# Syntheses of Chiral Cyclotriphosphazenes and Their Use in Cyclolinear Polymers

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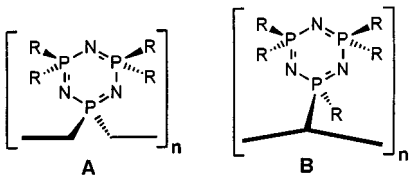
The reaction of hexachlorocyclotriphosphazene with two equivalents of the chelating diols 2,2′-dioxybiphenyl and 2′,2′′-dioxy-1′,1′′-bi-2-naphthyl was investigated. Although a mixture of different stereoisomers may be expected, only the formation of the *meso*-compounds [(*R,S*)-$(O,O)_2Cl_2P_3N_3$] is found (O,O stands for the diolate). Interestingly, when the remaining $PCl_2$ group undergoes reaction with hard nucleophiles like 4-methoxy phenolate, a change of configuration at one phosphorus center is observed and racemic mixtures of chiral [(*R,R*)-$(O,O)_2(RO)_2P_3N_3$] and [(*S,S*)-$(O,O)_2(RO)_2P_3N_3$] phosphazenes are observed. Enantiomerically pure cyclotriphosphazenes were obtaines from either the (*R*)- or (*S*)-form of 2′,2′′-dioxy-1′,1′′-bi-2-naphthyl. Soft nucleophiles like amines, however, do not affect the configuration at the phosphorus centers and allow the synthesis of *meso*-[(*R,S*)-$(O,O)_2(R^1RN)_2P_3N_3$] compounds. the bifunctional cyclotriphosphazenes [$(O,O)_2$(4-OH–$C_4H_4O)_2P_3N_3$] and [(*R,S*)-$(O,O)_2(H_2N)_2P_3N_3$] were used in polyaddition reactions with hexymethylene di(isocyanate) to give cyclolinea polymers of different stereochemical compositions corresponding to the stereochemistry of the phosphazene precursor (i.e. either a racemic mixture of homochiral polymer strands, enantiomerically pure polymers, or the *meso*-form of polymers was obtained). The properties of these polymers are discussed and a mechanism for the change of stereochemistry is proposed.

## Introduction

Polyurethanes are generally characterized by poor thermal stability due to the thermally labile urethane group. Their thermal decomposition starts in the region of 150−200°C. Several attempts to increase the thermal stability of polyurethanes by introducing thermally stable groups have been reported.[1−2] Phosphazenes are well-known to impart thermal stability and flame-retardant characteristics to polymer systems[3−6] and cyclomatrix phosphazene polymers containing cyclotriphosphazene rings are known for their excellent fire resistance.[7−12] The modification of different polymers such as polyesters, polyimides, etc. by phosphazenes has been reported previously.[10][11] These polymers may be divided into two groups: in cyclolinear polymers of type **A** the phosphorus centers of the cyclophosphazene moieties are incorporated into the polymer backbone, while in polymers of type **B** the phosphazene rings are attached as pendant groups on the backbone (Scheme 1).

Polymers of types **A** and **B** have commonly been prepared by polycondensation of chloro-substituted cyclotriphosphazenes, $Cl_{6-x}R_xP_3N_3$, with bifunctional substrates. However, these polymerizations are complicated by multiple displacements of chlorine atoms and generally lead to random mixtures of polymers, incorporating both geminally and vicinally substituted phosphazenes.[5,11,13−15] In this respect, the synthesis of spirocyclic cyclotriphosphazenes, $(O,O)Cl_4P_3N_3$ or $(O,O)_2Cl_2P_3N_3$, from sterically congested diols HO,OH (where O,O represents a chelating diol) and $Cl_6P_3N_3$ is interesting, since their preparation permits the selective synthesis of phosphazenes with one or two $PCl_2$ units.[8,16,17] These monomers should prove useful for the preparation of well-defined cyclolinear polymers of type **A**. Indeed, Kumar and Gupta[9] have reported the synthesis of cyclolinear polyphosphazene polyimides starting from a bis(amino)-bis(spiro)-substituted cyclotriphosphazene $(H_2N)_2(O,O)_2P_3N_3$. Recently, we described the synthesis of new cyclolinear phosphazene polyurethanes from diisocyanates and a bis(spiro)cyclotriphosphazene containing a geminal $P(O-C_6H_4-OH)_2$ unit.[8]




Scheme 1. Depiction of cyclolinear (**A**) and pendant (**B**) phosphazene polymers

The diols 2,2′-dioxybiphenyl and 2′,2′′-dioxy-1′,1′′-bis(2-naphthyl) (abbreviated throughout this paper as biphenoxy and binaphthoxy, respectively) have previously been used for the synthesis of spirocyclic phosphazenes.[8−9,16−19] Tris(2,2′-dioxybiphenylyl)cyclotriphos-

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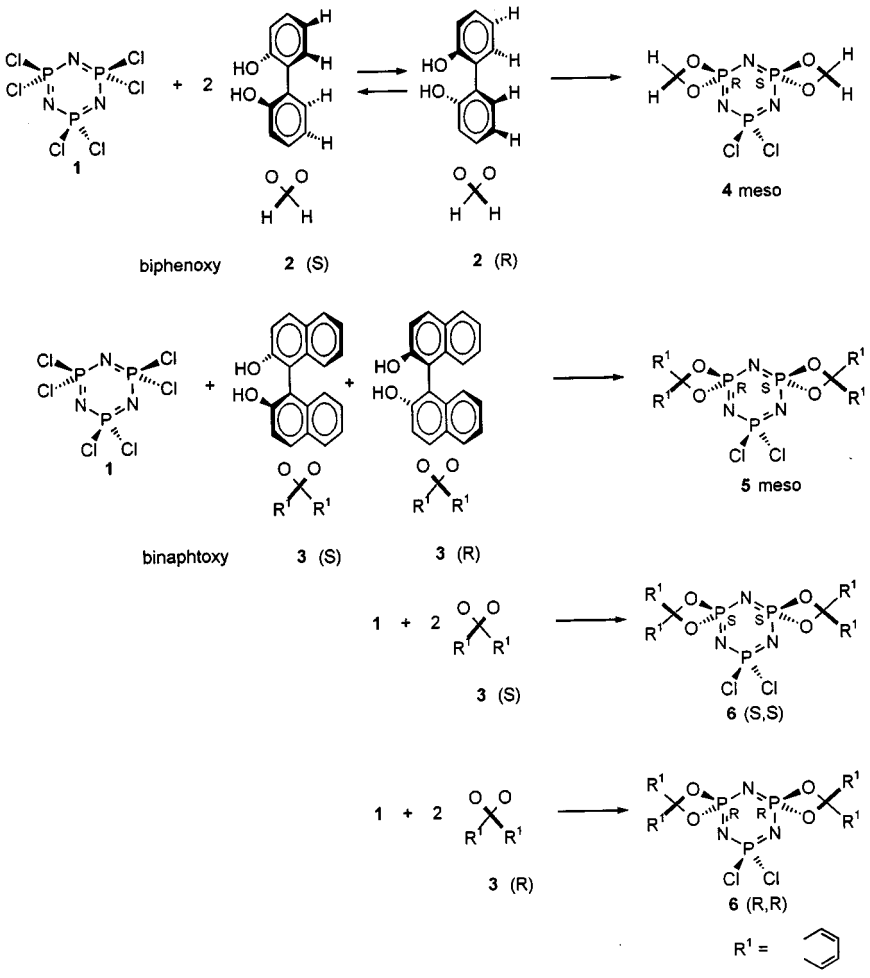
phazene[18] is stable up to at least 350°C and does not undergo polymerization by thermal ring-opening. Hence, increased thermal stability may be expected for polymers incorporating these motifs. Furthermore, binaphthoxy is commercially available in the form of two atropisomers, which do not interconvert at ambient temperature. This offers the possibility of achieving a simple synthesis of enantiomerically pure spirocyclic phosphazenes and hence of chiral polymers. The latter may have interesting properties as supports for catalysts. In this context, it is noteworthy that although the enantiomers of the sterically less hindered biphenoxy rapidly interconvert at ambient temperature, chiral (*R*) or (*S*)-configured phosphorus centers will be formed upon ring-closure by reaction with hexachlorocyclotriphosphazene. In particular, different diastereomers may be formed when racemic mixtures of diols are used and more than one O,O unit is bonded to an oligophosphazene. Thus, cyclotriphosphazenes made up of all (*R*)- or all (*S*)-configured phosphorus centers and/or having different (*R*)- or (*S*)-configured phosphorus centers within one $P_3N_3$ ring may be anticipated. Remarkably, although multiply-substituted cyclophosphazenes bearing biphenoxy or binaphthoxy groups are known, no particular attention has hitherto been focused on their stereochemistry. We have therefore investigated the synthesis of bis(spirocyclic) phosphazenes of the type $(O,O)_2Cl_2P_3N_3$ in more detail and report here on the somewhat unexpected results obtained. Furthermore, we also describe the incorporation of these phosphazenes into polyurethanes, allowing the synthesis of chiral polymers with improved thermal stabilities.

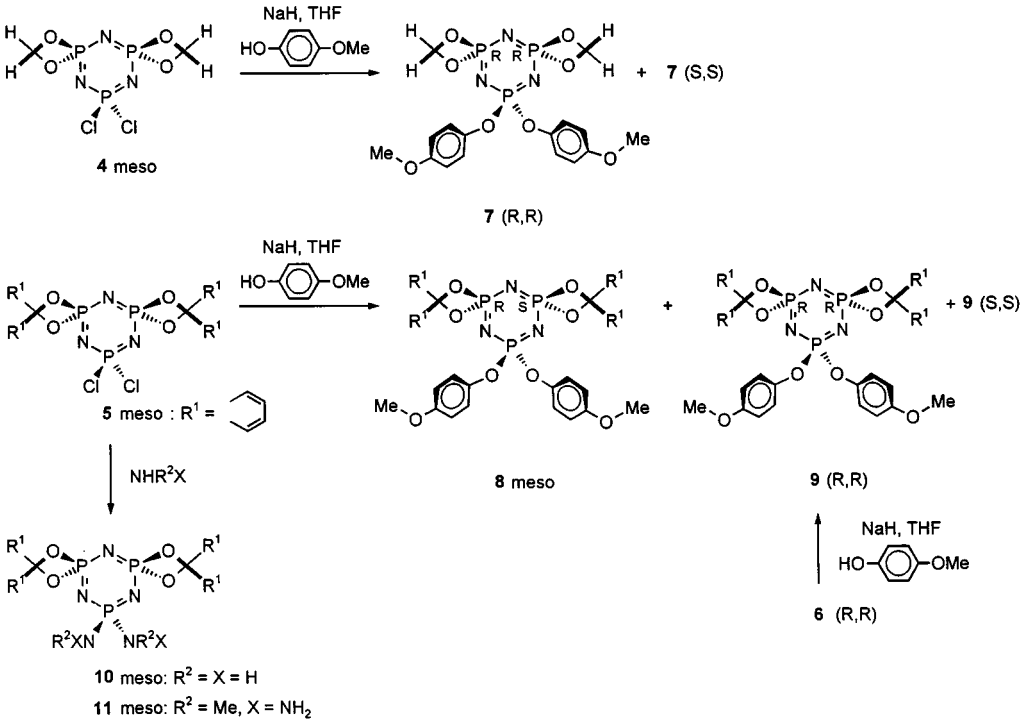
## Results

### Synthesis of Bis(spirocyclic) Phosphazenes

Starting from hexachlorocyclotriphosphazene **1** and two equivalents of biphenolate **2**, the bis(spirocyclic) cyclotriphosphazene **4** was obtained as described previously (Scheme 2).[8] Since **2** exists in the form of rapidly interconverting (*R*)- and (*S*)-isomers, the formation of three stereoisomers might have been expected, namely a pair of (*R*,*R*)- or (*S*,*S*)-configured enantiomers and the diastereotopic *meso* form. These diastereoisomers may be distinguished by $^{31}$P-NMR spectrometry. However, only one diastereoisomer was formed, as evidenced by the observation of a single set of resonances of an $AB_2$ spin system in the $^{31}$P-NMR spectrum of the crude reaction mixture. X-ray analysis (vide infra) showed that this isomer was, in fact, the *meso* diastereomer, [(*R*,*S*)-$(O,O)_2Cl_2P_3N_3$], containing one (*R*)- and one (*S*)-configured phosphorus center.




Scheme 2. Synthesis of bis(spirocyclic) phosphazenes *meso*-**4**, *meso*-**5**, **6**(*S,S*), and **6**(*R,R*)




Scheme 3. Synthesis of bis(spirocyclic) phosphazenes **7**(*R,R*), **7**(*S,S*), *meso*-**8**, **9**(*R,R*), *meso*-**10**, and *meso*-**11**

In a subsequent experiment, **1** was reacted with a racemic mixture of sodium binaphtholate **3**, consisting of one equivalent of **3**(*S*) and one equivalent of **3**(*R*), which do not interconvert at room temperature. Again only one of the possible stereoisomers of **5** was obtained. By subsequent chemical transformation (vide infra), it was unequivocally shown that here too only the *meso* isomer **5** had been formed. When **1** was reacted with two equivalents of either enantiomerically pure **3**(*S*) or **3**(*R*), the respective chiral cyclotriphosphazenes **6**(*S,S*) or **6**(*R,R*) were obtained. The optical rotation angle α of **6**(*R,R*) was determined as $[\alpha]^{25} = -103°$, which is considerably larger than the value found for unbonded binaphthol ($[\alpha]^{25} = -33°$).

The nonchiral bis(biphenoxy)-substituted cyclotriphosphazene *meso*-**4** was treated with two equivalents of sodium 4-methoxyphenolate in THF at room temperature (Scheme 3) and the reaction was followed by $^{31}$P-NMR spectrometry. The resonance of the $PCl_2$ unit in *meso*-**4** (δ = 30.4) disappeared, while a multiplet at δ = 11.2 was observed constituting the A part of a new $AB_2$ spin system. After 3 h, quantitative conversion into **7** had been achieved.

Surprisingly, in the $^1$H- and $^{13}$C-NMR spectra of **7**, only one signal for the $CH_3$ group of the methoxy substituents was observed. If we assume that the (*R,S*)-configuration at the phosphorus centers of the starting material *meso*-**4** is retained in the course of the substitution reaction, then the phenolate substituents are placed *within* the mirror plane and hence cannot be interconverted by this symmetry operation. Therefore, the methyl groups of the 4-methoxy substituents become diastereotopic and should give rise to two resonance signals. On the other hand, if the configuration at one phosphorus center is changed under the reaction conditions from (*R*) to (*S*) − or vice versa − chiral cyclotriphosphazenes **7**(*R,R*) or **7**(*S,S*) with (*R,R*)- and (*S,S*)-configured phosphorus centers will be obtained. In these, the methyl groups are related by a $C_2$ axis of symmetry and one resonance signal is to be expected. Indeed, X-ray analysis revealed that the configuration at one phosphorus center had changed and that the product corresponded to a racemic mixture of **7**(*R,R*) and **7**(*S,S*). Both enantiomers are present in the unit cell (space group $P\bar{1}$). Stimulated by this finding, we next re-investigated the synthesis of tris(biphenoxy)cyclotriphosphazene[18] by reacting *meso*-**4** with one further equivalent of **2**. Indeed, the sparingly soluble product showed only one $^{31}$P-NMR resonance at δ = 22.9 in DMF solution. Evidently, a change of configuration at the phosphorus centers also occurred, leading to a racemic mixture of chiral cyclotriphosphazenes having all (*R,R,R*)- or (*S,S,*S)-configured phosphorus centers.

When the binaphthoxy-substituted compound *meso*-**5** was reacted with 4-methoxyphenolate, a mixture of the stereoisomers *meso*-**8**, **9**(*R,R*), and **9**(*S,S*) was obtained, *meso*-**8** being the major product {ratio *meso*-**8**/[**9**(*R,R*) + **9**(*S,S*)] = 70:30}. As expected, in the $^1$H-NMR spectrum, the *meso* isomer shows two signals for the magnetically inequivalent methoxy substituents (δ = 3.80 and 3.95), while only one signal (δ = 3.87) is seen for the enantiomers **9**(*R,R*) and **9**(*S,S*). The latter was obtained in enantiomerically pure form by reacting **6**(*R,R*) with 4-methoxyphenolate, which led exclusively to **9**(*R,R*). This cyclotriphosphazene was characterized by X-ray structure analysis (vide infra). It is noteworthy that an equimolar mixture of **6**(*R,R*) and **6**(*S,S*) under identical reaction conditions (THF, room temp., 3 h)

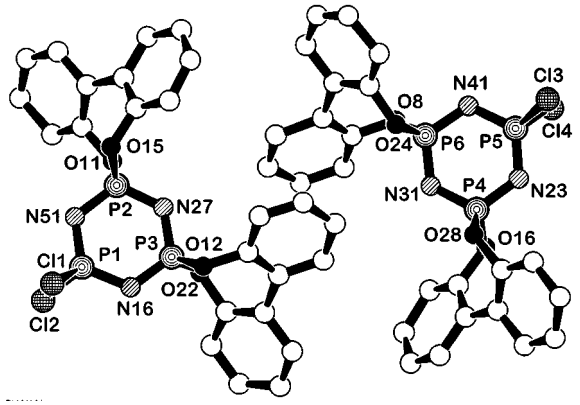



Figure 1. SCHAKAL view of *meso*-**4**

Table 1. Selected bond lengths [Å] and angles [°] in *meso*-**4**

| Bond | Length [Å] | Bond | Angle [°] |
|---|---|---|---|
| P(1)−N(51) | 1.567(7) | N(51)−P(1)−N(16) | 119.8(3) |
| P(1)−N(16) | 1.570(7) | Cl(1)−P(1)−Cl(2) | 99.62(14) |
| P(1)−Cl(1) | 2.001(3) | N(51)−P(1)−Cl(1) | 109.3(3) |
| P(1)−Cl(2) | 2.002(3) | N(16)−P(1)−Cl(1) | 108.8(3) |
| P(2)−N(27) | 1.560(6) | N(51)−P(1)−Cl(2) | 108.4(3) |
| P(2)−N(51) | 1.589(7) | N(16)−P(1)−Cl(2) | 109.0(3) |
| P(2)−O(11) | 1.567(5) | N(27)−P(2)−N(51) | 117.2(3) |
| P(2)−O(15) | 1.591(5) | O(11)−P(2)−O(15) | 103.7(3) |
| P(3)−N(27) | 1.567(6) | N(27)−P(2)−O(11) | 105.5(3) |
| P(3)−N(16) | 1.580(7) | O(11)−P(2)−N(51) | 111.5(3) |
| P(3)−O(12) | 1.564(5) | N(27)−P(2)−O(15) | 112.5(3) |
| P(3)−O(22) | 1.586(5) | N(51)−P(2)−O(15) | 105.6(3) |
| | | N(27)−P(3)−N(16) | 117.4(3) |
| | | O(12)−P(3)−O(22) | 103.6(3) |
| | | O(12)−P(3)−N(27) | 111.9(3) |
| | | O(12)−P(3)−N(16) | 105.5(3) |
| | | N(27)−P(3)−O(22) | 105.7(3) |
| | | N(16)−P(3)−O(22) | 112.0(3) |
| | | P(1)−N(16)−P(3) | 120.8(4) |
| | | P(1)−N(51)−P(2) | 120.9(4) |
| | | P(2)−N(27)−P(3) | 123.8(4) |

led exclusively to a mixture of **9**(*R*,*R*) and **9**(*S*,*S*) and no *meso*-**8** was observed.

Finally, we investigated the reactions of *meso*-**5** with aqueous ammonia[20] and methylhydrazine[21] in THF solution. Under mild reaction conditions, the replacement of both chlorine centers was observed and the products *meso*-**10** and *meso*-**11** were obtained quantitatively. In *meso*-**11**, the more basic methyl-substituted nitrogen center is bonded to the phosphorus center, as was observed previously.[22] Again, the magnetically inequivalent methyl groups in *meso*-**11** give rise to separate signals ($\delta$ = 3.11 and 2.86), proving that the configuration at the phosphorus centers is retained. The presence of the amino groups was also confirmed by the IR spectrum, which featured two bands at $\tilde{\nu}$ = 3340 and 3460 $cm^{-1}$.

## X-ray Structure Analyses

In order to unequivocally determine the stereochemistries of compounds *meso*-**4**, **7**(*R*,*R*), and **9**(*R*,*R*), X-ray crystal structure analyses were performed. Details of the data collections are given in Table 4.

The result obtained for *meso*-**4** is shown in Figure 1 and selected bond lengths and angles are listed in Table 1.

In the crystal, two molecules of *meso*-**4** are aligned in a coplanar fashion (the interplanar angle between the two $P_3N_3$ planes amounts to 8.3°) by intermolecular π-stacking of two arene moieties of the biphenoxy substituents. The $P_3N_3$ rings are almost planar [deviations (Å) from best planes: P1(−0.003)−P2(0.005)−P3(−0.004)−N16(0.007)−N27(0.002)−N51(−0.003) and P4(−0.029)−P5(−0.004)−P6(−0.052)−N23(0.005)−N31(0.054)−N41(0.026)] and slightly elongated along the axes running through P1−N27 and P5−N31, respectively. Nevertheless, all P−N and P−O distances, P−N−P (121.8°) and N−P−N (118.0°) angles lie within the expected ranges.[23] The Cl−P−Cl angle (99.4°) is slightly smaller than the O−P−O angles (103.7°). There are no unusually short repulsive intramolecular interactions. The (*R*)-(P2,P6) and (*S*)-(P3,P4) configurations of the two biphenoxy-substituted phosphorus centers within one molecule can clearly

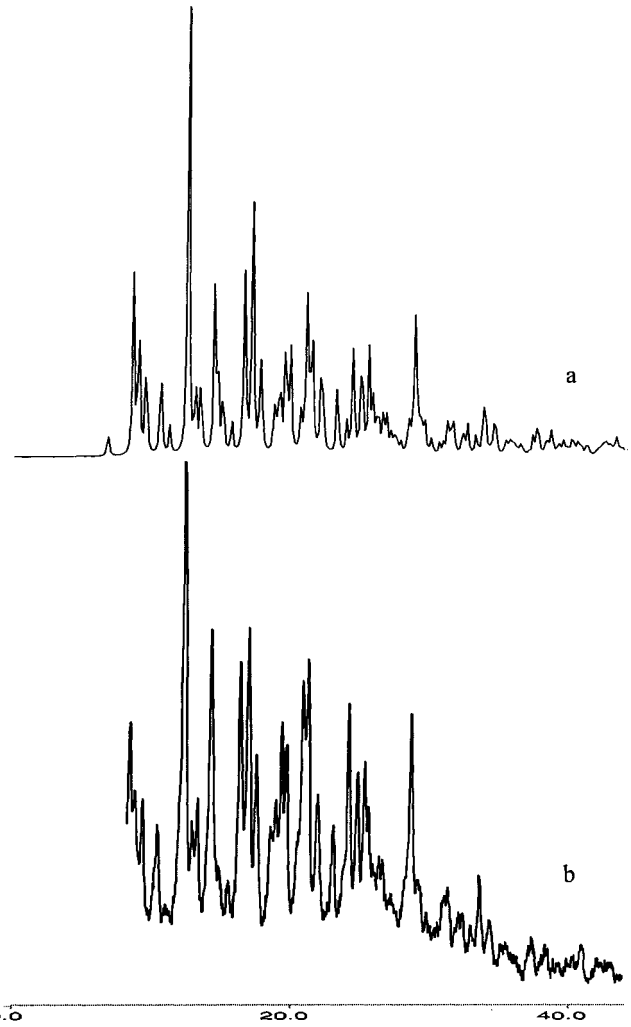



Figure 2. X-ray powder diffraction pattern of *meso*-**4**; a: calculated spectrum; b: experimental spectrum

be seen. In order to verify that the conformer found in the crystal corresponds to that observed in the bulk, we performed a powder diffraction study of microcrystalline material. In Figure 2, the experimental diffraction pattern (bottom) is compared with that calculated using the parameters derived from the single crystal used for the structure determination.

As can be seen, there is an almost perfect fit between the two patterns, which confirms that all synthesized material is of the *meso* form of **4**.

A plot of the molecular structure of the (*R*,*R*)-isomer of **7** is shown in Figure 3. Selected bond lengths and angles are given in Table 2.

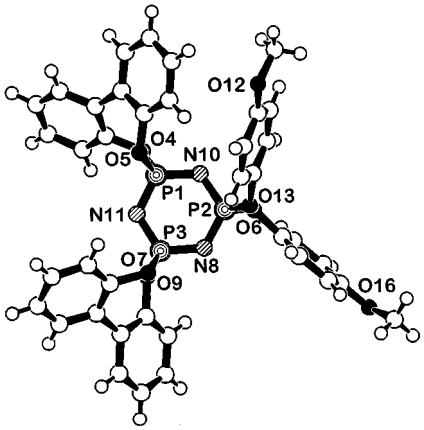



Figure 3. SCHAKAL view of **7**(*R*,*R*)

Table 2. Selected bond lengths [Å] and angles [°] in **7**(*R*,*R*)

| Bond | Length [Å] | Bond | Angle [°] |
|---|---|---|---|
| P(1)−N(10) | 1.561(3) | N(10)−P(1)−N(11) | 117.89(14) |
| P(1)−N(11) | 1.574(3) | O(4)−P(1)−O(5) | 102.6(6) |
| P(1)−O(4) | 1.585(2) | N(10)−P(1)−O(4) | 105.19(13) |
| P(1)−O(5) | 1.589(2) | N(11)−P(1)−O(4) | 112.13(14) |
| P(2)−N(10) | 1.578(3) | N(10)−P(1)−O(5) | 112.15(14) |
| P(2)−N(8) | 1.578(3) | N(11)−P(1)−O(5) | 105.87(14) |
| P(2)−O(13) | 1.563(3) | N(8)−P(2)−N(10) | 117.7(2) |
| P(2)−O(6) | 1.573(2) | O(13)−P(2)−O(6) | 103.63(14) |
| P(3)−N(8) | 1.563(3) | N(8)−P(2)−O(13) | 108.0(2) |
| P(3)−N(11) | 1.576(3) | O(6)−P(2)−N(8) | 109.64(14) |
| P(3)−O(7) | 1.585(3) | N(10)−P(2)−O(13) | 111.60(13) |
| P(3)−O(9) | 1.590(2) | N(10)−P(2)−O(6) | 105.44(13) |
| | | N(8)−P(3)−N(11) | 118.1(2) |
| | | O(7)−P(3)−O(9) | 102.87(12) |
| | | O(7)−P(3)−N(8) | 112.6(2) |
| | | O(7)−P(3)−N(11) | 104.5(2) |
| | | N(8)−P(3)−O(9) | 106.3314) |
| | | N(11)−P(3)−O(9) | 111.47(14) |
| | | P(1)−N(11)−P(3) | 121.7(2) |
| | | P(1)−N(10)−P(2) | 121.8(2) |
| | | P(2)−N(8)−P(3) | 122.0(2) |

The other enantiomer is also found in the unit cell (space group $P\bar{1}$), but is not shown. The $P_3N_3$ ring is almost planar [deviations (Å) from the best plane: P1(−0.053)−P2(−0.025)−P3(0.006)−N8(−0.005)−N10(0.055)−N11(0.022)] and all P−N distances are almost equal (largest variation 0.017 Å), indicating that no unusual steric interactions are involved. An idealized $C_2$ axis of symmetry runs through P2−N11 and interconverts the methyl groups bonded to O12 and O16.

The chiral cyclotriphosphazene **9**(*R*,*R*) crystallizes in the axial chiral space group $P_2(1)$. The molecule is shown in such a way that the idealized $C_2$ axis running through P1−N3 lies horizontal in the plane of the paper (Figure 4); selected bond lengths and angles are listed in Table 3.

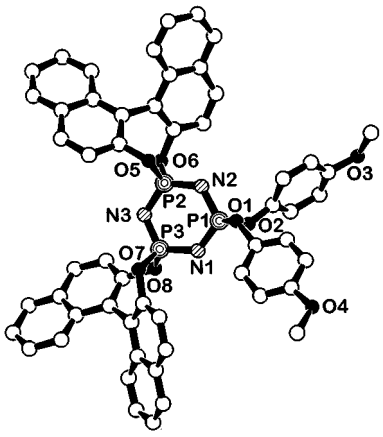



Figure 4. SCHAKAL view of **9**(*R*,*R*)

Table 3. Selected bond lengths [Å] and angles [°] in **9**(*R*,*R*)

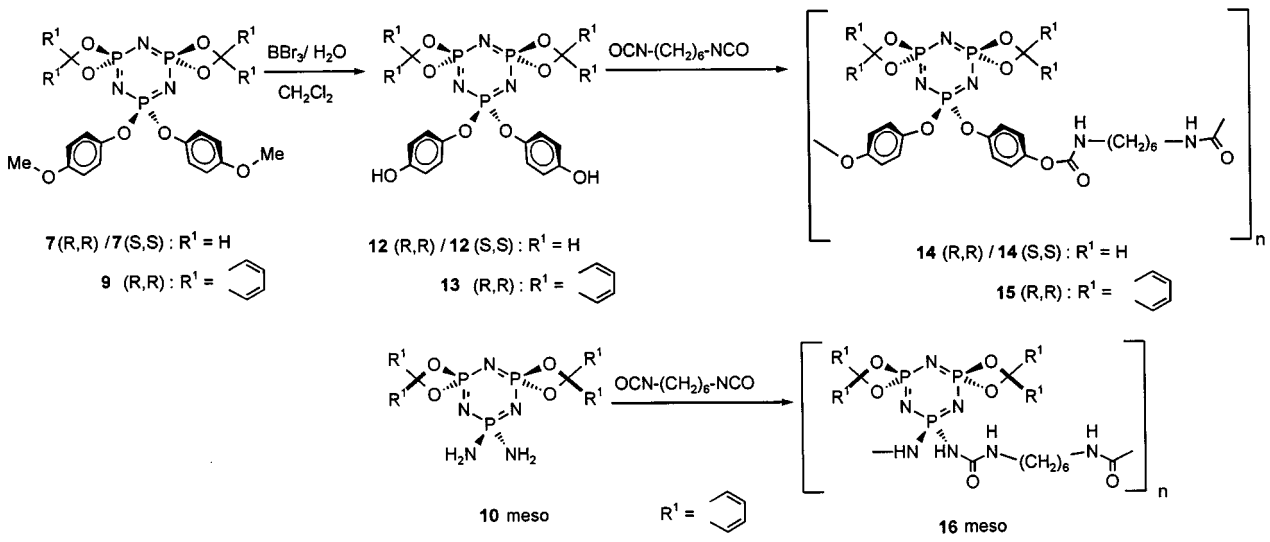
| Bond | Length [Å] | Bond | Angle [°] |
|---|---|---|---|
| P(2)−N(3) | 1.568(10) | N(3)−P(2)−O(5) | 112.4(5) |
| P(2)−O(5) | 1.582(8) | N(3)−P(2)−N(2) | 118.7(5) |
| P(2)−N(2) | 1.571(10) | O(5)−P(2)−N(2) | 104.7(5) |
| P(2)−O(6) | 1.612(7) | N(3)−P(2)−O(6) | 107.6(5) |
| P(3)−O(7) | 1.567(7) | O(5)−P(2)−O(6) | 101.8(4) |
| P(3)−N(3) | 1.566(11) | N(2)−P(2)−O(6) | 110.3(5) |
| P(3)−N(1) | 1.581(9) | O(7)−P(3)−N(3) | 107.7(5) |
| P(3)−O(8) | 1.620(7) | O(7)−P(3)−N(1) | 112.3(5) |
| P(1)−N(1) | 1.539(10) | N(3)−P(3)−N(1) | 116.0(5) |
| P(1)−O(1) | 1.564(8) | O(7)−P(3)−O(8) | 102.7(4) |
| P(1)−N(2) | 1.594(10) | N(3)−P(3)−O(8) | 110.6(5) |
| P(1)−O(2) | 1.610(8) | N(1)−P(3)−O(8) | 106.7(5) |
| | | N(1)−P(1)−O(1) | 114.3(5) |
| | | N(1)−P(1)−N(2) | 117.6(3) |
| | | O(1)−P(1)−N(2) | 102.9(5) |
| | | N(1)−P(1)−O(2) | 104.2(4) |
| | | O(1)−P(1)−O(2) | 104.6(4) |
| | | N(2)−P(1)−O(2) | 112.7(5) |
| | | P(2)−N(2)−P(1) | 120.5(6) |
| | | P(1)−N(1)−P(3) | 124.3(6) |
| | | P(2)−N(3)−P(3) | 122.6(4) |

Among the phosphazenes investigated in this work, **9**(*R*,*R*) is the most sterically encumbered. This is reflected in a larger variation of the bond lengths (P−N 1.539−1.594 Å; P−O 1.564−1.620 Å) and angles (P−N−P 116.0−118.7°; N−P−N 120.5−124.3°), and in a slight puckering of the $P_3N_3$ ring [deviations (Å) from the best plane: P1(0.022)−P2(0.024)−P3(−0.02)−N2(−0.38)−N1(0.006)−N3(0.005)]. The internal O5−P2−O6 (101.8°) and O7−P−O8 (102.7°) angles are slightly smaller than the rather open O1−P1−O2 (104.6°). Generally, however, no severe steric interactions leading to unusual distortions are observed.

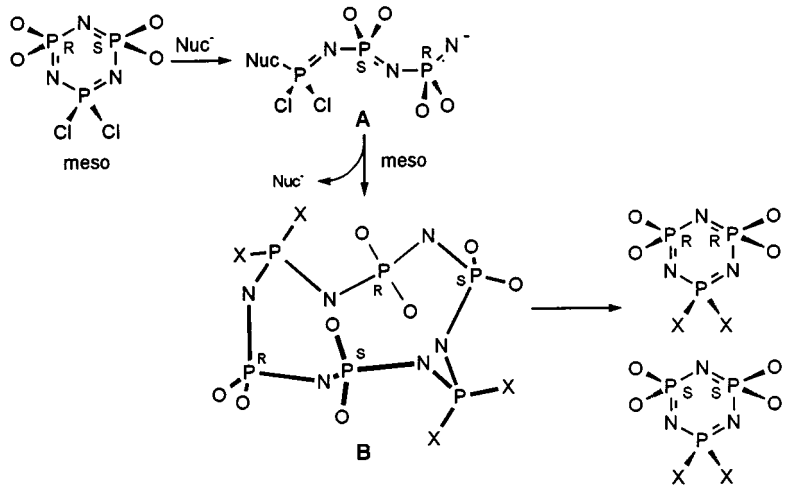
## Discussion

Clearly, the *meso* forms of the 1,1-P-dichloro-substituted cyclotriphosphazenes, *meso*-**4** and *meso*-**5**, respectively, seem to be favored when racemic mixtures of the diols **2** and **3** are used. It is quite remarkable that these are formed exclusively and we cannot offer a straightforward explanation as to why the chiral (*R*,*R*) or (*S*,*S*) forms are not found. On the other hand, an anionic nucleophile converts the *meso* forms either quantitatively, as in the case of *meso*-**4**, or at least partially, as is observed for *meso*-**5**, into the axial chiral isomers. This is even more surprising because the sterically more demanding 4-methoxyphenolate groups should give rise to increased steric interactions, which, at first glance, may be smaller in the *meso* isomers. However, just the opposite may be true and attractive interactions, for example between aromatic hydrogen centers and a π-system of a neighboring arene moiety, may determine the relative stabilities. Such an interaction (< 2.8 Å) is seen in the molecular structure of **7**(*R*,*R*) (Figure 3) between one hydrogen center of a biphenoxy group and the π-cloud of a 4-methoxyphenolate residue. In any case, a plausible mechanism for the change of the configuration at the phosphorus centers within one $P_3N_3$ unit must be found. While one may speculate about pentacoordinated phosphorus centers undergoing Berry rotation when the biphenoxy-substituted cyclotriphosphazene *meso*-**4** is reacted with an anionic nucleophile, such a possibility is highly unlikely for *meso*-**5**. Instead, a complete intermolecular exchange of (*R*)- or (*S*)-configured (O,O)P units must take place and we propose the mechanism outlined in Scheme 4 to explain this observation.

Nucleophilic attack on the electrophilic $PCl_2$ group leads to ring-opening and formation of intermediate **A**. This may act as a further nucleophile, attacking a second equivalent of *meso*-configured 1,1-dichlorocyclotriphosphazene. A dimer **B** containing a twelve-membered $P_6N_6$ ring could thus be formed, although higher oligomers cannot be ruled out. The structures of cyclophosphazenes $(R_2PN)_n$ have been comprehensively determined for $n = 3-12$.[23] It is found that the P−N−P angles in particular widen with ring size [e.g. 133° in $(Me_2PN)_6$]. This may increase the steric interactions between substituents on neighboring phosphorus centers and may be particularly unfavorable for (*R*,*S*)-configured pairs (see Figure 1). Finally, the larger ring **B** collapses into the thermodynamically more stable six-membered chiral phosphazenes. While this mechanism is admittedly highly speculative, it would explain why no *meso*-**8** is obtained when **6**(*R*,*R*) is reacted with 4-methoxyphenolate. It is even conceivable that the substitution of the chlorines by phenolate residues occurs at the stage of the larger-ring phosphazenes. It is noteworthy that no further *meso*-**8** is converted into **9**(*R*,*R*) or **9**(*S*,*S*) when the reaction is carried out for an extended period in the presence of excess phenolate after complete conversion has been already achieved. Raising the temperature to about 100°C led to nonspecific degradation of the reaction products. Thus, it seems that a $PCl_2$ group is necessary in order to observe the stereochemical phenomena. Furthermore, only hard nucleophiles lead to exchange of the (O,O)P groups, since amine bases do not alter the stereochemistry of the starting materials (cf. the synthesis of *meso*-**10** and *meso*-**11** from *meso*-**5**). Finally, we note that the interconversion of rings of different sizes has been described for anionic cyclosilazanes[24] and it is well-known that cyclosiloxanes, which are isoelectronic with phosphazenes, easily undergo a ring-opening polymerization (ROP) in the presence of base.[25] To the best of our knowledge, equilibria between rings of different sizes, as is




Scheme 4. Syntheses of cyclolinear polymers




Scheme 5. Proposed mechanism for exchange of (O,O)P groups

indirectly evidenced here by an exchange of stereochemically different (O,O)P groups, have not previously been described in cyclophosphazene chemistry.

## Syntheses of Polymers

In order to obtain cyclolinear polymers, we converted the racemic mixture of 4-methoxy-substituted phosphazenes **7**(*R*,*R*) and **7**(*S*,*S*) as well as enantiomerically pure **9**(*R*,*R*) into the hydroxylated compounds **12** and **13** by reacting them with $BBr_3$ and then hydrolyzing the intermediate boron compounds[26] (Scheme 5).

These reactions proceeded with complete retention of the stereochemistry at the phosphorus centers. For instance, using the mixture of isomers *meso*-**8**, **9**(*R*,*R*) and **9**(*S*,*S*) obtained according to Scheme 3, two $^1$H-NMR signals were observed for the OH groups of the *meso* isomer ($\delta$ = 4.05 and 4.11) and one ($\delta$ = 4.09) for the enantiomers, in the same ratio as the integrals of the methoxy resonances of the starting material. The enantiomerically pure compound **13**(*R*,*R*) exhibited an optical rotation angle of $[\alpha]^{25} = -119°$. The presence of hydroxyl groups in **12**(*R*,*R*)/**12**(*S*,*S*) and **13**(*R*,*R*) was evident from the IR spectra, which featured a broad band located near 3400 $cm^{-1}$ corresponding to the OH stretching vibration. Furthermore, the complete conversion of **7** and **9** into **12** and **13**, respectively, was evident from the $^1$H- and $^{13}$C-NMR spectra owing to the disappearance of the signals attributable to the methoxy functions.

Polyurethanes incorporating cyclotriphosphazene units were prepared by direct polyaddition of either the bifunctional hydroxylated racemic mixture of **12**(*R*,*R*)/**12**(*S*,*S*) or enantiomerically pure **13**(*R*,*R*) or the bis(amino)-substituted *meso* compound *meso*-**10** with hexamethylenediisocyanate (HDI). The reactions were performed in DMF at 80°C and the polymers **14**(*R*,*R*)/**14**(*S*,*S*), **15**(*R*,*R*), and *meso*-**16** were purified by precipitation and repeated extractions with methanol.[27] The $^{31}$P-NMR spectra in [$D_6$]DMSO solution were very similar to the spectra of the monomers.

The $^1$H-NMR and IR spectra confirmed the formation of polyurethane structures; the IR spectra of **14**(*R*,*R*)/**14**(*S*,*S*), **15**(*R*,*R*), and *meso*-**16** are given in Figure 5.

The spectra show the characteristic absorptions of the cyclotriphosphazene ring and aromatic groups at around $\tilde{\nu}$ = 1250, 1170, and 960 $cm^{-1}$, attributable to P=N, (P)−C−O and P−O−(C) stretching vibrations, respectively.[28] These results confirmed that the cyclotriphosphazene units remained unaffected when incorporated into the polymers. The urethane groups present in **14**(*R*,*R*)/**14**(*S*,*S*), **15**(*R*,*R*), and *meso*-**16** are characterized by NH stretching vibrations at $\tilde{\nu} \approx 3350$ $cm^{-1}$ and C=O stretching vibrations at $\tilde{\nu} \approx 1700$ $cm^{-1}$. In the $^1$H-NMR spectra of the polymers, a resonance at $\delta \approx 9.6$ can be attributed to the NH proton of the urethane linkage. The molecular weight of **14**(*R*,*R*)/**14**(*S*,*S*) was estimated by steric exclusion chromatography in THF to be $\overline{M}_w$bar = 17000 with a molecular weight distribution $\overline{M}_w$bar/$\overline{M}_n$bar = 1.7. The molecular weights of **15**(*R*,*R*) and *meso*-**16** could not be determined because of the poor solubilities of these polymers in THF.

In terms of the stereochemistries at the phosphorus centers, the polyurethanes prepared in this work are representatives of three different polymer types. Thus, **14**(*R*,*R*)/**14**(*S*,*S*) consists of a racemic mixture of homochiral polymer chains, **15**(*R*,*R*) is the first example of an enantiomerically pure cyclolinear phosphazene polymer (optical rotation angle $[\alpha]^{25} = -111°$), while *meso*-**16** contains (*R*)- and (*S*)-configured phosphorus centers within one polymer strand. The thermal behavior of these three polymers was investigated by dynamic thermogravimetric analysis (TGA) in air. Typical TGA curves for **14**(*R*,*R*)/**14**(*S*,*S*), **15**(*R*,*R*), and *meso*-**16** are shown in Figure 6.

It can be seen that the incorporation of cyclotriphosphazene moieties increases the thermal stability of all polyurethanes. Note that simple "organic" polyurethanes show thermooxidative decomposition starting at ca. 200°C. For **14**(*R*,*R*)/**14**(*S*,*S*), the temperature corresponding to 10%

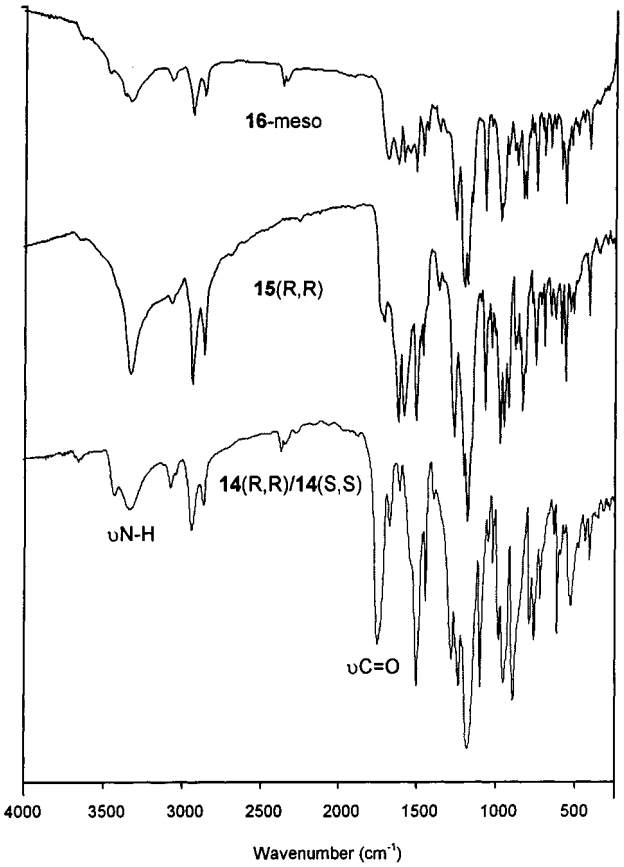



Figure 5. Infrared spectra of polymers **14**(*R*,*R*)/**14**(*S*,*S*), **15**(*R*,*R*), and *meso*-**16**

weight loss ($T_{10}$) is found to be 325°C. The value of $T_{10}$ is lower for **15**(*R*,*R*) (280°C), but lies in the same range for *meso*-**16** (315°C). At a temperature of 500°C, 72%, 60%, and 70%, respectively, of the original masses of **14**(*R*,*R*)/**14**(*S*,*S*), **15**(*R*,*R*), and *meso*-**16** still remain. This high char yield is characteristic of cyclotriphosphazene-containing polymers[8–10] and accounts for their flame-retardant properties. For comparison, the thermal behavior of a polyurethane synthesized from 1,3-bis(hydroxy)benzene and HDI was investigated. Its $T_{10}$ was found to be low (209°C) and complete decomposition was observed at just 600°C.[3] However, the thermal stability of **15**(*R*,*R*), in which only one stereoisomer of the diol is present, is significantly lower than those of **14**(*R*,*R*)/**14**(*S*,*S*) and *meso*-**16**. In the latter, both atropisomers of the diols are present. As can be deduced from Figure 1, a favorable packing by π-stacking of the arene moieties may be responsible for the enhanced thermal stabilities of these polymers.

## Conclusion

Reactions of hexachlorocyclotriphosphazene **1** with two equivalents of the chelating diols 2,2′-dioxybiphenyl, **2**(*S*), **2**(*R*), or 2′,2′′-dioxy-1′,1′′-bis(2-naphthyl), **3**(*S*), **3**(*R*), lead only to the formation of the *meso* compounds [(*R*,*S*)-$(O,O)_2Cl_2P_3N_3$] *meso*-**4** or *meso*-**5**, respectively. Remarkably, when the remaining $PCl_2$ group is reacted with a hard nucleophile such as 4-methoxyphenolate, either a racemic mixture of chiral [(*R*,*R*)-$(O,O)_2(RO)_2P_3N_3$], **7**(*R*,*R*), and [(*S*,*S*)-$(O,O)_2(RO)_2P_3N_3$], **7**(*S*,*S*), (O,O = 2,2′-dioxybiphenyl) is formed, or at least partial racemization occurs, leading to a mixture of all possible stereoisomers *meso*-**8**, **9**(*R*,*R*) and **9**(*S*,*S*) [O,O = 2′,2′′-dioxy-1′,1′′-bis(2-naphthyl)]. While one may speculate about five-coordinated phosphorus centers undergoing Berry rotation in the case of O,O = biphenoxy, this phenomenon is highly unlikely when O,O = binaphthoxy and does not explain the configurational change at the phosphorus centers. In order to explain the exchange of complete (O,O)P-units within the cycles, we

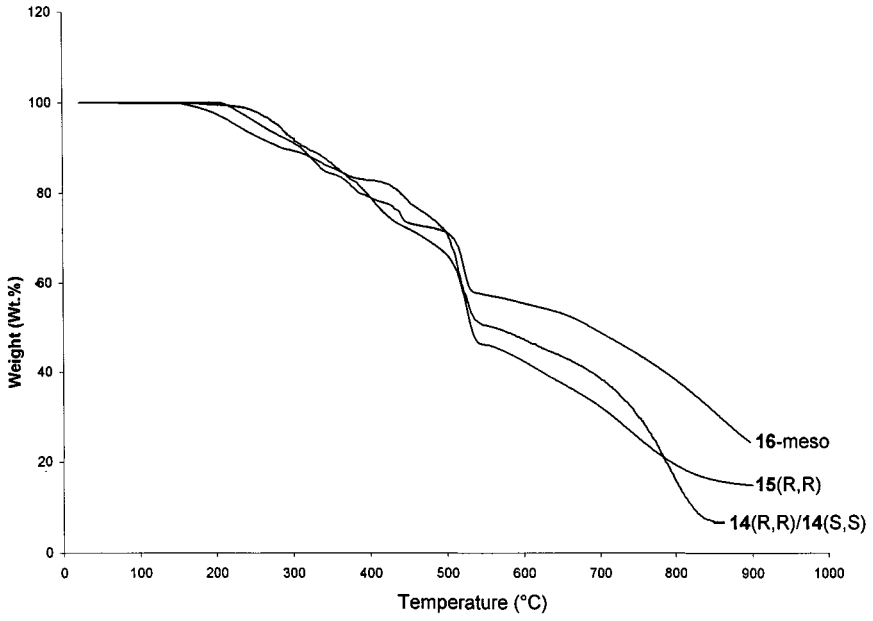



Figure 6. Thermogravimetric analysis of **14**(*R*,*R*)/**14**(*S*,*S*), **15**(*R*,*R*), and *meso*-**16** conducted at a heating rate of 8°C/min in air

Table 4. Crystal data and structure refinement for *meso*-**4**, **7**(*R*,*R*), and **9**(*R*,*R*)

| | *meso*-**4** | **7**(*R*,*R*) | **9**(*R*,*R*) |
|---|---|---|---|
| Empirical formula | $C_{24}H_{16}Cl_2N_3O_4P_3$ | $C_{38}H_{30}N_3O_8P_3$ | $C_{54}H_{38}N_3O_8P_3$ |
| Formula weight | 574.21 | 749.56 | 949 |
| Temperature [K] | 293(2) | 293(2) | 293(2) |
| Wavelength [Å] | 1.54178 | 1.54178 | 0.71073 |
| Space group | *Cc* | $P\bar{1}$ | *P*2(1) |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Unit cell dimensions [Å][°] | *a* = 11.078(5) | *a* = 11.669(6) | *a* = 9.657(2), |
| | *b* = 26.711(13) | *b* = 11.866(10) | *b* = 23.686(5), |
| | *c* = 17.403(9) | *c* = 13.919(12) | *c* = 10.487(2) |
| | α = 90 | α = 101.12(6) | α = 90 |
| | β = 101.75(4) | β = 96.88(6) | β = 90.30(3) |
| | γ = 90 | γ = 111.23(5) | – |
| Volume [Å$^3$] | 5042(4) | 1725(2) | 2398.7(8) |
| *Z* | 8 | 8 | 2 |
| Density [mg·m$^3$] (calcd.) | 1.513 | 1.444 | 1.437 |
| Absorption coefficient [mm$^{-1}$] | 4.447 | 2.091 | 0.297 |
| *F*(000) | 2336 | 776 | 1074 |
| Crystal size [mm$^3$] | 0.3 × 0.2 × 0.2 | 0.4 × 0.3 × 0.2 | 0.4 × 0.3 × 0.3 |
| θ range for data collection [°] | 3.31 to 50.01 | 3.31 to 49.99 | 1.72 to 20.08 |
| Index ranges | $-10 \le h \le 10$ | $-11 \le h \le 11$ | $-9 \le h \le 9$ |
| | $0 \le k \le 26$ | $-11 \le k \le 11$ | $-22 \le k \le 0$ |
| | $0 \le l \le 17$ | $0 \le l \le 13$ | $-10 \le l \le 10$ |
| Reflections collected | 2621 | 3539 | 4663 |
| Independent reflections | 2621 ($R_{int}$ = 0.0122) | 3539 ($R_{int}$ = 0.0000) | 2332 ($R_{int}$ = 0.0000) |
| Absorption correction | None | None | None |
| Refinement method | Full-matrix least-squares on $F^2$ | | |
| Data/restraints/parameters | 2611/0/648 | 3539/0/470 | 2332/465/641 |
| Goodness-of-fit on $F^2$ | 1.078 | 1.060 | 1.038 |
| Final *R* indices [$I>2\sigma(I)$] | *R*1 = 0.0444, *wR*2 = 0.1122 | *R*1 = 0.0411, *wR*2 = 0.1162 | *R*1 = 0.0355, *wR*2 = 0.0889 |
| R indices (all data) | *R* = 0.0450, *wR*2 = 0.1134 | *R*1 = 0.0425, *wR*2 = 0.1179 | *R*1 = 0.0374, *wR*2 = 0.0902 |
| Extinction coefficient [mm$^{-1}$] | 0.00023(6) | 0.0072(5) | 0.0093(15) |
| Largest diff. peak & hole [e.Å$^{-3}$] | 0.325 and −0.467 | 0.343 and −0.340 | 0.391 and −0.212 |
| Absolute structure parameter | −0.01(2) | – | 0.50(16) |

propose ring-opening and the formation of larger cycles, i.e. cyclohexaphosphazenes, which collapse to reform cyclotriphosphazenes with different stereochemistry. Chiral cyclotriphosphazenes such as **9**(*R*,*R*) and **9**(*S*,*S*) were obtained using either of the enantiomerically pure (*R*)- or (*S*)-forms of 2′,2′′-dioxy-1′,1′′-bis(2-naphthyl) **3** as starting materials. The change of configuration is furthermore related to the presence of a $PCl_2$ unit in the phosphazene ring, since the stereochemistry of all phenoxy-substituted phosphazenes [$(O,O)_2(RO)_2P_3N_3$] is retained, even when these are reacted with excess phenolate $RO^-$ under harsh conditions. Interestingly, soft nucleophiles such as amines do not affect the configuration at the phosphorus centers and thus allow the synthesis of *meso*-[(*R*,*S*)-$(O,O)_2(R^1RN)_2P_3N_3$] compounds. These observations show that seemingly simple substitution reactions on chloro-substituted phosphazenes are more complex than they might at first appear. The bifunctional cyclotriphosphazenes [(*R*,*R*)-$(O,O)_2$(4-HO−$C_4H_4O)_2P_3N_3$] and/or [(*S*,*S*)-$(O,O)_2$(4-HO−$C_4H_4O)_2P_3N_3$] and [(*R*,*S*)-$(O,O)_2(H_2N)_2P_3N_3$] are suitable monomers for polyaddition reactions with hexamethylenediisocyanate, which furnish cyclolinear polyurethane polymers. Depending on the stereochemistry of the phosphazene precursor, either a racemic mixture of homochiral polymer strands, an enantiomerically pure polymer, or the *meso* form of a polymer was obtained. The latter was found to show the highest thermal stability

## Experimental Section

**General Methods:** $^{31}$P-, $^1$H-, and $^{13}$C-NMR spectra were recorded in $CD_2Cl_2$ and $CDCl_3$ for most compounds, those of *meso*-**10** were recorded in [$D_8$]THF, while polymers where examined in [$D_6$]DMSO using Bruker DPX250 and DPX300 NMR spectrometers. Chemical shifts (ppm) are positive in the low-field direction and are quoted relative to external 85% $H_3PO_4$ ($^{31}$P) or external TMS ($^1$H, $^{13}$C). – Infrared spectra were recorded with a Perkin−Elmer 783 spectrometer. The samples were dispersed in KBr. – Mass spectra were recorded on a Finnigan MAT 8200 spectrometer operating in the EI (70 eV) mode. – Thermogravimetric measurements were performed in air on a Setaram NTB10−8 instrument at a heating rate of 8°C/min. – The optical rotation angles were measured on a Perkin−Elmer 241MC polarimeter [*c* = 1, $CHCl_3$ for **6**(*R*,*R*), **9**(*R*,*R*) and **13**(*R*,*R*); DMF for **15**(*R*,*R*)] using light of the Na D line (λ = 589 nm). – The X-ray powder diffraction pattern of *meso*-**4** was recorded using a Stoe STADIP powder diffractometer equipped with a position-sensitive detector (radiation: Cu-$K_{\alpha1}$).

Tetrahydrofuran (THF), chlorobenzene, dichloromethane, and dimethylformamide (DMF) were obtained from Aldrich. THF, $CH_2Cl_2$, and DMF were purified by distillation. Sodium hydride, biphenol, binaphthol [(+/−); *R*(+)], sodium hydroxide, 4-methoxyphenol, methylhydrazine, boron tribromide, ammonium hydroxide solution, and 1,6-hexamethylenediisocyanate (HDI) were purchased from Aldrich or Fluka and were used as received. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, (Nippon Soda) was

Table 5. Spectroscopic data for intermediate compounds and precursors

| Compd. | $^{31}$P NMR δ [ppm] | $^{1}$H NMR [$^{-1}$] | $^{13}$C NMR *m/z* | IR frequency | MS |
|---|---|---|---|---|---|
| *meso*-**4** | 20.72, 30.43, $J_{AB}$ = 79.28 Hz | 7.31−7.55 (m, Ar) | 147.3 (m, Ar), 129.9 (m, Ar), 129.7 (m, Ar), 128.5 (m, Ar), 126.5 (m, Ar), 121.8 (m, Ar) | 1226.7 (ν P=N), 1172, 962 (ν P−O−Ar) | 574 [M$^+$] |
| *meso*-**5** | 21.78, 30.44, $J_{AB}$ = 77.65 Hz | 7.23−7.55 (m, Ar), 7.65 (d, Ar), 7.75 (d, Ar), 8.00 (t, Ar), 8.09 (t, Ar) | | 1265 (ν P=N), 1184, 973 (ν P−O−Ar) | 773 [M$^+$] |
| **6**(*R*,*R*), **6**(*S*,*S*) | 21.97, 30.22, $J_{AB}$ = 78.59 Hz | 7.28−7.35 (m, Ar), 7.41−7.53 (m, Ar), 7.63 (d, Ar), 7.87 (m, Ar), 7.90 (s, Ar), 7.99 (d, Ar), 8.12 (d, Ar) | 121.8 (m, Ar), 126.1 (d, Ar), 127.0 (d, Ar), 127.6 (s, Ar), 128.9 (d, Ar), 131.5 (d, Ar), 132.4 (m, Ar), 136.6 (m, Ar), 147.1 (m, Ar) | 1263 (ν P=N), 1188, 973 (ν P−O−Ar) | 773 [M$^+$] |
| **7**(*R*,*R*), **7**(*S*,*S*) | 12.22, 26.59, $J_{AB}$ = 61.99 Hz | 3.93 (s, $CH_3$), 6.80 (d, Ar), 7.42 (d Ar), 6.90−7.31 (m, Ar) | 55.5 (s, $CH_3$), 114.4 (m, Ar), 122.2 (m, Ar), 122.6 (m, Ar), 125.9 (m, Ar), 128 (m, Ar), 129.5 (m, Ar), 129.6 (m, Ar), 146 (m, Ar), 147 (m, Ar), 155.5 (m, Ar) | 2836 (ν C−H, $OCH_3$), 1231 (ν P=N), 1173, 948 (ν P−O−Ar) | 749 [M$^+$] |
| *meso*-**8** | 12.03, 27.56, $J_{AB}$ = 61.36 Hz | 3.80, 3.95 (s, $OCH_3$), 7.15 (d, Ar), 7.28−7.54 (m, Ar), 7.61 (d, Ar), 7.97 (m, Ar), 8.03 (m, Ar), 8.13 (d, Ar) | 55.2, 55.5 (s, $OCH_3$), 114.0 (d, Ar), 114.3 (d, Ar), 120.7 (m, Ar), 120.9 (m, Ar), 121.3 (m, Ar), 121.9 (d, Ar), 122.0 (d, Ar), 125.1 (m, Ar), 126.1 (m, Ar), 126.8 (m, Ar), 128.0 (m, Ar), 130.3 (m, Ar), 131.4 (m, Ar), 132.1 (m, Ar), 147.0 (m, Ar) | 2833 (ν C−H,$OCH_3$), 1268 (ν P=N), 1170, 975 (ν P−O−Ar) | 949 [M$^+$] |
| **9**(*R*,*R*), **9**(*S*,*S*) | 11.76, 27.87, $J_{AB}$ = 61.79 Hz | 3.88 (s, $OCH_3$), 6.96 (d, Ar), 7.06 (d, Ar), 7.28−7.49 (m, Ar), 7.85 (d, Ar), 7.93−7.95 (m, Ar) | 55.4 (s, $OCH_3$), 114.2 (d, Ar), 121.1 (m, Ar), 121.3 (m, Ar), 121.7 (d, Ar), 125.1 (d, Ar), 126.9 (d, Ar), 128.1 (s, Ar), 130.3 (d, Ar), 131.3 (d, Ar), 131.7 (d, Ar), 144.4 (m, Ar), 146.8 (t, Ar), 147.0 (t, Ar) | 2830 (ν C−H, $OCH_3$), 1260 (ν P=N), 1162, 970 (ν P−O−Ar) | 949 [M$^+$] |
| *meso*-**10** | 20.29, 27.43, $J_{AB}$ = 47.63 Hz | 7.28−8.15 (m, Ar) | 121.5 (m, Ar), 122.6 (m, Ar), 125.7 (m, Ar), 126.5 (m, Ar), 127.8 (m, Ar), 129.7 (d, Ar), 131.3 (m, Ar), 132.0 (m, Ar), 136.0 (m, Ar), 146.9 (m, Ar) | 3460, 3340 (ν N−H), 1544 (δ N−H), 1256 (ν P=N), 1176, 969 (ν P−O−Ar) | |
| *meso*-**11** | 28.31, 29.34, $J_{AB}$ = 58.32 Hz | 2.84 (d, $CH_3$), 3.11 (d, $CH_3$), 7.25−7.65 (m, Ar), 7.75 (d, Ar), 8.01−8.22 (m, Ar) | | 3412, 3324 (ν N−H), 2790 (ν C−H), 1566 (δ N−H), 1255 (ν P=N), 1170, 966 (ν P−O−Ar) | 791 [M$^+$] |
| **12**(*R*,*R*), **12**(*S*,*S*) | 12.74, 26.83, $J_{AB}$ = 62.27 Hz | 6.79 (d, Ar), 7.60 (d, Ar), 6.88−7.32 (m, Ar), 8.33 (s, OH) | 116.8 (m, Ar), 122.7 (m, Ar), 122.8 (m, Ar), 122.9 (m, Ar), 127.1 (m, Ar), 129.4 (m, Ar), 129.4 (m, Ar), 143 (m, Ar), 148.9 (m, Ar), 155.2 (m, Ar) | 3358 (ν O−H), 1231 (ν P=N), 1175, 951 (ν P−O−Ar) | 721 [M$^+$] |
| **13**(*R*,*R*) | 12.32, 28.19, $J_{AB}$ = 61.81 Hz | 5.18 (s, OH), 6.92 (d, Ar), 7.19−7.54 (m, Ar), 7.90 (d, Ar), 8.04 (m, Ar) | 115.6 (m, Ar), 121.1 (m, Ar), 121.5 (m, Ar), 121.8 (d, Ar), 125.0 (d, Ar), 126.9 (d, Ar), 17.0 (d, Ar), 128.1 (s, Ar), 130.4 (d, Ar), 131.4 (d, Ar), 131.9 (d, Ar), 144.3 (d, Ar), 146.8 (m, Ar), 152.5 (m, Ar) | 3401 (ν O−H), 1259 (ν P=N), 1166, 973 (ν P−O−Ar) | 921 [M$^+$] |

purified by vacuum sublimation. All reactions and manipulations were carried out under inert atmosphere.

Compounds *meso*-**4**, **7**(*RR*)/**7**(*S*,*S*), and **12**(*R*,*R*)/**12**(*S*,*S*) were synthesized according to a procedure reported elsewhere.[8]

**Crystallographic Analyses of *meso*-4, 7(*R*,*R*), and 9(*R*,*R*):** The data sets for the single-crystal X-ray studies were collected on either a Nonius CAD4 or a fully automated Siemens−Stoe AED2 four-circle diffractometer. All calculations were performed on a Digital Corporation VAX system using the SHELXS-86 and SHELXS-93 program suites.[29][30]

Specific data relating to the crystal structures and refinements are collected in Table 4. The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$.

The graphical representations of the molecular structures were drawn using the SCHAKAL program.[31]

**Synthesis of 2,2-Dichloro-4,4,6,6-bisspiro(2′,2′′-dioxy-1′,1′′-binaphthyl)]cyclotriphosphazene [*meso*-5, 6(*R*,*R*), 6(*S*,*S*)]:** A three-necked round-bottomed flask was charged with chlorobenzene (12 mL), water (20 mL), $N_3P_3Cl_6$ (1.13 g, 3.25 mmol), 2,2′-dihydroxy-1,1′-binaphthyl (2.16 g, 6.51 mmol), sodium hydroxide (0.52 g, 13.01 mmol), and TBA (0.10 g, 0.324 mmol). The reaction mixture was stirred rapidly at room temperature for 3 h and then heated at 70°C for a further 3 h. The solvents were then removed under reduced pressure to leave a brown residue, which was washed with chlorobenzene and acetone and dried. A white solid was obtained (2.4 g, 85%); m.p. > 250°C. Spectroscopic data are given in Table 5.

**Synthesis of 2,2-Bis(4-methoxyphenyloxy)bisspiro(2′,2′′-dioxy-1′,1′′-binaphthyl)]cyclotriphosphazene [*meso*-8, 9(*R*,*R*), 9(*S*,*S*)]:** A solution of 4-methoxyphenol (0.73 g, 5.92 mmol) in THF was added dropwise to a solution of *meso*-**5** [or **6**(*R*,*R*) or **6**(*S*,S)] (2.56 g, 2.96 mmol) in THF containing suspended NaH (0.14 g, 20 mmol). The mixture was stirred at room temperature for 3 h and then the THF was removed under reduced pressure. The residue was redissolved in dichloromethane and the resulting solution was extracted twice with 10% aqueous NaOH, washed with water (three times),

Table 6. Spectroscopic data for polymers **14**(*R*,*R*)/**14**(*S*,*S*), **15**(*R*,*R*) and *meso*-**16**

| Compd. | $^{31}$P NMR δ [ppm] | $^{1}$H NMR δ [ppm] | IR frequency [cm$^{-1}$] |
|---|---|---|---|
| **14**(*R*,*R*), **14**(*S*,*S*) | 26.13, 12.08, $J_{AB}$ = 62.60 Hz | 1.32 ($CH_2$), 1.47 ($CH_2$), 3.07 ($CH_2$-NH-), 7.15−7.80 (m, Ar), 9.65 (s, NH) | 3389 (ν N−H), 1745 (ν C=O), 1230 (ν P=N), 1171, 946 [ν (P−O−Ar)] |
| **15**(*R*,*R*) | 27.32, 12.21, $J_{AB}$ = 60.02 Hz | 1.25 ($CH_2$), 1.50 ($CH_2$), 3.10 ($CH_2$-NH-), 6.90−8.20 (m, arom.), 9.61 (s, NH) | 3319 (ν N−H), 1731 (ν C=O), 1259 (ν P=N), 1170, 973 [ν (P−O−Ar)] |
| *meso*-**16** | 27.43, 20.29, $J_{AB}$ = 47.79 Hz | 1.23 ($CH_2$), 1.46 ($CH_2$), 2.96 ($CH_2$-NH-), 7.22−8.30 (m, arom.) | 3363 (ν N−H), 1545 (δ N−H), 1686 (ν C=O), 1256 (ν P=N), 1181, 969 [ν (P−O−Ar)] |

and dried over anhydrous sodium sulfate. After filtration and removal of the solvent under reduced pressure, 2.33 g (83%) of *meso*-**8** [or **9**(*R*,*R*) or **9**(*S*,S)] was obtained; m.p. 199°C. − $C_{54}H_{38}N_3O_8P_3$: calcd. C 67.1, H 4.0, N 4.3; found C 66.8, H 3.8, N 4.3. − Spectroscopic data are given in Table 5.

**Synthesis of 2,2-Bis(4-hydroxyphenyloxy)bisspiro(2′,2′′-dioxy-1′,1′′-binaphthyl)]cyclotriphosphazene [13(*R*,*R*)/13(*S*,*S*)]:** A solution of 1.07 g (4.26 mmol) of boron tribromide in anhydrous $CH_2Cl_2$ (10 mL) was added dropwise to a solution of **6**(*R*,*R*) or **6**(*S*,*S*) (2.02 g, 2.13 mmol) in anhydrous $CH_2Cl_2$ (15 mL). The reaction mixture was stirred at room temperature for 3 h and then poured into water (50 mL). The residue obtained was dissolved in $CH_2Cl_2$ and the resulting solution was washed with water (three times). The solvent was finally removed under reduced pressure to leave 1.37 g (70%) of **13**(*R*,*R*); m.p. 210°C. − $C_{52}H_{34}N_3O_8P_3$: calcd. C 67.8, H 3.7, N 4.6; found C 67.7, H 3.8, N 4.5. Spectroscopic data are given in Table 5.

**Synthesis of 2,2-Bis(amino)-bisspiro(2′,2′′-dioxy-1′,1′′-binaphthyl)]-cyclotriphosphazene (*meso*-10):** A solution of 0.605 mL (8.11 mmol) of ammonium hydroxide in THF (10 mL) was added dropwise to a solution of *meso*-**5** (1.57 g, 2.03 mmol) in the same solvent (10 mL). The reaction mixture was stirred at 40°C for 1 h and at room temperature for 2 h and then the THF was removed under reduced pressure. The residue obtained was washed with water (three times) and dried, furnishing 1.16 g (78%) of *meso*-**10**; m.p. >250°C. Spectroscopic data are given in Table 5.

**Synthesis of 2,2-Bis(methylhydrazino)bisspiro(2′,2′′-dioxy-1′,1′′-binaphthyl)]cyclotriphosphazene (*meso*-11):** To a solution of *meso*-**5** (1.56 g, 2.01 mmol) in THF was added a solution of methylhydrazine (0.43 mL, 8.05 mmol) in THF (4 mL) at 0°C. The resulting mixture was stirred for 2 h at room temperature and then the solvent was evaporated. The residue was taken up in chloroform and the mixture was filtered by passage through Celite. Evaporation of the solvent from the filtrate furnished 1.11 g (70%) of *meso*-**11**. Spectroscopic data are given in Table 5.

**Synthesis of Polyurethanes [14(*R*,*R*)/14(*S*,*S*), 15(*R*,*R*), and *meso*-16]:** A solution of **12**(*R*,*R*)/**12**(*S*,*S*) or **13**(*R*,*R*) or *meso*-**10** together with HDI (molar ratio, diol or diamine/diisocyanate = 1:1) in DMF was stirred at 80°C for 48 h. The reaction mixture was then poured into cold methanol to precipitate the polymer, which was washed several times with methanol, and finally dried in vacuo at 100°C for 12 h to give a white-yellow solid soluble in DMF and DMSO. − **14**(*R*,*R*)/**14**(*S*,*S*): $C_{44}H_{36}N_5O_{10}P_3$: calcd. C 59.4, H 4.3, N 7.9; found C 58.6, H 4.5, N 8.2. **15**(*R*,*R*): $C_{60}H_{46}N_5O_{10}P_3$: calcd. C 66.1, H 4.2, N 6.4; found C 68.3, H 4.0, N 6.3. *meso*-**16**: $C_{48}H_{40}N_7O_6P_3$: calcd. C 63.8, H 4.4, N 10.8; found C 66.2, H 4.6, N 11.1. Spectroscopic data are given in Table 6.

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