) react readily with **1** to form analogues of the intermediates **4a**−**h** (to be published[22]). These two sets of results confirm that a host−guest complex (such as **3a**−**h**) can be formed by hydrogen-bonding one of the NH_2 groups of the diamines **2a**−**h** in the macrocyclic cavity of **1**, which then assists the substitution reaction at the macrocycle-bearing P-atom to form the intermediate compounds **4a**−**h**, regardless of the length of the linear diamine (Scheme 1).

Diaminolysis reactions of unsubstituted hexachlorocyclotriphosphazatriene have been found to occur by a two-step mechanism, as revealed by ^{31}P NMR kinetic studies at low-temperature (180 K).[23] The intermediates were dangling moieties, in which only one amino function was grafted onto the N_3P_3 ring. The second step of diami-

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(22) The results of studies on the regioselective substitution of **1** with aliphatic monoamino-compounds and sodium cation-paired arylate anions will be published elsewhere together with the structural parameters of the respective mono- and di-gem-to-macrocycle substituted amino- and aryloxy-derivatives.

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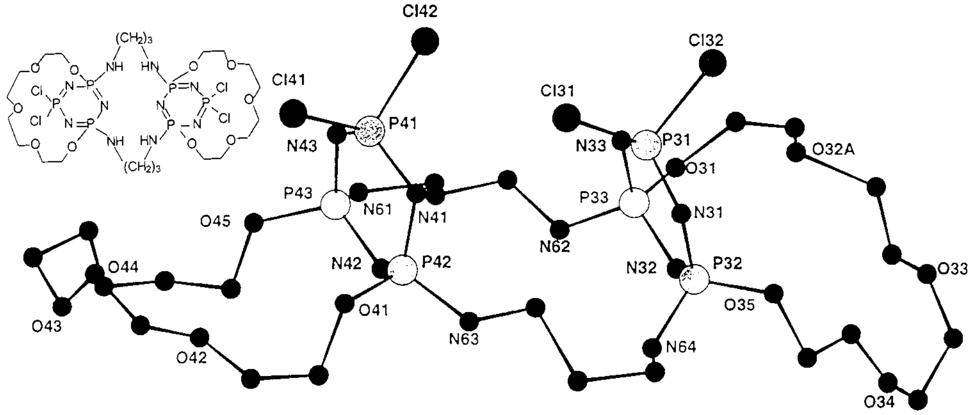

Figure 1. X-ray crystallographic structure of the bis-bino cyclophosphazene-macrocyclic compound **8b**.

nolysis was so fast that the dangling entities could not be prepared under typical reaction conditions at room temperature, but were successfully achieved using a solid support approach.[24] In the present work the reaction of **1** with diamine **2a** was followed by ^{31}P NMR spectroscopy in toluene-d_8 at a temperature of 253 K to observe intermediates of the reaction shown in Scheme 1. Under initial conditions of an excess of **1**, it was found that the main reaction was formation of **6a** via the "intermediate **4a**" which occurred up to a mole ratio of 1:1 and then, on successive addition of diamine to a mole ratio of 1:2 for **1:2a**, formation of the bis-bino compound **8a** via the "intermediate 7a"; it should be noted that, under these reaction conditions, the ansa compound **5a** was not observed. (^{31}P NMR spectra of the reaction of **1** with **2a** showing successive formation of **4a**, **6a**, **7a**, and **8a** has been provided in Supporting Information).

It should be noted in Scheme 1 that there are three possible routes to formation of compound **8** from the intermediate **4** that all go via compound **7** as the key intermediate; one route is by direct intermolecular condensation of **4**, and the other two by further stepwise reaction of **4** with both **1** and **2**, the route depending on the order of addition of reactants. The ^{31}P NMR studies of the reaction at 253 K (Figures S1, S2) provided direct evidence for the route from **4** to **8** via **6** and **7**, i.e., addition to **4** of **1** then **2**, as indicated by arrows with unbroken lines for stages II and III of the reaction in Scheme 1. The other two routes to **8** are denoted by arrows with broken lines because no direct evidence has been provided in this work.

Effect of Molar Ratios and Concentration of Reactants. The relative ratios of the products (estimated from ^{31}P NMR spectra of the crude reaction mixtures) have been found to depend primarily on the molecular ratio of the reactants and to some extent on concentration (Tables S1, S4). In general at a 1:1 molar ratio of **1** to diamine **2** (*half the amount of the diamine serving as HCl scavenger*) formation of singly bridged bino-derivatives **6a**−**h** predominates whereas, when the diamine was used in excess, the distribution between ansa-cyclosubstituted derivatives **5a**−**h** and doubly bridged bis-bino derivatives **8a**−**h** (the two main products formed) could be varied by changing the amount of solvent used.

On increasing the ratio of **1** to **2a** from 1:1 to 1:2 and 1:4, formation of the doubly bridged bis-bino derivative **8a** was favored at the expense of the singly bridged bino derivative **6a**, as expected. Intramolecular cyclocondensation of **4a**,**b** to **5a**,**b** is favored in more dilute solutions and, concomitantly, formation of **8a**,**b** is more pronounced at higher concentrations (Table S4).

Preliminary Screening of Complexation Properties by a TLC Method. The metal-cation complexation properties of the ligands **5**, **6**, **8** have been investigated using a simple TLC method which is based on the different rates of migration of the free ligand and its complex, and the assumption that differences in R_f values are related to the stability constants of complexation.[25] In several cases formation of complexes has been confirmed by mass spectrometric investigations (LSIMS) in which the molecular ions of the respective metal−ligand complexes were observed. The TLC results (Table 3) show that in all cases the complexing properties of the ligands **5**, **6**, **8** containing polymethylenediamino units, capable of cooperating with the PNP-macrocycle in binding cations in *lariat* (*l*asso-*r*ope-*a*nd-*t*ie) mode,[26] are much better than those of the parent crown **1**.

Most of the ligands **5**, **6**, **8** display a marked preference toward binding potassium (and sometimes sodium and rubidium) and silver ion; a significant affinity of some of them toward divalent cations, such as Mg^{2+} (**5a**, **5b**, **6g**, **8a**, Ca^{2+} **8c**, **8e**), and Ni^{2+} (**5a**, **5e**) is also observed. The cylindrical macrotricycles **8** exhibit the broadest spectrum of complexation properties with metal cations (especially **8c** and **8e**) and have the potential to complex molecules.[15] More detailed studies on the complexing abilities of the new ligands **5**, **6**, **8** are currently under way and will be reported in due course.

Summary

Supramolecular assistance[8a−c,17] to regioselectivity has been found to be significant in the synthesis of intra- and intermolecularly diamino-bridged PNP-crown derivatives. The stereoelectronic information contained in the regiodirecting macrocyclic unit, (Cl)PNP(Cl)[O(CH$_2$CH$_2$O)$_3$-CH$_2$CH$_2$O], enables the chlorocyclophosphazene-containing PNP-crown, **1**, to be regarded as a useful synthon for the regioselective preparation of unusual *gem*-to-macrocycle diamino-linked cyclophosphazene derivatives **5**−**8**,

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[26] For definition of *lariat* ethers, see Gokel, G. W. *Crown Ethers & Cryptands*; The Royal Society of Chemistry: Cambridge, 1991; pp 141−142.

Table 2. ^{31}P NMR and MS Data of Bino Derivatives 6a−h (polymethylenediamino-bridged cyclophosphazenic bola-amphiphiles): $N_3P_3Cl_3[O(CH_2CH_2O)_4]$-$NH(CH_2)_nNH$-$N_3P_3Cl_3$-$[O(CH_2CH_2O)_4]$

cmpd			^{31}P NMR {−^{1}H}, AMX spin system[a]						^{31}P NMR {+^{1}H}		
n	no.	*M* found/calcd (*m*/*z*)	δP_A, ppm[b] >P(OR)NH	J_{A-M}[d] [Hz]	δP_M, ppm[b] >P(OR)Cl	J_{M-X}[d] [Hz]	δP_X, ppm[b] >PCl_2	J_{A-X}[d] [Hz]	J_{PA}−H [Hz][e]	J_{PM}−H [Hz][f]	J_{PX}−H [Hz][g]
2	**6a**	923/922	15.8[c]	56.2	21.1[c]	71.6	25.7	62.5	10.9	15.8	−
3	**6b**	937/936	15.8[c]	55.0	21.2[c]	71.6	25.7	63.2	13.3	16.0	−
4	**6c**	953/950	16.1[c]	54.8	21.4[c]	70.8	26.0	56.6	12.5	15.7	−
5	**6d**	967/964	15.9[c]	54.6	21.3[c]	73.2	25.8	54.8	12.9	15.6	−
6	**6e**	979/978	15.8[c]	54.7	21.2[c]	71.1	25.7	63.6	11.5	15.5	−
8	**6f**	1009/1006	15.9	54.7	21.3	71.3	25.8	63.5	13.3	15.2	−
10	**6g**	1035/1034	15.9	54.7	24.3	71.2	25.8	63.5	12.1	15.3	−
12	**6h**	1063/1062	15.9	54.7	21.3	71.0	25.8	63.5	12.1	15.5	−

[a] AMX spin system denoted according to ref 21. [b] Doublet of doublets. [c] Doubling-up of signals observed, with small chemical shift separation ca. 0.02−0.05 ppm, decreasing with *n* value (similar splitting has been observed in analogous compounds in ref 30, and the problem of the conformational explanation will be published elsewhere. [d] J_{P-P} values calculated according to ref 21 for AMX coupling system. [e] Observed as a broad multiplet. [f] Each peak of the doublet of doublets is split into three signals. [g] No proton coupling.

Table 3. Comparison of Metal Cation Complexation Properties of Ansa (5), Bino (6), and Bis-Bino (8) Polymethylenediamino PNP-crown Derivatives with Respect to Those of the Parent Tetrachloro Precursor 1[a]

compound[b]		$\lvert B\rvert$[e] $= (R_{f\,2} - R_{f1})/\,R_{f\,2}$ [%]; (hexane−THF = 2:3), silica gel[f]											
no.	*n*[c]	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Cu^{2+}	Ca^{2+}	Mg^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}
1[d]	−	0	9	16	19	6	4	0	0	0	0	0	0
5a	2	50	64	67	53	35	61	13	28	47	26	36	0
5b	3	33	37	52	36	28	13	0	14	27	15	0	0
5c	4	17	20	31	22	28	63	0	0	12	0	0	0
5e	6	6	23	63	43	30	67	10	0	29	9	37	0
5f	8	0	22	66	46	24	62	0	6	9	6	6	0
5g	10	0	29	67	52	28	65	0	0	9	12	9	0
8a	2	50	45	82	92	78	50	0	0	31	13	0	0
8c	4	29	60	58	48	33	83	31	33	18	14	14	14
8e	6	27	70	92	88	57	92	11	50	37	24	21	8
8f	8	27	22	66	46	24	32	0	6	9	6	6	0
8h	12	18	63	89	57	88	84	0	19	24	0	13	15
6c	4	29	60	91	60	71	99	0	6	9	6	6	0
6f	8	18	61	94	83	76	77	0	16	22	13	17	0
6g	10	70	50	64	46	35	50	0	18	41	17	15	18

[a] According to a TLC test; ref 25. [b] For structural formula see Scheme 1. [c] *n* = number of CH_2 groups in the polymethylene chain. [d] Parent tetrachloro-PNP-crown **1**. [e] The difference of R_f value of a ligand on a silica gel plate and on the gel pre-impregnated with a salt containing the given metal cation. [f] Merck alumina plates.

inaccessible by other synthetic routes. These compounds can be considered as new polytopic macrocyclic ligands of lateral macrobicycle (**5a**−**h**), bola-amphiphilic bis-crown (**6a**−**h**), and cylindrical macrotricycle (**8a**−**h**) types.

Experimental Section

Materials. Hexachlorocyclotriphosphazatriene was obtained from the Nippon Fine Chemical Co. Ltd. (Japan) and purified by fractional crystallization from hexane. Sodium hydride (60% dispersion in mineral oil, Aldrich Chemie), *n*-hexane (Merck), and 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,8-diaminooctane, 1,10-diaminodecane, and 1,12-diaminododecane (Fluka AG) were used as received. Tetraethylene glycol (Aldrich Chemie, 99%) was dried over 4 Å molecular sieves. Tetrahydrofuran (POCh, Gliwice) was distilled over $CuCl_2$, next over calcium hydride, and then twice over a sodium−potassium alloy under an atmosphere of dry argon. For column chromatography silica gel 60 (230−400 mesh, Merck) was used.

Methods. The low temperature ^{31}P NMR spectra of the reactions in toluene-d_8 were recorded at 253 K. Mass spectra were recorded using chemical ionization (positive and negative) with an isobutane matrix; liquid secondary ion mass spectrometry (LSIMS) was used to investigate metal-cation complexation using glycerol and *m*-nitrobenzyl alcohol (NBA) matrixes. The observed and calculated mass values are based on the ^{35}Cl isomer for the appropriate isotope pattern for compounds containing two (**5**, **10b**), four (**8**), or six (**6**) chlorine atoms. Flash column chromatography was done with silica gel (100−200 mesh, Merck) and eluted with hexane−THF. TLC experiments were performed on Merck precoated silica gel 60 plates. TLC complexation experiments were carried out as previously described;[25] the values of parameter B% for complexes of the ligands **5**, **6**, **8** with various metal cations are given in Table 3. It should be noted that B [= $(R_{f\,2} - R_{f1})/R_{f\,2}$ for the ligand on a silica gel plate, R_{f1}, and on the plate pre-impregnated with a salt containing the metal cation, $R_{f\,2}$] is expected to be proportional to the stability constants of metal cation complexation with the ligand.[25]

Crystal Data. Data were collected using a crystal size 0.16 × 0.22 × 0.15 mm on a Delft instruments FAST TV area detector diffractometer at the window of a rotating anode generator (50 kV, 50 mA) using a molybdenum target [$\lambda_{(Mo-K\alpha)}$ = 0.71069 Å), controlled by the MADNES software.[27] The crystal was of poor quality and showed anisotropic mosaicity.

Crystal data: $C_{22}H_{48}N_{10}O_{10}P_6Cl_4$ (solv), $M = 936.29$ (+solv), monoclinc, space group $P2_1/n$, $a = 8.979(10)$, $b = 42.284(6)$, $c = 23.854(2)$ Å, $\beta = 98.486(9)°$, $U = 8957.4$ Å^3, $T = 150(2)$K, $Z = 8$, μ(Mo−Kα) = 0.534 mm^{-1}, $F(000) = 3872$. In all, 32340 reflections were collected, θ range 1.79 to 25.05° (index ranges: $h = -9$ to 10, $k = -45$ to 50, and $l = -27$ to 23), which merged to give 13049 unique reflections ($R_{int} = 0.14$).

The structure was solved by direct methods (SHELX-S)[28] and refined by full matrix least-squares on F_o^2 (SHELX-93).[29]

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As a result of disorder in parts of the polyether fragments, and in the solvent pockets, it was not possible to complete the refinement to the usually desired levels, but the identity of the compound and the common structure of the two independent molecules present are confirmed beyond doubt. Final R indices were $wR_2 = 0.1508$ and $R_1 = 0.0702$ [$I > 2\sigma I$] and 0.1814 and 0.2249, respectively, for all data. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$. Residual electron densities were 0.754 and −0.583 eÅ^{-3}

Synthesis. All reactions were performed under an atmosphere of dry argon.

Preparation of 1,3-[oxy(tetraethylenoxy)]-1,3,5,5-tetrachlorocyclotriphosphazatriene (1) was carried out as previously reported,[1] compound **1** (reactive PNP-crown precursor) being separated from the crude reaction mixture by column chromatography on silica gel, eluted with hexane−THF (2:1).

Reaction of 1 with Diamines 2a−h at a Mole Ratio of 1:2 i.e., toward Preferred Formation of the Ansa Derivatives (5a−h), $N_3P_3Cl_2[O(CH_2CH_2O)_4]$-$[NH(CH_2)_nNH]$, and Bis-Bino Derivatives (8a−h), $\{N_3P_3Cl_2[O(CH_2CH_2O)_4]$-$[NH(CH_2)_nNH]\}_2$. The respective diamine **2a**−**h** (2 mmol) and **1** (0.469 g, 1 mmol) were placed in 50 mL of dry benzene in a 100 mL three-necked round-bottomed flask and the solution stirred at room temperature for ca. 2.5 h and filtered to remove the amine hydrochloride, and the solvent was removed at reduced pressure. The resulting colorless oil was extracted with benzene (50 mL), concentrated to 5 mL, and subjected to chromatography, using hexane−THF (1:1) as eluant. The yields of the respective ansa (**5**), bino (**6**), and bis-bino (**8**) derivatives (estimated from ^{31}P NMR spectra) are given in Table S1.

Referring to the amount of crude reaction mixture subjected to silica gel column chromatography, the relative yields of the pure fractions corresponding to the particular series of derivatives **5**, **6**, **8** (Table S1) varied from 6% (**5a**) to 35% (**5c**) and were in most cases over one-half of those estimated from ^{31}P NMR, which may result from the strong adsorption on silica of the respective derivatives or even some decomposition on the silica gel column during elution.

The analytical data (MS, ^{31}P NMR) for all derivatives **5**, **6**, **8** (**10b**) are shown in Tables 1, 2; auxiliary data (EA, ^{1}H NMR, R_f) are given in Supporting Information (Tables S2, S3).

Reactions of 1 with Diamines 2a−h at Molar Ratios of 1:1, i.e., toward the Preferred Formation of Bino-Derivatives of General Formula: $N_3P_3Cl_3[O(CH_2CH_2O)_4]$-$NH(CH_2)_nNH$-$N_3P_3Cl_3[O(CH_2CH_2O)_4]$, 6a−h. The respective diamine **2a**−**h** (2 mmol as a solution in 75 mL of benzene) was added dropwise from an addition funnel to a solution of **1** (0.934 g, 2 mmol in 75 mL of benzene) in a 250 mL three-necked round-bottomed flask. The solution was stirred at room temperature for 3 h and filtered to remove the amine hydrochloride, and the solvent was removed at reduced pressure. The resulting colorless oil was extracted with benzene (50 mL), concentrated to 5 mL, and subjected to chromatography using hexane−THF (1:1) as eluant. After column separation, the yield of the respective bino(1,n)-ansa-cyclophosphazenes varied from 45% ($n = 12$) to 75% ($n = 6$) of the theoretical value. The analytical data (MS, ^{31}P NMR; Table 2: ^{1}H NMR, elemental analysis; Table S2) were in good agreement with expected values. The products were stable in air for about 2 weeks and then lost their solubility, probably due to reaction of the heterogenic functions (NH and PCl) resulting in degradation and/or formation of polymeric material.

Reactions of 1 with 1,2-Diaminoethane (2a) and 1,3-Diaminopropane (2b) under Various Reaction Conditions. In a 100 mL three-necked round-bottomed flask was placed **1** (0.469 g, 1 mmol) and the respective diamine **2a** or **2b** (1 or 2 mmol); the various molar ratios of the reagents and concentrations of solutions are given in Table S4. The reaction mixture was stirred at room temperature for 3 h, and the reaction was followed on TLC silica gel plates using hexane−THF (1:2). When the reaction was complete, the amine hydrochloride precipitate was filtered off and the solution concentrated at reduced pressure to ca. 5 mL and subjected to chromatography, using hexane−THF (1:1) as eluant. The relative proportion of products formed was found to depend on the molecular ratio of reactants, their concentration, and the molecular size of the dinucleophile (Table S4). The products were characterized as above.

The reaction was also carried out in other solvents. In general it was found that the same set of products was formed for reactions in aromatic solvents such as benzene and toluene, as well as in THF and in solvent mixtures such as hexane/THF (1:1). In a chlorinated solvent (dichloromethane) polymerization reactions gave resinous residues that were initially soluble in organic solvents, but precipitate after about 1 day.

Preparation and Crystallization of 8b Suitable for X-ray Crystallographic Studies. To promote formation of the bis-bino derivative, **8b**, a solution of 1,3-diaminopropane, **2b**, (0.63 g, 8.56 mmol) in 10 mL of benzene was added dropwise to a solution of **1** (2 g, 4.28 mmol) in 90 mL of benzene in a 250 mL round-bottomed flask fitted with a magnetic stirrer; initially, reactant **1** is in great excess which promotes formation of **6b** as an intermediate in the formation of **8b**. To minimize formation of other products such as the ansa-ansa compound **5b** and the spiro compound **10b**, the reaction was carried out at relatively high concentrations and in an ice-bath. The reaction was followed by TLC to completion over 3 h. The crude reaction products were filtered off, and further precipitation of unwanted products occurred on addition of hexane to the benzene solution. The benzene−hexane solution was evaporated to dryness under reduced pressure and dried over anhydrous sodium sulfate. A concentrated solution of the products in 5 mL of benzene was separated into four components by column chromatography on silica gel, the first two products (ansa-ansa **5b**, spiro-ansa **10b**) were separated by elution with hexane−acetone (1:1 by volume) and then 1:2 by volume to separate the two remaining products (bino **6b** and bis-bino **8b**). Most reaction products were recrystallized from benzene with a few drops of light petroleum (bp 40−60 °C); the ansa-ansa compound (**5b**) is stable [and the X-ray structure of the analogous compound **5a** has been published previously[7]] whereas crystals of spiro-ansa (**10b**) and bino (**6b**) were found to be unstable and unsuitable for X-ray crystallographic analysis. On the other hand, the bis-bino compound (**8b**) is stable and was crystallized from hexane−acetone (1:1) to provide crystals suitable for X-ray crystallographic analysis after five recrystallizations.

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Supporting Information Available: Analytical and ^{1}H NMR data for the series of compounds, **5**, **6**, **8a**−**h**, **10b** (Tables S2, S3); influence of reaction conditions (chain length of diamine **2**, molar ratio of the reactants (**1** to **2**) and concentration on the distribution of the products **5**−**8**, **10** (Tables S1, S4); observed and calculated structure factors, crystal data and structure refinement, anisotropic displacement parameters, bond lengths and angles, selected torsion angles, and least-squares planes for the compound **8b** (Tables S5 (four); ^{31}P NMR spectra (Figures S1, S2) of the reaction of **1** with **2a** indicating the subsequent reaction stages to **6a** and **8a** and the formation of dangling intermediates **4a** and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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