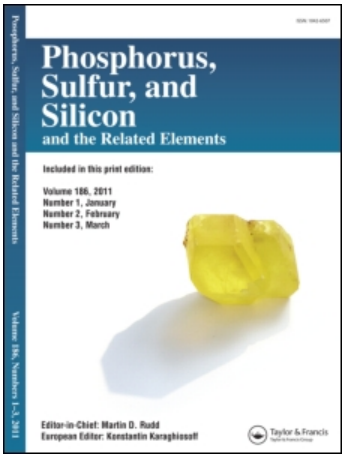

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SYNTHESIS OF NEW PHOSPHORUS CONTAINING MACROCYLES

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SYNTHESIS OF NEW PHOSPHORUS CONTAINING MACROCYLES

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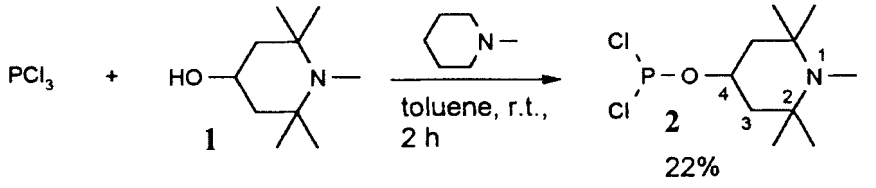
The reaction of 1,2,2,6,6-tetramethylpiperidin-4-ol **1** with PCl_3 gives the phosphorous acid monoester dichloride **2**. This compound forms the macrocycles **4** and **6**, respectively, in a (2 + 2) cyclocondensation with the bisphenols **3** and **5**. Macrocycle **6** could be oxidized to the phosphate macrocycle **7**. In the reaction of **6** with sulfur the thiophosphate macrocycle **8** was obtained. A multi-step one-pot reaction of bisphenol **5** with PCl_3 leads to the phosphorus containing *out,out*-cryptand **9** and *in,out*-cryptand **10**. The *in*-phosphorus in cryptand **10** showed an approximately 3000 times lower oxidation rate than the *out*-phosphorus in the reaction with cumenehydroperoxide.

Keywords: Macrocycles; cryptands; phosphites; phosphates; thiophosphates; piperidines

INTRODUCTION

Phosphorus containing macrocycles have become increasingly more interesting in recent years because of their interesting complexing abilities. Crown ether analogues, phosphorous hydrazides and cyclophosphazenes occupy the largest section in this field aside biochemical phosphorus containing macrocycles such as cyclic DNA.[1,2] Macrocyclic phosphites are relatively rare although they may be interesting for further modification reactions to obtain more complex structures.

Nifantev[3] and Blokhin[4,5] synthesized macrocyclic phenylphosphonites based on 4,4′-isopropylidenediphenol (**3**), bis(4-hydroxyphenyl)sulfid and various dihydroxynaphthols. Herein we report the synthesis of macrocylic phosphites bridged with 4,4′-isopropylidenediphenol (**3**) and 4,4′-[1,4-phenylenebis(1-methylethylidene)]bis[2,6-dimethylphenol] (**5**) units. Some of our macrocycles also bear exocyclic hindered piperidine groups which are widely used



SCHEME 1 Synthesis of the phosphorous acid monoester dichloride **2**

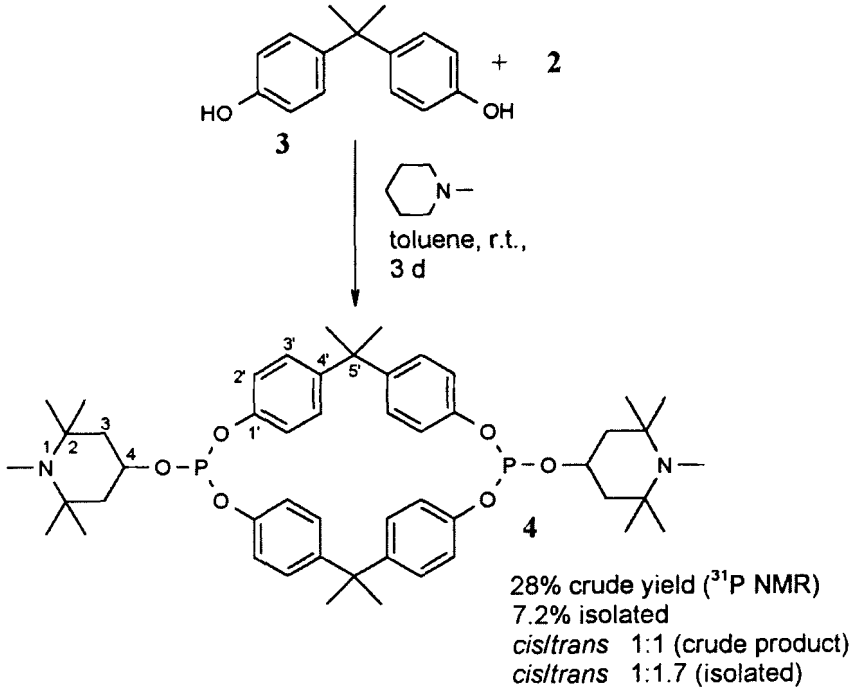
in light stabilizers for polymers. Organic phosphites containing sterically hindered piperidine groups, so-called 'HALS-phosphites' (HALS = *H*indered *A*mine *L*ight *S*tabilizer), are able to protect polymers against different damaging influences (light, long term thermal stress, damaging during processing) as it was reported in ref. 6.

RESULTS AND DISCUSSION

Synthesis of HALS Containing Phosphorus Macrocycles

The reaction of 4-hydroxy-1,2,2,6,6-pentamethylpiperidine (**1**) with an excess of PCl_3 was carried out in toluene using 1-methylpiperidine as a base (Scheme 1). Phosphorous acid monoester dichloride **2** was obtained only in 22% yield but could be purified by distillation *in vacuo* and used as a building block for macrocyclic phosphites. Byproducts are phosphorous acid bis(1,2,2,6,6-pentamethylpiperidin-4-yl-ester) monochloride (^{31}P NMR: δ = 168.9) and phosphorous acid tris(1,2,2,6,6-pentamethylpiperidin-4-yl ester) (^{31}P NMR: δ = 138.8).[7] The use of TEA instead of 1-methylpiperidine as a base leads to the formation of the hydrochloride of **2**.

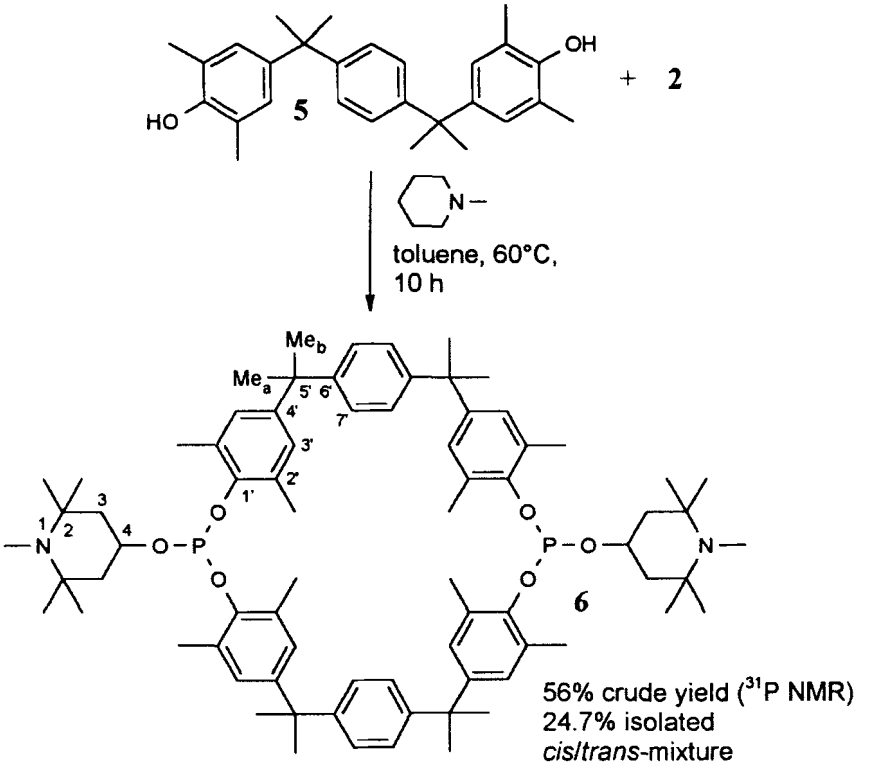
Phosphorous acid monoester dichloride **2** reacts with bisphenol **3** under conditions of high dilution (2.7 mmol of **2** and **3** per litre solvent) in a (2 + 2) cyclocondensation reaction to give the macrocycle **4** (Scheme 2) in low yield. It could be separated from oligomeric compounds (^{31}P NMR: δ = 130.8) by their different solubility in *n*-hexane. *Cis*- and *trans*-diastereomers of **4** are formed in a 1:1 ratio. They could be distinguished by means of ^{31}P NMR in the crude product giving one singlet each at 136.8 and 137.2 ppm, respectively. One diastereomer could be enriched by recrystallization from toluene/acetonitrile. The cyclic structure was proved for the mixture of isomers by CI mass spectrometry showing the expected mass peak of the protonated macrocyclic product **4** at 855.5 [MH^+].



SCHEME 2 Synthesis of the macrocycle **4**

Phosphorous acid monoester dichloride **2** also reacts with bisphenol **5** in a (2 + 2) cyclocondensation to afford the phosphite macrocycle **6** as a mixture of *cis*- and *trans*-diastereomers (Scheme 3). In this case the crude yield of macrocycle **6** according to the ^{31}P NMR spectrum (δ = 138.3) in comparison with oligomeric products (δ = 139.7) is higher than the yield obtained for macrocycle **4**. This suggests that a favorable preorganization of the very flexible bisphenol **5** leads to the preferred formation of the macrocyclic product **6**. It can be recrystallized from toluene/acetonitrile without further pre-treatment. The two diastereomers of **6** could not be distinguished by means of ^{31}P, ^{1}H or ^{13}C NMR spectroscopy. This became only possible after oxidation to the corresponding phosphates as shown below. The non-equivalence of 5′-Me_a and 5′-Me_b according to their *cis*- or *trans*-position in the macrocyclic ring was not resolved either by ^{1}H NMR or ^{13}C NMR spectroscopy. The cyclic structure was again proved by mass spectrometry (CI, MALDI-TOF).

The oxidation of **6** with cumenehydroperoxide gives the corresponding phosphate **7** (Scheme 4). In this case the two diastereomers can be distinguished in the ^{31}P NMR spectrum (δ = −12.4, −12.2). The ratio of the diastereomers



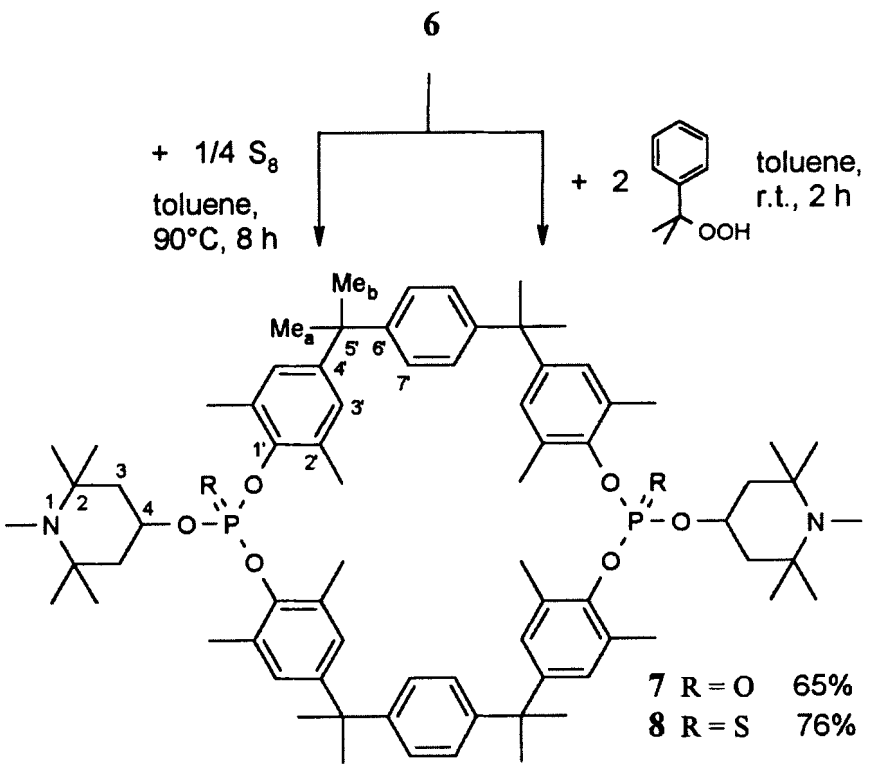
SCHEME 3 Synthesis of the macrocycle **6**

after recrystallization was about 1:8. Besides mass spectrometry an important indication for the existence of the macrocyclic structure is given by ^{13}C NMR spectroscopy. The two methyl groups 5′-Me$_a$ and 5′-Me$_b$ which are in a *cis*- or *trans*-position in respect to the exocyclic piperidine moiety attached to the phosphorus are not equivalent and show two singlets in the ^{13}C NMR spectrum at 30.9 and 30.8 ppm.

The sulfurization of **6** leads in a straightforward reaction to the *cis/trans*-mixture of the macrocyclic thiophospate **8** (Scheme 4).

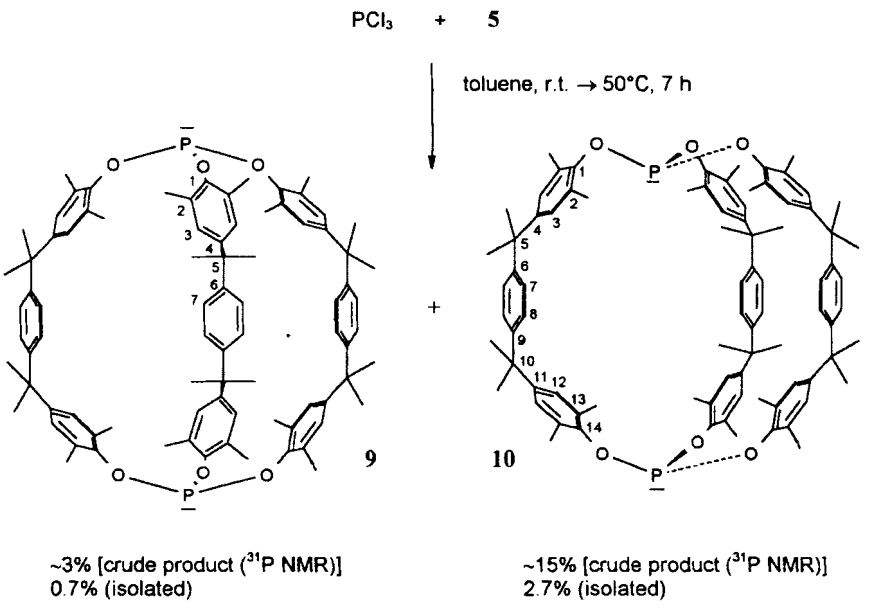
Phosphite Cryptands

The one-pot reaction of PCl_3 with bisphenol **5** under conditions of high dilution (5.4 mmol of **5** per liter solvent) yields the cryptands **9** and **10** in low to medium yields (Scheme 5).



SCHEME 4 Synthesis of the macrocycles **7** and **8**

This fact is remarkable as two cyclization steps must be involved in the formation of the cryptands. The reaction probably proceeds via a (2 + 2) cyclocondensation of PCl_3 and bisphenol **5** followed by a (1 + 1) cyclocondensation of the macrocyclic intermediate **11** and bisphenol **5** (Scheme 6a). Alternative routes, for instance via a (1 + 1) cyclocondensation of the open chain phosphite **12** with PCl_3 (Scheme 6b), seem to be less likely. The latter would require the simultaneous existence of PCl_3 and phosphite **12** which is only possible if the esterification of the phosphorous acid mono- and diester intermediates proceeds faster than those of PCl_3. In this system, however, a stepwise esterification was observed. So it could be shown that at room temperature the last esterification step is very slow due to the steric hindrance by the methyl groups in *ortho*-position of bisphenol **5**. After 1 h stirring at room temperature almost no phosphorous triesters could be observed by means of ^{31}P NMR spectroscopy. During that time the macrocyclic phosphorous acid diester monochloride intermediate **11** is formed [^{31}P NMR: δ = 173.6, 173.1 (*cis*- and *trans*-isomer)] which was

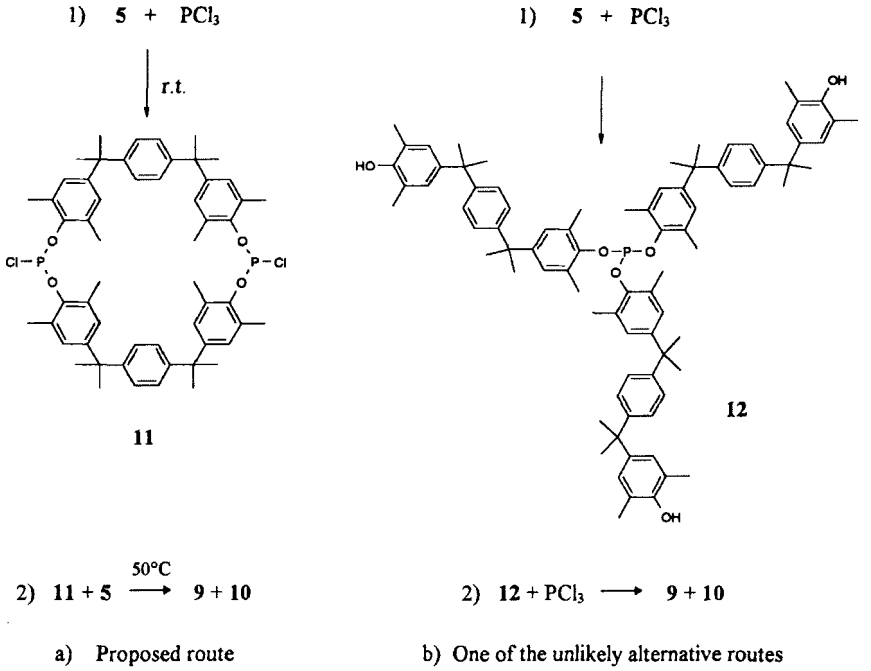


SCHEME 5 Synthesis of the macrocycles **9** and **10**

not isolated. Subsequent heating to 50°C initiates the final esterification step. Now in a (1 + 1) cyclocondensation the cryptands **9** and **10** can be formed (Scheme 6a).

The diastereomers **9** and **10** can be isolated in the same way as compound **6**. The cryptands without free OH groups are more soluble in benzine than oligomers or simple macrocycles containing free OH groups. These products give a broad peak in the ^{31}P NMR spectrum at 142.1–141.8 ppm. **9** and **10** can even be separated by fractional crystallization from *i*-PrOH/$CHCl_3$ under cooling with a dry ice/acetone mixture. The cooling seems necessary because a partial transformation of **10** into **9** is possible during heating of the solution. This means that the *in*-lone pair in compound **10** can invert at higher temperatures. *Out,out*-cryptand **9** is probably thermodynamically more stable than **10**.

It is interesting to note that the ^{31}P NMR shifts for the *in*- and *out*-phosphorus in **10** are extremely different [**10**: ^{31}P NMR: δ = 147.2 (*in*), 128.0 (*out*)]. The chemical shift of the *in*-phosphorus belongs to the highest ^{31}P NMR shifts observed for phosphites whereas the shift for the *out*-phosphorus lies in the normal region for this type of compounds. The non-equivalence of the two sides of molecule **10** is also reflected in the ^{1}H and ^{13}C NMR spectra. ^{1}H NMR shows different signals each for 3- and 12-H, 2- and 13-Me and 5- and 10-Me. 7- and

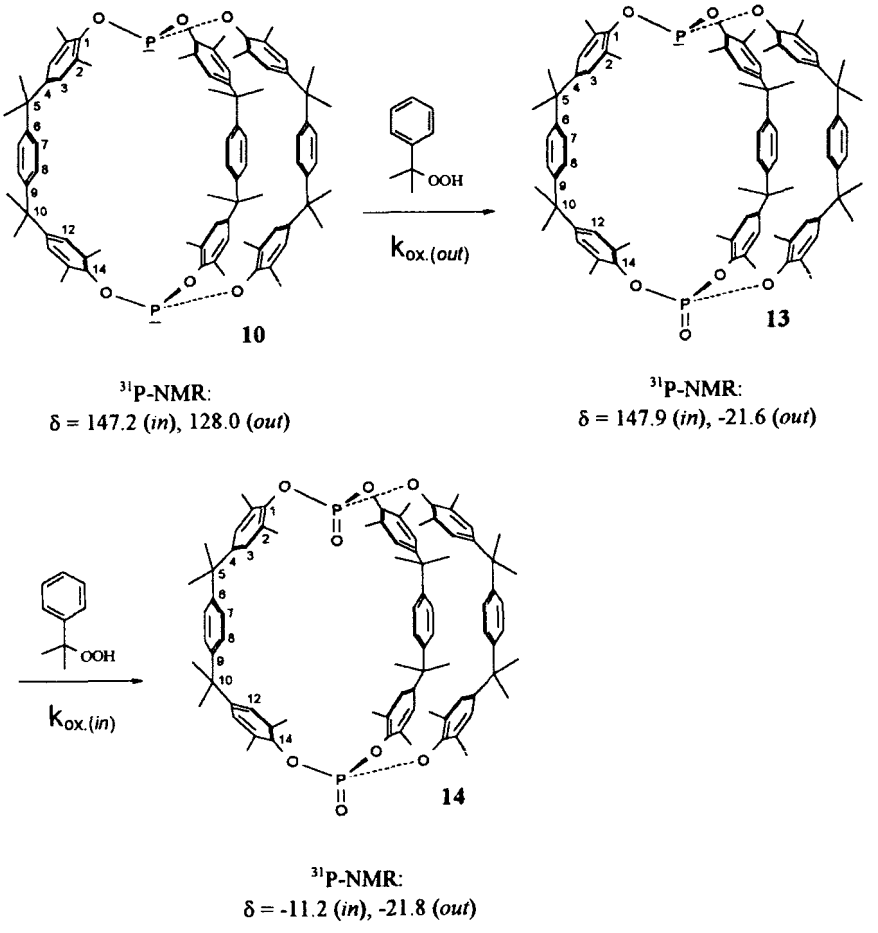


SCHEME 6 Two ways of the formation of **9** and **10** from the reaction of **5** with PCl_3

8-H give an AB-type spectrum. The same is true for ^{13}C NMR. All pairs of corresponding carbon atoms from the two non-equivalent sides of the molecule give two signals each.

In compound **9**, however, both sides of the molecule are equivalent which is demonstrated by the ^{31}P, ^{1}H and ^{13}C NMR spectra showing only one signal for each corresponding pair of atoms.

Another important indication for the existence of structures **9** and **10** is provided by an oxidation experiment (Scheme 7, Figure 1). Compound **10** containing about 10% of isomer **9** was oxidized directly in the NMR tube with an excess of cumenehydroperoxide at room temperature. It could be proved that the *in*-phosphorus in **10** is much less reactive (about 3000 times) than the *out*-phosphorus (Figure 1, Table I). The *out*-phosphorus (^{31}P NMR: δ = 128.0) was completely oxidized within 25 min to give the ^{31}P NMR phosphate peak of compound **13** at −21.6 ppm. This caused a shift of the ^{31}P NMR peak of the *in*-phosphorus from 147.2 ppm (see compound **10**) to 147.9 ppm (see compound **13**). In contrast, the oxidation rate of the *in*-phosphorus in compound **10** is unusually low (Table I). Only half of the phosphite is converted into the completely oxidized phosphate **14** after 10 days. Thereby the ^{31}P NMR peak of the



10

^{31}P-NMR:
δ = 147.2 (*in*), 128.0 (*out*)

13

^{31}P-NMR:
δ = 147.9 (*in*), -21.6 (*out*)

14

^{31}P-NMR:
δ = -11.2 (*in*), -21.8 (*out*)

SCHEME 7 Oxidation of cryptand **10** with cumenehydroperoxide

in-phosphorus slowly turns into the *in*-phosphate peak of **14** at −11.2 ppm. This oxidation also influences the ^{31}P NMR shift of the already oxidized *out*-phosphorus, slightly shifting the signal from −21.6 (see compound **13**) to −21.8 ppm (see compound **14**). The isomer **9** is completely oxidized with the same rate as the *out*-phosphorus in **12** to give the *out,out*-cryptand **15**.

The slow oxidation of the *in*-lone pair in **10** strongly supports the structural proposal for this molecule demonstrating that the lone pair is efficiently shielded inside the cryptand. The isomeric mixture of the entirely oxidized products **14** and **15** was isolated. The ^{31}P NMR shifts for the two phosphorus atoms in **14** are again remarkably different [**14**: ^{31}P NMR: δ = −11.2 (*in*), −21.8 (*out*)].

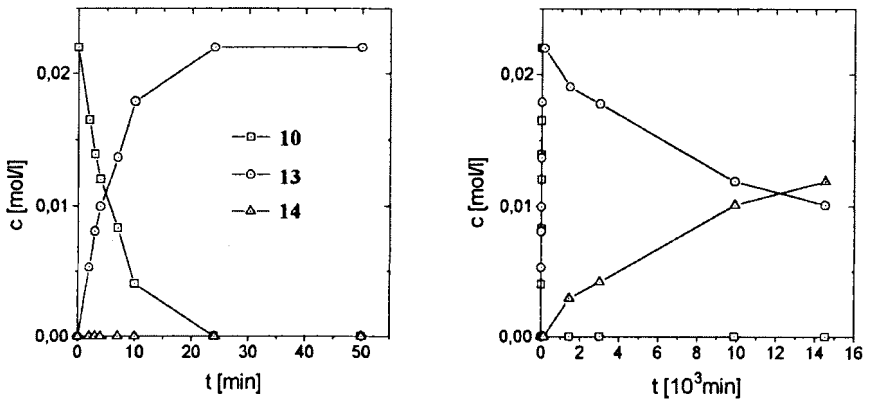


FIGURE 1 Concentrations of compounds **10**, **13** and **14** during the oxidation of **10** with an excess of cumenehydroperoxide

In the ^{1}H NMR spectrum of **14** the two non-equivalent sides of the molecule also lead to different chemical shifts for corresponding protons from the two sides of the molecule. As in compound **10** two different signals each for 3- and 12-H, 2- and 13-Me and 5- and 10-Me are obtained. 7- and 8-H also give an AB-type spectrum.

EXPERIMENTAL

The melting points were determined on a Boëtius melting point apparatus. ^{1}H NMR (TMS internal reference), ^{13}C NMR (TMS internal reference) and ^{31}P NMR spectra (85% H_3PO_4 external reference) were recorded on a Bruker AC-200 P spectrometer. ^{13}C NMR peaks were assigned by means of DEPT (Distortionless Enhancement by Polarisation Transfer). The atoms in the schemes are numbered according to their theoretical magnetic non-equivalence excluding non-equivalence phenomena caused by hindered rotation. This effect is not always resolved in the NMR spectra, however. IR spectra were performed on a Nicolet 250 FT-IR spectrometer. The mass spectra were recorded on a Finnigan MAT 95-A spectrometer and MALDI-TOF mass spectra were performed on a Kratos Kompact MALDI II (Shimadzu Europa GmbH, Duisburg,

TABLE I Oxidation rates of the two different phosphorus atoms in **10**

	$k_{ox}[s^{-1}]$ (298 K)
out-phosphorus	$2.74*10^{-3}$
in-phosphorus	$1*10^{-6}$

Germany) using a N_2-laser source (λ = 337 nm), a pulse duration of 3 ns, a positive polarity and 20 kV acceleration voltage. The microanalyses were recorded on a CHN-S analyzer (Carlo Erba). The solvents were purified by conventional methods. 4-Hydroxy-1,2,2,6,6-pentamethyl-piperidine **1** was kindly donated by HÜLS AG. Bisphenol **5** was kindly donated by MITSUI PETROCHEMICALS CO.

Phosphorous acid 1,2,2,6,6-pentamethyl-4-piperidinyl ester dichloride (2)

65 g (0.473 mol) of PCl_3 were dissolved in 500 ml of toluene and placed in a 1 l three-neck flask equipped with a condenser, dropping funnel and a gas inlet tube under nitrogen atmosphere. The flask was cooled with ice/NaCl. A solution of 27.6 g (0.161 mol) of 4-hydroxy-1,2,2,6,6-pentamethylpiperidine (**1**) and 18 g (0.182 mol) of 1-methylpiperidine in 250 ml of toluene was added within one hour under continuous stirring and cooling. Following this the solution was allowed to warm to room temperature and was stirred for another two hours. The precipitated hydrochloride was filtered off. The toluene was evaporated to yield a yellow oil. The product **2** could be purified by distillation *in vacuo*. Yield: 10 g (22%); b.p. 76–86°C/0.1 torr (colorless oil, very sensitive to moisture).

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = 177.7.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 5.04 (m_c, 1 H, 4-H), 2.20 (s, 3 H, 1-Me), 1.93 (dd, J = 4.3, 12.2 Hz, 2 H, *trans*-3-H), 1.61 (dd, J = 11.7, 11.7 Hz, 2 H, *cis*-3-H), 1.14, 1.07 (2 s, 6 H each, *cis*-2-Me, *trans*-2-Me).

^{13}C NMR ($CDCl_3$, 50.3 MHz): 76.2 (d, $^{2}J_{PC}$ = 9.7 Hz, C-4), 55.6 (C-2), 47.9 (C-3), 33.1, 20.8 (2 Me each, *trans*-2-Me, *cis*-2-Me), 27.9 (1-Me).

1,2,2,6,6-pentamethyl-4{[2,2,14,14-tetramethyl-20-[(1,2,2,6,6-pentamethyl-4-piperidyl)oxy]-7,9,19,21-tetraoxa-8,20-diphosphapentacyclo[20.2.2.2^{3,6}.2^{10,13}.2^{15,18}]dotriaconta-1(24),3,5,10,12,15,17,22,25,27,29,31-dodecaen-8-yl]oxy}piperidine 4

1 l of toluene was placed in a flame-dried 2 l flask. A solution of 1.0 g (4.4 mmol) of bisphenol **3** and 4.0 g (40.0 mmol) of 1-methylpiperidine in 400 ml of toluene and simultaneously a solution of 1.2 g (4.4 mmol) phosphorous acid dichloride **2** in 200 ml of toluene were slowly dropped into the solvent. The solution was stirred for three days at room temperature. The precipitated hydrochloride was filtered off and the solvent was evaporated. The residue was refluxed for 10 min with *n*-hexane (500 ml) and kept at 0°C overnight. The

precipitated solid was filtered off and disposed. After evaporation of the solvent macrocycle **4** crystallized from the colorless oily residue after three days. It was recrystallized from toluene/acetonitrile to give **4** as a mixture of *cis*- and *trans*-diastereomers in a 1:1.7 ratio. M.p. 202–208°C; yield: 136 mg (7.2%) (colorless crystals).

The two diastereomers could be distinguished and assigned in the ^{1}H- and ^{13}C NMR spectra because of their different intensities. NMR data are given for the main isomer. Where distinguishable data for the other diastereomer are indicated (#). Otherwise the NMR peaks of the isomers coincide.

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = 136.8, 137.2#.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 6.94 (d, J = 8.6 Hz, 8 H, 3′-H), 6.58 (d, J = 7.9 Hz, 8 H, 2′-H), 6.56# (d, J = 8.6 Hz, 8 H, 2′-H), 4.93 (m_c, 2 H, 4-H), 2.19 (s, 6 H, 1-Me), 1.99 (dd, J = 3.6, 12.0 Hz, 4 H, *trans*-3-H), 1.64* (dd, J = 12.0, 12.0 Hz, 4 H, *cis*-3-H), 1.54 (s, 24 H, 5′-Me), 1.13 (s, 12 H, *cis*- or *trans*-2-Me), 1.04 (s, 12 H, *cis*- or *trans*-2-Me).* The signal is partly covered.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 149.5 (d, $^{2}J_{PC}$ = 5.7 Hz, C-1′), 149.4# (d, $^{2}J_{PC}$ = 5.9 Hz, C-1′), 146.5# (d, $^{5}J_{PC}$ = 1.7 Hz, C-4′), 146.4 (d, $^{5}J_{PC}$ = 1.7 Hz, C-4′), 127.9 (C-3′), 121.0# (d, $^{3}J_{PC}$ = 5.8 Hz, C-2′), 120.9 (d, $^{3}J_{PC}$ = 6.0 Hz, C-2′), 68.3 (C-4), 55.5 (C-2), 48.9 (d, $^{3}J_{PC}$ = 2.6 Hz, C-3), 42.1 (C-5′), 33.3, 20.81 (*trans*-2-Me, *cis*-2-Me), 30.8 (5′-Me), 28.01 (1-Me).

IR (KBr): **** tilde error **** = 2968 cm^{-1} (C-H), 2920 (C-H), 2855 (C-H), 1600 (C = C_{ar}), 1500 (C = C_{ar}), 1445, 1370 (H-C-H), 1360, 1237, 1208, 1173, 1027 (P-O-C), 871, 857, 838.

MS (CI, pos., methane); m/z (%): 855.5 (100) [MH^+].

$C_{50}H_{68}N_2O_6P_2$ (855.0) calcd. C 70.23 H 8.02 N 3.28%

found: C 70.17 H 8.27 N 3.27%

1,2,2,6,6-pentamethyl-4-{[2,2,7,7,10,16,19,19,24,24,27,33,36,37,42,43-hexadecamethyl-30-[(1,2,2,6,6-pentamethyl-4-piperidyl)oxy]-12,14,29,31-tetraoxa-13,30-diphosphaheptacyclo[30.2.2.2^{3,6}.2^{8,11}.2^{15,18}.2^{20,23}.2^{25,28}]-hexatetraconta-1(34),3,5,8,10,15,17,20,22,25,27,32,35,37,39,41,43,45-octadecaen-13-yl]oxy}piperidine 6

A solution of 2.2 g (8.1 mmol) of phosphorous acid dichloride **2** in 1.5 l of toluene was placed in a flame-dried 2 l flask. A solution of 3.3 g (8.1 mmol) of bisphenol **5** and 2.0 g (20.2 mmol) of 1-methylpiperidine in 200 ml of toluene was dropped into the mixture at room temperature within 5 h. The reaction mixture was heated to 60°C and continuously stirred at this temperature for 10 h. The hydrochloride formed was filtered off and the solvent was evaporated. A

viscous oil was obtained which crystallized after few hours. Phosphite **6** could be obtained as a *cis/trans*-mixture by recrystallization from toluene/acetonitrile. Yield: 1.2 g (24.7%); m.p. 243–247°C (colorless crystals). The diastereomers could not be distinguished by means of ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = 138.3.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 7.00 (s, 8H, 3′- or 7′-H), 6.70 (s, 8 H, 3′- or 7′-H), 4.86 (m_c, 2 H, 4-H), 2.17 (s, 6 H, 1-Me), 2.05 (s, 24 H, 2′-Me), 1.95 (dd, J = 4.3, 13.6 Hz, 4 H, *trans*-or *cis*-3-H), 1.60* (d, br., J = 13.6 Hz, 4 H, *cis*-or *trans*-3-H), 1.53 (s, 24 H, 5′-Me), 1.08 (s, 12 H, *cis*- or *trans*-2-Me), 0.98 (s, 12 H, *cis*- or *trans*-2-Me). *The signal is partly covered.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 147.5, 146.9 (C-4′, C-6′), 146.3 (d, $^{2}J_{PC}$ = 1.8 Hz, C-1′), 129.6 (d, $^{3}J_{PC}$ = 2.9 Hz, C-2′), 127.3, 126.2 (C-3′, C-7′), 67.9 (d, $^{2}J_{PC}$ = 5.7 Hz, C-4), 55.4 (C-2), 48.9 (d, $^{3}J_{PC}$ = 2.6 Hz, C-3), 41.9 (C-5′), 33.3, 20.61 (*trans*-2-Me, *cis*-2-Me), 31.0 (5′-Me), 28.01 (1-Me), 18.1 (d, $^{4}J_{PC}$ = 5.8 Hz, 2-Me, or two singlets due to hindered rotation).

IR (KBr): **** tilde error **** = 2968 cm^{-1} (C-H), 2925 (C-H), 2850 (C-H), 1482 (H-C-H), 1370 (H-C-H), 1350, 1300, 1220, 1195, 1167, 1120, 1003 (P-O-C), 900, 837.

MS (CI pos., methane); m/z (%): 1204 (100) [MH^+].

MALDI-TOF-MS (matrix 2,4,6-trihydroxyacetophenone); m/z (%): 1202 (100) [MH^+].

$C_{76}H_{104}N_2O_6P_2$ (1203.6) calcd. C 75.84 H 8.71 N 2.33%

found: C 75.72 H 9.07 N 2.25%

2,2,7,7,10,16,19,19,24,24,27,33,36,37,42,43-hexadecamethyl-13,30-di[(1,2,2,6,6-pentamethyl-4-piperidyl)oxy]-12,14,29,31-tetraoxa-13λ^5,30λ^5-diphosphaheptacyclo[30.2.2.2^{3,6}.2^{8,11}.2^{15,18}.2^{20,23}.2^{25,28}]-hexatetraconta-1(34),3,5,8,10,15,17,20,22,25,27,32,35,37,39,41,43,45-octadecaen-13,30-dione 7

121 mg (0.1 mmol) of macrocyclic phosphite **6** and 61 mg (0.4 mmol) of cumenehydroperoxide were dissolved in 20 ml of toluene. The solution was stirred for two hours at room temperature. Afterwards toluene was evaporated. The colorless oil obtained could be crystallized from acetonitrile to yield **7** as a mixture of *cis*- and *trans*-diastereomers in an about 1:8 ratio. Yield: 81 mg (65.6%); m.p. > 360°C (white crystals).

NMR data are given for the main isomer. Where distinguishable data for the other diastereomer are indicated (#). Otherwise the NMR peaks of the isomers coincide.

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = −12.4, −12.2#.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 6.97 (s, 8 H, 3′- or 7′-H), 6.71 (s, 8 H, 3′- or 7′-H), 4.69 (m_c, 2 H, 4-H), 2.13 (s, 6 H, 1-Me), 2.11 (s, 24 H, 2′-Me), 1.83 (dd, J = 4.3, 12.1 Hz, 4 H, *trans*-3-H), 1.52 (s, 24 H, 5′-Me), 1.46* (dd, J = 11.7, 11.7 Hz, 4 H, *cis*-3-H), 1.05 (s, 12 H, *cis*- or *trans*-2-Me), 0.93 (s, 12 H, *cis*- or *trans*-2-Me).* The signal is partly covered.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 147.5 (C-4′, C-6′), 146.1 (d, $^2J_{PC}$ = 9.3 Hz, C-1′), 129.5 (d, $^3J_{PC}$ = 3.2 Hz, C-2′), 127.4, 126.2 (C-3′, C-7′), 74.2 (d, $^2J_{PC}$ = 6.4 Hz, C-4), 55.3 (C-2), 47.4 (d, $^3J_{PC}$ = 4.4 Hz, C-3), 41.9 (C-5′), 33.3, 20.41 (*trans*-2-Me, *cis*-2-Me), 30.9, 30.8 (5′-Me_a, 5′-Me_b), 27.91 (1-Me), 17.2 (2′-Me).

IR (KBr): **** tilde error **** = 2968 cm^{-1} (C-H), 2932 (C-H), 2872 (C-H), 1483 (H-C-H), 1379 (H-C-H), 1363, 1284, 1233, 1180, 1160, 1112, 1029, 1008 (P-O-C), 985, 974, 934, 890.

MS (CI pos., methane); m/z (%): 1235 (42) [MH^+], 1082 (90) [MH^+-pip], 929 (100) [MH^+-2 pip].

$C_{76}H_{104}N_2O_8P_2$ (1235.6) calcd.: C 73.87 H 8.48 N 2.27%

found:. C 73.93 H 8.81 N 2.34%

2,2,7,7,10,16,19,19,24,24,27,33,36,37,42,43-Hexadecamethyl-13,30-di[(1,2,2,6,6-pentamethyl-4-piperidyl)oxy]-12,14,29,31-tetraoxa-13λ^5,30λ^5-diphosphaheptacyclo-[30.2.2.2^{3,6}.2^{8,11}.2^{15,18}.2^{20,23}.2^{25,28}]-hexatetraconta-1(34),3,5,8,10,15,17,20,22,25,27,32,35,37,39,41,43,45-octadecaen-13,30-dithione 8

253 mg (0.21 mmol) of macrocyclic phosphite **6** and 54 mg (1.69 mmol) of sulfur were dissolved in 20 ml of toluene. The solution was heated to 90°C and stirred for 8 h. After cooling to room temperature acetonitrile (20 ml) was added which led to the precipitation of **8** as mixture of *cis*- and *trans*-diastereomers. Yield: 203 mg (76.3%); m.p. 248–52°C (colorless crystals).

NMR data are given for the main isomer. Where distinguishable data for the other diastereomer are indicated (#). Otherwise the NMR peaks of the isomers coincide.

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = 54.1, 54.0#.

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 6.99 (s, 8 H, 3′- or 7′-H), 6.67 (s, 8 H, 3′- or 7′-H), 4.80 (m_c, 2 H, 4-H), 2.13 (s, 6 H, 1-Me), 2.12 (s, 24 H, 2′-Me), 1.75 (dd, J = 3.9, 12.1 Hz, 4 H, *trans*-3-H), 1.54 (s, 24 H, 5′-Me), 1.43 (dd, J = 11.9, 11.9 Hz, 4 H, *cis*-3-H), 1.04 (s, 12 H, *cis*- or *trans*-2-Me), 0.94 (s, 12 H, *cis*- or *trans*-2-Me).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 147.7 (d, $^5J_{PC}$ = 2.3 Hz, C-4′), 147.6 (C-6′), 146.9 (d, $^2J_{PC}$ = 10.7 Hz, C-1′), 129.8 (d, $^3J_{PC}$ = 3.6 Hz, C-2′), 128.2,

126.3 (C-3', C-7'), 75.0 (d, $^2J_{PC}$ = 5.9 Hz, C-4), 55.4 (C-2), 47.0 (d, $^3J_{PC}$ = 4.3 Hz, C-3), 41.9 (C-5'), 33.3, 20.41 (*trans*-2-Me, *cis*-2-Me), 30.6 (br., 5'-Me), 27.91 (1-Me), 18.0 (2'-Me).

IR (KBr): **** tilde error **** = 2967 cm^{-1} (C-H), 2931 (C-H), 2871 (C-H), 1509 (C-H_{ar}), 1482 (H-C-H), 1378 (H-C-H), 1362, 1308, 1259, 1215, 1174, 1158, 1111, 1028, 1005 (P-O-C), 982, 953, 926, 884, 832, 761, 753.

MS (CI pos., methane); m/z (%): 1268 (2) [MH^+], 1114 (100) [MH^+-pip], 961 (57) [MH^+-2 pip].

$C_{76}H_{104}N_2O_6S_2P_2$ (1267.7) calcd.: C 72.00 H 8.27 N 2.21 S 5.06%
found: C 71.55 H 8.54 N 2.14 S 4.87%

4,7,7,12,12,15,21,24,24,29,29,32,37,40,40,45,45,48,51,56,57,62,63,68-tetracosamethyl-2,17,19,34,35,50-hexaoxa-1,18-diphosphaundecacyclo-[15.15.15.2^{3,6}.2^{8,11}.2^{13,16}.2^{20,23}.2^{25,28}.2^{30,33}.2^{36,39}.2^{41,44}.2^{46,49}]octahexaconta-3,5,8,10,13,15,20,22,25,27,30,32,36,38,41,43,46,48,51,53,55,57,59,61,63,65,67-heptacosaene (9 and 10)

4 g (9.9 mmol) of bisphenol **5** and 4 g (39.6 mmol) of TEA were dissolved in 1.8 l of toluene in a flame-dried 2 l flask. 0.9 g (6.6 mmol) of PCl_3 in 50 ml of toluene were added. The solution was stirred for 1 h at room temperature. Afterwards it was heated to 50°C and stirred for another 6 h at this temperature. The hydrochloride formed was removed and the solvent was evaporated. A viscous oil was obtained. The crude product was refluxed with 200 ml of benzine (boiling range 90–110°C). The solution was separated from the insoluble residue and kept at 0°C for two days. During that time a white precipitate appeared which mainly consisted of oligomers and hydrolysis and oxidation products. The solid was separated and disposed. The solvent was evaporated from the solution to yield again a viscous oil. The whole procedure with benzine was repeated twice. The oily product now obtained crystallized and contained only compounds **11** and **12**. The two isomers could be separated by repeated fractional crystallization from *i*-PrOH/$CHCl_3$ under cooling with dry ice/acetone.

Out, out-*phosphite cryptand 9*

Yield: 30 mg (0.7%); decomposition at ~320°C (white crystals).

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = 129.7.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 7.10 (s, 12 H, 7-H), 6.59 (s, 12 H, 3-H), 1.93 (s, 36 H, 2-Me), 1.61 (s, 36 H, 5-Me).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 147.3 (C-6), 147.1 (d, C-1 or C-4, J_{PC} not determined), 146.7 (d, C-1 or C-4, J_{PC} not determined), 129.0 (d, $^3J_{PC}$ =

2.3 Hz, C-2), 127.6 (C-3), 126.4 (C-7), 41.9 (C-5), 30.6 (5-Me), 17.9 (d, $^4J_{PC}$ = 5.8 Hz, 2-Me).

In, out-*phosphite cryptand 10*

Yield: 115 mg (2.7%); decomposition at ~320°C (white crystals).

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = 147.2 (*in*), 128.0 (*out*).

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 6.93 (d, J = 8.1 Hz, 6 H, 7- or 8-H), 6.91 (d, J = 8.1 Hz, 7- or 8-H), 6.74 (s, 6 H, 3- or 12-H), 6.53 (s, 6 H, 3-or 12-H), 2.08 (s, 18 H, 2-or 13-Me), 1.89 (s, 18 H, 2-or 13-Me), 1.53 (s, 18 H, 5-or 10-Me), 1.51 (s, 18 H, 5-or 10-Me).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 148.2, 146.8 (C-6, C-9), 147.4 (d, $^2J_{PC}$ = 6.1 Hz, C-1 or C-14), 147.1 (d, $^5J_{PC}$ = 2.5 Hz, C-4 or C-11), 146.6 (d, $^5J_{PC}$ = 1.3 Hz, C-4 or C-11), 145.9 (d, $^2J_{PC}$ = 4.6 Hz, C-1 or C-14), 130.0 (d, $^3J_{PC}$ = 3.8 Hz, C-2 or C-13), 129.2 (d, $^3J_{PC}$ = 2.1 Hz, C-2 or C-13), 127.6 (d, $^4J_{PC}$ = 1.3 Hz, C-3 or C-12), 127.3 (br., C-3 or C-12), 126.4 (C-7 or C-8), 126.2 (C-7 or C-8), 42.2 (C-5 or C-10), 42.0 (C-5 or C-10), 31.2 (5-Me or 10-Me), 31.1 (5-Me or 10-Me), 18.2 (d, $^4J_{PC}$ = 5.4 Hz, 2-Me or 13-Me), 17.5 (d, $^4J_{PC}$ = 5.0 Hz, 2-Me or 13-Me).

$C_{84}H_{96}O_6P_2$ (1262.67) MS (mixture of **9** and **10**, CI pos., methane); m/z (%): 1263 (100) [MH^+].

Oxidation of a mixture of cryptands 9 and 10

The experiment was carried out directly in the NMR tube and the fate of the phosphorus compound was monitored by means of ^{31}P NMR spectroscopy. 31 mg (0.024 mmol) of a mixture of cryptands **9** and **10** (ratio 1:10) were placed in an NMR tube and dissolved in 0.95 ml of C_6D_6. 51 mg (50 μl, 0.338 mmol) of cumenehydroperoxide (freshly distilled) were added. The temperature was kept at 25°C by air flow thermostatting. At the beginning of the reaction every 60 s spectra were recorded. At a later stage of the reaction the periods were extended according to the reaction rate. The degree of conversion was determined by the ratio of the ^{31}P NMR peak heights to the total of all peak heights.

4,7,7,12,12,15,21,24,24,29,29,32,37,40,40,45,45,48,51,56,57,62,63,68-tetracosamethyl-2,17,19,34,35,50-hexaoxa-1λ^5, 18λ^5-diphosphaundecacyclo-[15.15.15.2^{3,6}.2^{8,11}.2^{13,16}.2^{20,23}.2^{25,28}.2^{30,33}.2^{36,39}.2^{41,44}.2^{46,49}]octa-hexaconta-3,5,8,10,13,15,20,22,25,27,30,32,36,38,41,43,46,48,51,53,55,57,59,61,63,65,67-heptacosaen-1,18-dione (14 and 15)

The mixture of the *in,out*- and *out,out*-phosphate cryptands **13** and **14** was taken from the oxidation experiment of compounds **9** and **10** after completion of the reaction. C_6D_6 was evaporated and the residue was washed with *n*-BuOH to

yield a mixture of **13** and **14** (ratio ~1:10) as a white powder. M.p. > 360°C.

^{31}P NMR signals could be assigned according to the different oxidisability of the phosphite peaks and the appearance of the corresponding phosphate peaks during the oxidation experiment and from the molar ratio of the two isomers. ^{1}H NMR data for **14** could be assigned taking the molar ratio of the isomers **14** and **15** into account.

In, out-***phosphate cryptand 14***

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = −11.2 (*in*), −21.8 (*out*).

^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 7.01 (d, J = 9.2 Hz, 6 H, 7- or 8-H), 6.99 (d, J = 9.2 Hz, 6 H, 7- or 8-H), 6.82 (s, 6 H, 3- or 12-H), 6.62 (s, 6 H, 3- or 12-H), 2.16 (s, 18 H, 2- or 13-Me), 2.02 (s, 18 H, 2- or 13-Me), 1.59 (s, 18 H, 5- or 10-Me), 1.58 (s, 18 H, 5- or 10-Me).

Out, out-***phosphate cryptand 15***

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = −21.0.

$C_{84}H_{96}O_8P_2$ (1295.55) MS (mixture of **14** and **15**, DCI pos., methane); m/z (%): 1296 (100) [MH^+].

4,7,7,12,12,15,21,24,24,29,29,32,37,40,40,45,45,48,51,56,57,62,63,68-tetracosamethyl-2,17,19,34,35,50-hexaoxa-1λ^5,18-diphosphaundecacyclo-[15.15.15.2^{3,6}.2^{8,11}.2^{13,16}.2^{20,23}.2^{25,28}.2^{30,33}.2^{36,39}.2^{41,44}.2^{46,49}]octahexaconta-3,5,8,10,13,15,20,22,25,27,30,32,36,38,41,43,46,48,51,53,55,57,59,61,63,65,67-heptacosaen-1-one (13)

^{31}P NMR data were taken from the oxidation experiment.

^{31}P NMR (C_6D_6, 81.1 MHz): δ = 147.9 (*in*), −21.6 (*out*).

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