elusive to optical spectroscopic methods. The HMD radical cation, on the other hand, appears to be more stable and may be accessible by gentle oxidation of either HMP or HMD. Several approaches to $HMD^{\bullet+}$ will be pursued.

Our calculations further indicate that the adduct formed by interaction of cyclopropenylium cation and cyclopropenyl radical may have a structure altogether different from that considered before. We plan to further pursue this problem. Finally, we note that of the five radical cations of composition $(CH)_6$, the prismane species discussed here is the third one on which we have performed calculations. The interesting features of a fourth isomer, benzvalene, will be reported shortly.

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Novel Ditopic Receptors Based on the P_2N_2 Diphosphazane Ring: Synthesis and X-ray Structural Characterization of Cis and Trans Bis(crown ether) Annellated $1,3,2\lambda^5,4\lambda^5$-Diazadiphosphetidine 2,4-Disulfide

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Abstract: The 1,3,2,4-diazadiphosphetidine ring is used for the construction of the bis(crown ether) derivative **1**, which occurs as cis and trans isomers. Refluxing triethylene glycol dianilino ether **3** with hexamethylphosphorous triamide (HMPT) in toluene followed by addition of sulfur gave **1** as a crystalline material in isolated yields ranging from 25% to 73%. The compounds have been characterized by a combination of ^1H, ^{13}C, and ^{31}P NMR and mass spectral data. The structural assignments of the two diastereoisomers are based on X-ray structural analysis. Crystal data at 291 K are as follows: *cis*-**1**·H_2O [Cu Kα (λ = 1.541 78 Å)] a = 11.030 (9) Å, b = 11.169 (3) Å, c = 18.101 (13) Å, α = 85.68 (4)°, β = 87.06 (6)°, γ = 86.57 (4)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.087 for 5888 reflections with $I \geq 2.5\sigma(I)$; *trans*-**1**·$2CH_2Cl_2$ [Mo Kα (λ = 0.710 69 Å)] a = 11.757 (3) Å, b = 11.140 (4) Å, c = 9.393 (1) Å, α = 65.51 (2)°, β = 101.12 (2)°, γ = 100.63 (3)°, Z = 1, triclinic, space group $P\bar{1}$, R = 0.054 for 3531 reflections with $I \geq 2.5\sigma(I)$. In the cis isomer, a water molecule is encapsulated in the cavity formed by the two macrocyclic moieties facing each other. The trans isomer, which crystallizes with two dichloromethane molecules, lies on a crystallographic center of symmetry. The macrocyclic intermediate precursor **4** is characterized together with the bis(crown) derivative **5**. The tervalent parent compounds are extremely sensitive to moisture. The macrocycle **8** containing a P(O)H fragment is a degradation product.

Numerous macrocyclic compounds have been designed and prepared for complexation of metal ions and neutral guests, and interest in macrocyclic polyhetero ligand systems continues unabated. The search for new macrocyclic hosts with higher specificities toward binding of ionic and neutral species is particularly attractive and exemplified by the recently reported preorganized structures of spherands,[1] cavitands,[2] calixarenes,[3] and cryptophanes.[4] Thus far, the majority of such systems contains the crown ether structure with oxygen, nitrogen, or sulfur atoms as binding subunits, although some phosphorus-containing ligands have also been reported and are being actively studied. Polyphosphamacrocycles have received considerable attention as potential ligands only in recent years, and interest in their synthesis and complexing properties is growing very rapidly.[5] Besides the macrocyclic phosphanes, macrocyclic compounds containing phosphorus atoms directly bonded to oxygen, sulfur, or nitrogen atoms have been reported.[6,7]

Our studies in this area are focused on the design of phosphorus macrocycles that involve aminophosphine groups with connectivities to crown ether like structure.[7] This choice is considered attractive for the following reasons: (1) di- and triaminophosphine provide an efficient building block for the preparation of phosphorus macrocycles with a well-defined structure around the phosphorus atoms; (2) aminophosphines and phosphoramides are potentially powerful ligands and can considerably enhance the

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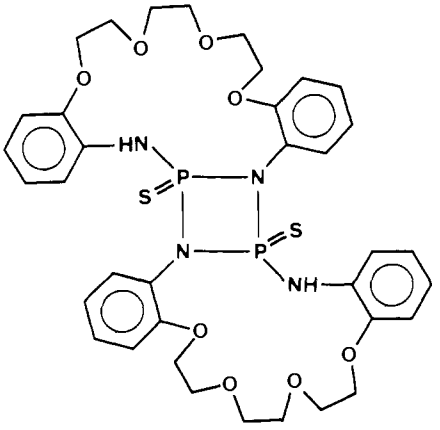
complexing properties of these new receptors; (3) the various coordinations of the phosphorus atom offer new possibilities in complexing chemistry.

We report here the preparation and structural characterization of the bismacrocyclic compound **1**, where two 17-membered rings



1

are joined at a diazadiphosphetidine ring, forming a tricyclic structure. 1,3,2,4-Diazadiphosphetidines have received much attention from both synthetic and structural chemists.[8] For this ring system it is possible to assign geometric isomers depending on the bond orientations of the phosphorus substituents. Therefore, two different structures are expected for **1** that exhibit different orientations of the two macrocyclic rings toward each other. The two isomers give rise to novel bismacrocycles with syn or anti relationships, and we have undertaken the structural characterization and solution study of both isomers. In addition to **1**, other species are formed in the course of the reaction. Some have been isolated and characterized as new macrocyclic compounds. Their formation and structure also attracted our attention as they are examples of phosphorus derivatives including the aminophosphine group in a macrocyclic structure. It was therefore crucial to identify these species unambiguously. The results of this work are described thereafter.

Experimental Section

General Methods. All manipulations involving tervalent phosphorus compounds were carried out under N_2 or Ar atmosphere. Solvents were freshly distilled under N_2 from Na (toluene) or CaH_2 (DMF) before use. Mass spectra were obtained with a Nermag R10-10C spectrometer from the Centre d'Analyse USTMG/CNRS in Grenoble. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker WP80SY and AM300 spectrometer at room temperature unless otherwise noted. ^1H and ^{13}C chemical shifts were measured relative to $(CH_3)_4Si$; ^{31}P chemical shifts were measured relative to H_3PO_4; δ (ppm) values downfield from the standard are defined as positive. ^{13}C and ^{31}P NMR spectra are proton-decoupled unless otherwise noted. The reported multiplicities of ^{13}C NMR spectra represent ^{31}P–^{13}C couplings. For compound **1**, aromatic carbon-13 atoms may belong to A_2X (NC_6H_5) or AA'X (NHC_6H_5) systems, where A and A' are the phosphorus atoms. Consequently, the splittings measured between the outer and inner lines of the corresponding triplet patterns are reported as J values. Analytical size exclusion chromatography (SEC) was performed on Lichrogel PS columns (E. Merck) with CH_2Cl_2 as the mobile phase. Elemental analyses were performed by the Service Central d'Analyses, CNRS. Melting points are uncorrected.

Triethylene Glycol Bis(2-nitrophenyl ether) (2).[7] Triethylene glycol ditosylate[9] (39.55 g, 86 mmol) was added to a mixture of 2-nitrophenol (24 g, 172 mmol) and K_2CO_3 (23.84 g, 172 mmol) in DMF (200 mL). After being stirred and heated to reflux for 16 h, the resulting solution was partly concentrated in vacuo and then poured into 750 mL of water. The precipitate that had formed was collected, washed with water, and recrystallized from MeOH to give **2** (25.7 g, 76%, pale yellow): mp 63 °C; ^1H NMR ($CDCl_3$) δ 3.67–4.40 (m, 12 H, CH_2), 6.83–7.90 (m, 8 H, Ar). Anal. Calcd for $C_{18}H_{20}N_2O_8$: C, 55.10; H, 5.14; N, 7.14. Found: C, 55.31; H, 5.12; N, 7.10. The same yield was obtained by using the commercially available 1,2-bis(2-chloroethoxy)ethane instead of triethyleneglycol ditosylate.

Triethylene Glycol Bis(2-aminophenyl ether) (3).[7] A solution of triethylene glycol bis(2-nitrophenyl) ether (**2**, 10 g, 25.5 mmol) in EtOH (180 mL) was warmed until complete dissolution. Catalyst (1 g of 5% Pd–C) was then added, and hydrazine monohydrate (7.42 mL, 7.66 g, 153 mmol) was slowly added from an addition funnel. The mixture was refluxed for 1 h and then filtered through a pad of Celite. The solvent was removed under reduced pressure, and the residue recrystallized from MeOH–Et_2O at −20 °C to give 7.8 g (92%) of **3**: mp 53 °C; ^1H NMR ($CDCl_3$) δ 3.63–4.25 (m, 16 H, CH_2 and NH_2), 6.50–6.95 (m, 8 H, Ar); ^{13}C NMR ($CDCl_3$) δ 68.35, 69.77, 70.68 (CH_2), 112.95, 115.16, 118.10, 121.71, 136.93, 146.11 (Ar). Anal. Calcd for $C_{18}H_{24}N_2O_4$: C, 65.04; H, 7.28; N, 8.43. Found: C, 65.27; H, 7.40; N, 8.47.

Synthesis of the Bis(crown ether) Annellated 1,3,2λ⁵,4λ⁵-Diazadiphosphetidine 2,4-Disulfide (1).[10] Hexamethylphosphorous triamide (HMPT) (1.9 mL, 10.4 mmol) was added to a dry toluene (1 L) solution of **3** (3.32 g, 10 mmol). The mixture was stirred and heated at 110–115 °C for 3–4 days until no more evolution of dimethylamine was observed. The dimethylamine formed during the reaction was evacuated by a stream of dry N_2. The reaction was monitored by ^{31}P NMR and size exclusion chromatography on sulfurized samples of the reaction mixture. After completion of the reaction, sulfur (0.37 g, 11.5 mmol) was added, and the mixture further stirred and heated for 1 h. A trans/cis ratio of approximately 9:1 was estimated from the ^{31}P NMR spectra of the crude mixture. It was mainly constant within the experimental conditions described here. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was redissolved in a minimum amount of a hot mixture of toluene–CH_2Cl_2. The solution was cooled to room temperature and then stored in a −20 °C freezer. Collection of the first fraction of crystallized material yielded pure *trans*-**1**: mp 266–268 °C; ^{31}P NMR (CD_2Cl_2) δ 44.9; ^1H NMR (CD_2Cl_2) δ 3.56–3.88 (m, 14 H, CH_2O), 3.95–4.30 (m, 10 H, CH_2O), 6.78–7.15 (m, 14 H, Ar, NH), 7.38, 7.74 (m, 4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 67.90, 68.92, 69.40, 69.87, 70.72, 72.34 (CH_2O), 112.43, 112.57, 120.93, 121.26, 123.99, 124.24, 124.47, 125.29 (t, J = 6.0 Hz), 125.83, 129.05 (t, J = 1.8 Hz), 150.39 (t, J = 4.4 Hz), 152.29 (t, J = 4.3 Hz, Ar); FAB MS 785 (M + 1). Anal. Calcd for $C_{36}H_{42}N_4O_8P_2S_2$: C, 55.09; H, 5.39; N, 7.14; P, 7.89; S, 8.17. Found: C, 54.40; H, 5.57; N, 7.02; P, 7.94, S, 7.89.

Further crystallization yielded samples contaminated with *cis*-**1**. Repeated recrystallization from CH_2Cl_2 yielded more *trans*-**1** and pure *cis*-**1** as colorless crystals: mp 259–261 °C; ^{31}P NMR (CD_2Cl_2) δ 47.5; ^1H NMR (CD_2Cl_2) δ 3.37 (m, 2 H, CH_2O), 3.45–3.70 (m, 12 H, CH_2O), 3.81 (m, 4 H, CH_2O), 4.14 (m, 6 H, CH_2O), 6.70–7.10 (m, 12 H, Ar, NH), 7.27, 7.41, 7.93 (m, 6 H, Ar); ^{13}C NMR (CD_2Cl_2) δ 68.87, 69.27, 69.27, 69.67, 70.98, 71.50 (CH_2O); 113.12, 113.36, 121.17, 121.37, 122.47, 123.91, 123.96, 128.38, 129.33 (t, J = 4.6 Hz), 130.12, 149.73 (t, J = 4.6 Hz), 155.15 (t, J = 4.2 Hz, Ar); EI MS m/e 784 (M^+). Anal. Calcd for $C_{36}H_{42}N_4O_8P_2S_2$: C, 55.09; H, 5.39; N, 7.14; P, 7.89; S, 8.17. Found: C, 54.90; H, 5.39; N, 7.06; P, 8.38; S, 8.57.

Overall yields ranging from 25% to 73% were observed from several runs. This large variation was mainly explained by the high sensitivity of the phosphorus(III) species to moisture. Crystals of *trans*-**1** and *cis*-**1** recrystallized from toluene or CH_2Cl_2 are mainly solvates. They become cloudy when heated under vacuum at 100 °C or after standing at room temperature for several days. They probably lose trapped solvent and/or water molecules. Toluene and/or water were indeed observed in the NMR spectra of the freshly recrystallized compounds. Crystals of *trans*- and *cis*-**1** were dried at 80–100 °C under vacuum for several hours.

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(10) Systematic name for **1**: 6,7,9,10,12,13,27,28,30,31,33,34-dodecahydro-21*H*,42*H*-tetrabenzo[*b*,*b*',*g*,*g*'][1,3,2,4]diazadiphospheto[1,2-*d*:3,4,-*d*']bis[1,9,12,15,4,6,5]tetraoxadiazaphosphacycloheptadecine 20,41-disulfide.

20,20′-[Ethylenebis(oxyethyleneoxy-*o*-phenyleneimino)]bis-[6,7,9,10,12,13,20,21-octahydro-19*H*-dibenzo[*b*,*g*][1,9,12,15,4,6,5]-tetraoxadiazaphosphacycloheptadecine] 20,20′-Disulfide (5). After successive removal of **1**, the residual mother solution was concentrated under reduced pressure. Chromatography of the residue on silica gel using ethyl acetate as eluent yielded a small amount of **5** as a white solid, which turned resinous at around 120–150 °C. **5** was also isolated by successive washings of the residue with ethyl acetate. The remaining white precipitate was recrystallized from hot ethyl acetate to give pure **5**: ^{31}P NMR ($CDCl_3$) δ 42.6; ^{1}H NMR ($CDCl_3$) δ 3.55–3.86 (m, 24 H, CH_2O), 3.99–4.22 (m, 12 H, CH_2O), 6.20 (d, $J_{P,H}$ = 8.2 Hz, 4 H, N*H*), 6.28 (d, $J_{P,H}$ = 11.9 Hz, 2 H, N*H*), 6.69–6.96 (m, 18 H, Ar), 7.47 (m, 2 H, Ar), 7.63 (m, 4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 68.66, 69.30, 70.44 (CH_2O, cycle), 68.90, 69.62, 70.96 (CH_2O), 113.10, 118.82 (d, J = 3.8 Hz), 121.82, 121.92, 130.42 (d, J = 2.6 Hz), 147.99 (d, J = 8.8 Hz, Ar, cycle), 112.70, 117.72 (d, J = 3.1 Hz), 121.60, 121.70, 130.34 (d, J = 2.8 Hz), 147.52 (d, J = 8.7 Hz, Ar); FAB MS 1117 (M + 1). Anal. Calcd for $C_{54}H_{66}N_6O_{12}P_2S_2$: C, 58.05; H, 5.95; N, 7.52; P, 5.54; S, 5.74. Found: C, 57.63; H, 5.59; N, 7.37; P, 5.76; S, 5.80.

20-(Dimethylamino)-6,7,9,10,12,13,20,21-Octahydro-19*H*-dibenzo-[*b*,*g*][1,9,12,15,4,6,5]tetraoxadiazaphosphacycloheptadecine 20-Sulfide (4).[7] Experimental conditions similar to those used for the synthesis of **1** were followed, but the reaction time was reduced to 15–20 h. At this time, sulfur was added, and the mixture further stirred and heated for 1 h. After cooling to room temperature, the solvent was evaporated to dryness, and the residue was flash chromatographed (SiO_2, 2% CH_3OH/CH_2Cl_2) to give **4** as a white crystalline solid (36%, yield not optimized): mp 140–142 °C; ^{31}P NMR ($CDCl_3$) δ 53.7; ^{1}H NMR ($CDCl_3$) δ 2.88 (d, $J_{P,H}$ = 11.5 Hz, 6 H, NCH_3), 3.65–3.85 (m, 8 H, CH_2O), 4.06–4.25 (m, 4 H, CH_2O), 6.04 (d, $J_{P,H}$ = 8.9 Hz, 2 H, N*H*), 6.79–6.99 (m, 6 H, Ar), 7.31 (d, 2 H, Ar); ^{13}C NMR ($CDCl_3$) δ 37.22 (d, J = 5.8 Hz, NCH_3), 69.11, 69.34, 70.55 (CH_2O), 113.70, 117.28 (d, J = 3.8 Hz), 121.17, 122.19, 131.31 (d, J = 3.5 Hz), 147.47 (d, J = 9.0 Hz, Ar); EI MS m/e 437 (M^+). Anal. Calcd for $C_{20}H_{28}N_3O_4PS$: C, 54.91; H, 6.45; N, 9.60; P, 7.08; S, 7.33. Found: C, 54.52; H, 6.57; N, 9.56; P, 7.15; S, 7.29.

6,7,9,10,12,13,20,21-Octahydro-19*H*-dibenzo[*b*,*g*][1,9,12,15,4,6,5]-tetraoxadiazaphosphacycloheptadecine 20-Oxide (8). Prolonged heating of the reaction mixture containing the tervalent derivatives resulted inevitably in the formation of an insoluble product. When the solution was allowed to cool to room temperature, more precipitate formed, and the crystalline compound was recovered by filtration. Similarly, once the reaction mixture has been exposed to air, a yellowish insoluble product was recovered together with a variable quantity of a white solid compound. The latter was obtained by a tentative recrystallization of the crude material in toluene to give a crystalline product identical with the former precipitate and identified as **8**: mp 170–171 °C (dec); yields as high as 45% were obtained from some runs. Formation of **8** is attributed to moisture, which cannot be rigorously excluded from the reaction apparatus. **8** is only slightly soluble in common solvents and slowly decomposes in solution. ^{31}P NMR ($CDCl_3$) δ 0.12; ^{1}H NMR ($CDCl_3$) δ 3.65–3.82 (m, 8 H, CH_2O), 4.09–4.17 (m, 4 H, CH_2O), 6.02 (d, br, $J_{P,H}$ = 8.7 Hz, 2 H, N*H*), 6.80–6.94 (m, 6 H, Ar), 7.31–7.39 (m, 2 H, Ar), 7.72 (dt, br, $J_{P,H}$ = 630.3 Hz, $J_{H,H}$ = 1.8 Hz, 1 H, P*H*); ^{13}C NMR ($CDCl_3$) δ 69.37, 69.73, 70.57 (CH_2O), 114.81, 118.63 (d, J = 4.6 Hz), 122.38, 122.68, 131.16, 147.82 (d, J = 7.0 Hz, Ar); FAB MS 379 (M + 1). Anal. Calcd for $C_{18}H_{23}N_2O_5P$: C, 57.14; H, 6.13; N, 7.40; P, 8.19. Found: C, 57.17; H, 6.18; N, 7.34; P, 8.09.

Characterization of the Diphosph(III)azane Compounds. Samples of the hot reaction mixture containing the phorphorus(III) species were examined by ^{31}P NMR. For this purpose a sample was periodically transferred into a 10-mm-o.d. NMR tube mounted on a side arm of the appropriate glassware to prevent any contact with the air. The NMR tube was immediately fitted on a vacuum line, 0.4 mL of C_6D_6 was added for lock purpose, and the tube was sealed under argon. Often upon cooling a precipitate appeared, and strong heating was needed to redissolve the product. Phosphorus-31 NMR spectra of the clear solution were immediately recorded, the probe temperature being maintained at 50–80 °C.

Crystallographic Structure Determinations. Crystals of *cis*-**1**·H_2O and *trans*-**1**·$2CH_2Cl_2$ were obtained upon recrystallization from dichloromethane. Care was taken to mount the crystals wet with solvent and to seal them in capillaries, as they become cloudy when standing in the open air for several days.

***cis*-1·H_2O.** X-ray data were collected at ambient temperature with a Huber 424+511 four-circle automated diffractometer equipped with a graphite monochromator. The unit-cell parameters were obtained by least-squares refinement of the setting angles of 17 reflections in the range 8° ≤ 2θ ≤ 26°. No significant change was detected in the intensity of the standard reflection (1,−2,2) measured every 50 reflections. Empirical absorption corrections were applied to the intensity data between 0.67 and 1.25. Table I provides other details of crystal parameters, data collection, and refinement.

Table I. Crystallographic Parameters for *cis*-**1** and *trans*-**1**

	cis-**1**·H_2O[a]	*trans*-**1**·$2CH_2Cl_2$[b]
T, K	291	291
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.030 (9)	11.757 (3)
b, Å	11.169 (3)	11.140 (4)
c, Å	18.101 (13)	9.393 (1)
α, deg	85.68 (4)	65.51 (2)
β, deg	87.06 (6)	101.12 (2)
γ, deg	86.57 (4)	100.63 (3)
vol, Å^3	2217 (2)	1091.0 (6)
d(calcd), g cm^{-3}	1.20	1.45
formula wt	802.84	954.69
Z	2	1
cryst size, mm	0.2 × 0.4 × 0.4	0.14 × 0.22 × 0.35
F(000), electrons	844	496
radiation λ, Å	Cu Kα, 1.541 78	Mo Kα, 0.710 69
scan mode	2θ–θ	ω
scan rate, deg/min	4–20	1.3–30
abs coeff μ, cm^{-1}	21.5	4.92
2θ range, deg	3–135	3–55
total rflctns	7999	5022
$I \geq 2.5\sigma(I)$	5888	3531
R	0.087	0.054
R_w	0.118	0.059
goodness of fit, S	1.52	1.85
max shift/esd	0.11	0.21
max peak in diff map, e Å^{-3}	0.56	0.72
min density in diff map, e Å^{-3}	−0.61	−0.70

[a] $C_{36}H_{42}N_4O_8P_2S_2 \cdot H_2O$. [b] $C_{36}H_{42}N_4O_8P_2S_2 \cdot 2CH_2Cl_2$.

The crystal structure was solved by direct methods using SHELXS 86[11] and refined by full-matrix least-squares calculations (SHELX 76)[12] to a final R index of 0.087. Hydrogen atoms were placed at idealized positions and refined with a common isotropic temperature factor (B = 10 Å^2). The non-hydrogen atoms were refined anisotropically by using F ($w = 1/(\sigma^2 + 0.011F^2)$). In addition to the main molecule and a water molecule (O(53)) in the cavity, a number of positions appeared in the difference Fourier synthesis, outside the cavity. These could not be interpreted properly and are tentatively attributed to disordered solvent and/or water molecules. The atoms labeled O(54) to O(59) represent these positions (Table II). The high values of their temperature factors are in agreement with the assumption of a disorder.

***trans*-1·$2CH_2Cl_2$.** X-ray data were collected at room temperature with a Syntex $P2_1$ automated diffractometer equipped with a graphite monochromator. The lattice parameters were obtained by least-squares refinement of the setting angles of 15 reflections in the range 5° ≤ 2θ ≤ 30°. No significant deviation was detected in the intensity of the standard reflection (1,0,3) checked every 50 reflections. The structure, solved by direct methods using SHELXS 86,[11] was refined by full-matrix least-squares calculations (SHELX 76)[12] to an R index of 0.054. Hydrogen atoms were located from a difference Fourier synthesis and were refined isotropically with a common thermal parameter (B = 6 Å^2). Other non-hydrogen atoms were refined anisotropically by using F ($w = 1/(\sigma^2 + 0.00077F^2)$). Crystal data and details of the structure determination and refinement are reported in Table I.

During the refinement a disorder appeared around the solvent molecule, due to different orientations of the chlorine atoms of the dichloromethane around a common carbon atom. One site occupation factor was refined for these secondary positions (C11B to C14B) and one for the main positions (C128, C129), keeping the total value in respect with the stoichiometry. Tables II and III provide the atomic coordinates for *cis*-**1**·H_2O and *trans*-**1**·$2CH_2Cl_2$, respectively, and Tables IV and V list bond distances and angles. Additional crystallographic data are available as supplementary material (see the paragraph at the end of the paper).

Results and Discussion

Synthesis. Treatment of 2-nitrophenol and triethylene glycol ditosylate[9] (or triethyleneglycol dichloride) in a suspension of

(11) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175–189.

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Table II. Atomic Coordinates (×10⁴) and Equivalent Temperature Factors (Å²) for *cis*-**1**·H_2O

atom	x/a	y/b	z/c	B_{eq}[a]
N1	1268 (3)	7515 (3)	7212 (2)	4.15 (2)
P2	1448 (1)	7574 (1)	8135 (1)	4.26 (2)
N3	317 (3)	8329 (3)	8533 (2)	4.28 (2)
C4	−597 (4)	7908 (4)	9074 (3)	4.77 (2)
C5	−1211 (4)	8799 (4)	9464 (2)	4.67 (2)
O6	−881 (3)	9945 (3)	9290 (2)	5.08 (2)
C7	−1550 (4)	10914 (5)	9612 (3)	6.22 (2)
C8	−1093 (5)	12067 (5)	9267 (3)	6.93 (2)
O9	−1421 (4)	12207 (4)	8516 (3)	7.52 (2)
C10	−1184 (5)	13345 (5)	8139 (4)	9.82 (2)
C11	148 (5)	13567 (5)	8039 (4)	10.17 (2)
O12	767 (5)	12704 (4)	7644 (4)	10.52 (2)
C13	1962 (5)	12847 (5)	7484 (5)	26.51 (2)
C14	2774 (5)	12240 (5)	7425 (5)	13.38 (2)
O15	2721 (4)	10981 (4)	7574 (3)	7.49 (2)
C16	3435 (4)	10403 (5)	8085 (3)	5.89 (2)
C17	3301 (4)	9184 (5)	8225 (3)	4.95 (2)
N18	2427 (3)	8637 (3)	7832 (2)	3.97 (2)
P19	2420 (1)	8401 (1)	6922 (1)	4.04 (1)
N20	1744 (3)	9521 (3)	6443 (2)	4.17 (2)
C21	2233 (4)	10385 (4)	5911 (2)	4.19 (2)
C22	1398 (4)	11129 (4)	5522 (3)	4.49 (2)
O23	200 (3)	10895 (3)	5691 (2)	5.02 (2)
C24	−694 (5)	11664 (4)	5320 (3)	5.99 (2)
C25	−1918 (5)	11285 (5)	5641 (3)	6.90 (2)
O26	−2083 (4)	11698 (4)	6362 (3)	7.71 (2)
C27	−3270 (5)	11487 (5)	6714 (4)	9.86 (2)
C28	−3513 (5)	10174 (5)	6866 (4)	9.64 (2)
O29	−2683 (4)	9655 (5)	7331 (3)	9.89 (2)
C30	−2893 (5)	8557 (6)	7698 (4)	11.17 (2)
C31	−2500 (5)	7569 (5)	7312 (4)	10.00 (2)
O32	−1155 (3)	7490 (3)	7292 (2)	7.03 (2)
C33	−581 (4)	6656 (4)	6884 (3)	5.56 (2)
C34	684 (4)	6669 (4)	6821 (2)	4.99 (2)
C35	−901 (4)	6731 (4)	9199 (3)	6.55 (2)
C36	−1818 (4)	6431 (4)	9750 (3)	8.02 (2)
C37	−2393 (4)	7324 (5)	10129 (3)	7.29 (2)
C38	−2131 (4)	8494 (4)	9993 (3)	5.88 (2)
C39	4308 (4)	10987 (5)	8445 (3)	8.21 (2)
C40	4982 (4)	10296 (5)	8949 (4)	11.33 (2)
C41	4841 (4)	9106 (5)	9113 (4)	11.05 (2)
C42	3985 (4)	8511 (5)	8737 (3)	7.22 (2)
C43	3475 (4)	10549 (4)	5770 (3)	5.95 (2)
C44	3846 (4)	11446 (4)	5230 (3)	7.08 (2)
C45	3003 (4)	12172 (4)	4858 (3)	6.80 (2)
C46	1769 (4)	12014 (4)	4987 (3)	5.94 (2)
C47	−1180 (5)	5807 (4)	6531 (3)	7.38 (2)
C48	−522 (5)	5043 (4)	6097 (4)	9.22 (2)
C49	719 (5)	5062 (4)	6011 (4)	9.40 (2)
C50	1351 (5)	5887 (4)	6387 (3)	7.19 (2)
S51	1985 (2)	6095 (2)	8669 (1)	7.27 (2)
S52	3917 (2)	7731 (2)	6492 (1)	6.54 (2)
O53	−167 (3)	10282 (3)	7470 (2)	5.06 (2)
O54	3948 (5)	5532 (4)	4616 (4)	13.85 (2)
O55	4422 (5)	6039 (5)	784 (5)	20.51 (2)
O56	4626 (5)	4999 (5)	1220 (4)	19.66 (2)
O57	4723 (5)	5231 (5)	2113 (4)	21.63 (2)
O58	4432 (4)	5489 (4)	2673 (4)	12.36 (2)
O59	4371 (5)	5217 (5)	5192 (5)	44.67 (2)

[a] $B_{eq} = (^8/_3)\pi^2\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$.

K_2CO_3 in DMF at reflux temperature gave the intermediate dinitro derivative **2** (76%).[7,13] Reduction of **2** with hydrazine–palladium–carbon in ethanol produced the corresponding triethylene glycol bis(2-aminophenyl) ether **3** (92%).[7,13] The macrocyclization described here involves the reaction of the diamine **3** with hexamethylphosphorous triamide (HMPT) in refluxing toluene for 3–4 days, with a **3**:HMPT mole ratio of 1:1.04. The procedure is similar to that used to prepare 1,3-diaryl-2,4-dianilino-1,3,2λ³,4λ³-diazadiphosphetidines.[14] The bismacrocycle **1** was obtained by the in situ sulfurization of the thus-formed tervalent parent compound.

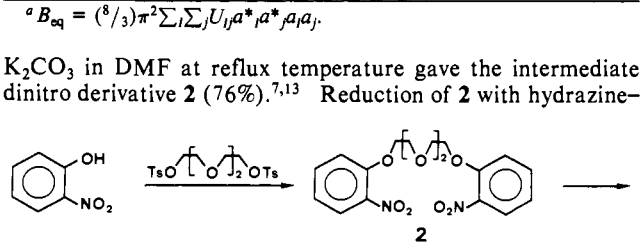

Table III. Atomic Coordinates (×10⁴) and Equivalent Temperature Factors (Å²) for *trans*-**1**·$2CH_2Cl_2$

atom	x/a	y/b	z/c	B_{eq}[a]
N1	5273 (2)	4568 (3)	1295 (3)	2.49 (4)
P2	3985 (1)	5056 (1)	256 (1)	2.41 (1)
N3	2994 (2)	3803 (3)	331 (3)	2.94 (5)
C4	3095 (3)	2665 (3)	68 (4)	3.05 (5)
C5	2284 (3)	2364 (4)	−1096 (4)	3.79 (7)
O6	1534 (2)	3273 (3)	−2009 (3)	4.73 (5)
C7	322 (4)	2805 (6)	−2129 (7)	6.01 (10)
C8	−111 (4)	2183 (5)	−585 (7)	6.01 (10)
O9	208 (3)	3054 (3)	197 (4)	5.37 (6)
C10	−317 (4)	2614 (5)	1596 (6)	5.42 (9)
C11	221 (4)	3505 (5)	2446 (6)	5.41 (9)
O12	1372 (2)	3165 (3)	3176 (4)	4.57 (5)
C13	1966 (3)	4016 (4)	3905 (5)	4.12 (7)
C14	3114 (3)	3557 (4)	4750 (4)	3.90 (7)
O15	3841 (2)	3740 (3)	3591 (3)	3.63 (4)
C16	4989 (3)	3570 (3)	4105 (4)	2.87 (5)
C17	5725 (3)	3995 (3)	2927 (3)	2.59 (5)
C18	3938 (3)	1825 (4)	947 (5)	4.15 (7)
C19	3956 (4)	687 (4)	688 (6)	5.20 (9)
C20	3145 (5)	375 (5)	−412 (7)	5.90 (11)
C21	2321 (4)	1212 (4)	−1305 (6)	5.06 (9)
C22	5455 (4)	3010 (4)	5683 (4)	3.76 (6)
C23	6632 (4)	2852 (4)	6090 (4)	4.18 (7)
C24	7336 (3)	3262 (4)	4951 (4)	3.80 (7)
C25	6899 (3)	3848 (3)	3360 (4)	3.29 (6)
S26	3353 (1)	6472 (1)	374 (1)	3.48 (2)
C27	7417 (7)	−266 (6)	5813 (8)	9.00 (18)
Cl28[b]	6817 (4)	288 (3)	3899 (4)	11.96 (10)
Cl29[b]	8903 (5)	470 (4)	5917 (8)	14.94 (16)
Cl1B[c]	8497 (9)	184 (11)	6975 (13)	6.33 (24)
Cl2B[c]	8508 (12)	366 (12)	4737 (17)	8.15 (36)
Cl3B[c]	8857 (10)	431 (12)	5294 (14)	4.47 (17)
Cl4B[c]	6235 (7)	−67 (9)	4711 (13)	5.41 (18)

[a] $B_{eq} = (^8/_3)\pi^2\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$. [b] Occupation factor 0.70. [c] Occupation factor 0.15.

The product of the reaction was shown by ^{31}P NMR spectroscopy to consist of essentially **1** as cis and trans isomers ($\delta(^{31}P)$ 47.5 and 44.9, respectively). In addition to **1**, the two macrocyclic compounds **4** ($\delta(^{31}P)$ 53.7) and **5** ($\delta(^{31}P)$ 42.6) were isolated. However, small quantities of other products were evident as well. These were not isolated nor characterized. They are assumed to be other condensation products of **3** and HMPT, including oligomeric materials. Their low abundance did not allow further investigations.

The new compounds *cis*-**1**, *trans*-**1**, **5**, and the previously reported macrocycle **4**[7] were characterized by spectral (^1H, ^{13}C, and ^{31}P NMR and MS) data. The *cis*-**1** isomer is a chiral molecule that is recovered as the racemic mixture, whereas the *trans*-**1** isomer is in the meso form. *cis*-**1** and *trans*-**1** isomers belong to systems of C_2 and C_i molecular symmetry, respectively, an insufficient condition to characterize easily both diastereoisomers, although the NMR spectra are distinguishable. The ^1H and ^{13}C NMR data for *cis*-**1** and *trans*-**1** do not provide any significant information about the configurational assignment. The expected AA′XX′ systems, formed by the NH protons and the phosphorus

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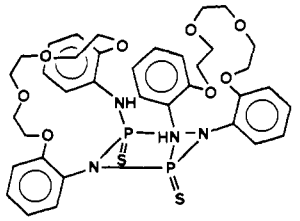
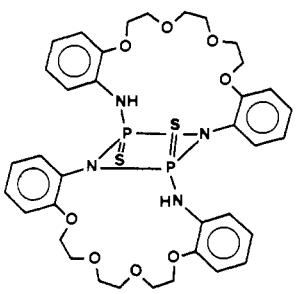
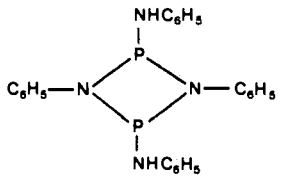


CIS-1



TRANS-1

atoms, were not resolved enough for an unambiguous analysis. $^{31}P,^{1}H$ coupled NMR spectra were recorded and exhibited different patterns: a broad multiplet with a width of 5 Hz at half-height for *cis*-**1**, and a broad triplet with external lines separated by 12 Hz for *trans*-**1**. The NH protons are shifted down field (6.8–7.0 ppm) as compared with the 5.65 ppm observed with the known $1,3,2\lambda^5,4\lambda^5$-diazadiphosphetidine 2,4-disulfide **7** $[(C_6H_5NH)P(S)NC_6H_5]_2$;[15] this is characteristic of hydrogen



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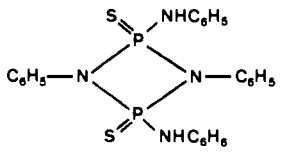
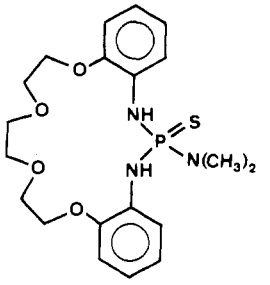


7

bonding, probably with molecules of water incorporated in the crown ether units.[16] Change of solvent resulted in slight modifications of the NMR spectra, an indication of specific interactions between **1** and solvent molecules. The configurational assignment of *cis*-**1** and *trans*-**1** was based on the X-ray crystallographic study (vide infra).

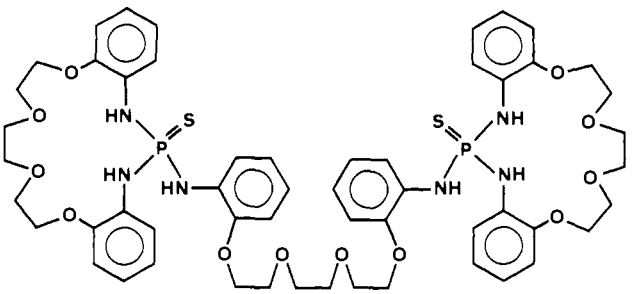
The macrocycle **4** is the first one formed in the early stages of the synthesis. When the reaction is quenched with sulfur after a 15–20-h refluxing time, **4** is the major compound recovered.[7]



4

It slowly disappears in the course of the reaction as observed on sulfurized samples periodically withdrawn and subjected to ^{31}P NMR analysis. From this result, we can conclude that **4** is directly obtained from the sulfurization of its parent tervalent derivative. Successive elimination of dimethylamine from HMPT results in the formation of the P(III) analogue of **4** ($\delta(^{31}P)$ 81.2 (toluene, 50 °C)), followed by condensation of two of these macrocycles, which leads to the formation of the stable diphosphazane ring. Other intermediates such as bis(dimethylamino) phosphorus compounds were not directly observed. If their formation does occur, they are rapidly transformed to the more stable cyclic compounds, within our experimental conditions.

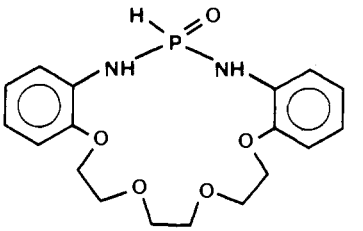
After successive removal of *trans*-**1** and *cis*-**1**, a chromatography of the remaining material was attempted to characterize other products from the reaction mixture. The bismacrocycle **5** was



5

thus isolated and clearly identified as a solid material, for which analysis and spectral data are consistent with the proposed formula. NMR spectra of **5** show two sets of resonances in relative areas 2:1 for the two macrocyclic units and the linear aminophenyl ether linkage, respectively. **5** might be formed by the condensation reaction of two molecules **4** with the starting compound **3**, a structure already found with phosphorus compounds involving a similar condensation reaction.[17] NMR spectra of **5** are subject to changes when traces of water are present in the solution. A low-field shift of 0.4 ppm is observed for the NH signal of the macrocyclic part, whereas the NH signal of the bridge chain shows no noticeable shift. Concomitantly, the water signal is shifted to low field. This is indicative of hydrogen bonds formation and suggests participation in specific hydrogen bonds of water molecules incorporated in the macrocyclic unit rather than with the linear polyether part of the molecule. **5** was also detected at the beginning of the reaction prior to the formation of the diazadiphosphetidine derivative. The products obtained depend critically upon reaction conditions. Compound **5** might be obtained in higher yield by using different conditions and more particularly a different 3:HMPT mole ratio. This aspect is being currently pursued. So far, bis(crown ether) derivatives have been designed and synthesized that show remarkable cation-complexing properties mostly due to their ability to form sandwich-type complexes.[18] In this connection, **5** would probably provide new complexes of cationic or neutral guests. The amido–phosphorus group may act as a binding subunit and enhance the complexing properties of such bismacrocyclic compounds.

In solution, the tervalent phosphorus species were very sensitive to degradation by atmospheric moisture, in contact with which they hydrolyzed after only a few minutes. The $1,3,2\lambda^3,4\lambda^3$-diazadiphosphetidine **6** $[(C_6H_5NH)PNC_6H_5]_2$ has been noted to decompose very rapidly in the air.[19] The macrocyclic phosphine oxide **8** containing a P–H bond ($\delta(^{31}P)$ 0.12, $^{1}J_{P,H}$ = 630.3 Hz)



8

was isolated from the reaction mixture eventually exposed to air. It must be pointed out that ^{31}P NMR signals corresponding to P(O)H group were possibly observed from samples withdrawn from the toluene solution of the P(III) species under nonstrictly anaerobic conditions. Similarly, some runs failed completely to produce **1**, probably for the same reasons. **8** was not the sole compound thus obtained, but other oxidation products were not

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Table IV. Bond Lengths and Angles for *cis*-1·H_2O

	Bond Lengths, Å		
P2–N1	1.699 (0.004)	P19–N1	1.695 (0.004)
C34–N1	1.426 (0.006)	N3–P2	1.631 (0.004)
N18–P2	1.695 (0.004)		
S51–P2	1.927 (0.002)	C4–N3	1.442 (0.006)
C5–C4	1.388 (0.006)	C35–C4	1.376 (0.007)
O6–C5	1.362 (0.006)	C38–C5	1.398 (0.006)
C7–O6	1.418 (0.006)	C8–C7	1.492 (0.007)
O9–C8	1.420 (0.008)	C10–O9	1.428 (0.007)
C11–C10	1.504 (0.008)	O12–C11	1.372 (0.008)
C13–O12	1.351 (0.008)	C14–C13	1.097 (0.008)
O15–C14	1.416 (0.007)	C16–O15	1.347 (0.007)
C17–C16	1.381 (0.007)	C39–C16	1.407 (0.007)
N18–C17	1.419 (0.006)	C42–C17	1.376 (0.007)
P19–N18	1.687 (0.004)	N20–P19	1.633 (0.004)
S52–P19	1.924 (0.002)	C21–N20	1.421 (0.006)
C22–C21	1.386 (0.006)	C43–C21	1.401 (0.006)
O23–C22	1.376 (0.006)	C46–C22	1.395 (0.006)
C24–O23	1.428 (0.006)	C25–C24	1.514 (0.007)
O26–C25	1.415 (0.008)	C27–O26	1.451 (0.007)
C28–C27	1.509 (0.008)	O29–C28	1.351 (0.008)
C30–O29	1.376 (0.008)	C31–C30	1.386 (0.009)
O32–C31	1.480 (0.006)	C33–O32	1.342 (0.006)
C34–C33	1.394 (0.006)	C47–C33	1.398 (0.007)
C50–C34	1.374 (0.006)	C36–C35	1.420 (0.007)
C37–C36	1.360 (0.007)	C38–C37	1.356 (0.007)
C40–C39	1.369 (0.008)	C41–C40	1.357 (0.008)
C42–C41	1.416 (0.008)	C44–C43	1.410 (0.007)
C45–C44	1.367 (0.007)	C46–C45	1.388 (0.007)
C48–C47	1.357 (0.007)	C49–C48	1.371 (0.007)
C50–C49	1.420 (0.008)		
	Distances from the Water Molecule		
O53···P2	3.58	O53···N3	2.84
O53···O9	3.18	O53···O12	2.99
O53···P19	3.58	O53···N20	2.87
O53···O23	3.25	O53···O26	3.25
O53···O29	2.93		
	Bond Angles, deg		
P19–N1–P2	96.3 (0.2)	C34–N1–P2	130.5 (0.3)
C34–N1–P19	129.5 (0.3)	N3–P2–N1	111.7 (0.2)
N18–P2–N1	82.6 (0.2)	N18–P2–N3	104.1 (0.2)
C4–N3–P2	129.2 (0.3)	S51–P2–N1	116.6 (0.2)
S51–P2–N3	115.5 (0.2)	S51–P2–N18	121.9 (0.2)
C5–C4–N3	114.9 (0.4)	C35–C4–N3	124.8 (0.4)
C35–C4–C5	120.2 (0.4)	O6–C5–C4	116.5 (0.4)
C38–C5–C4	119.7 (0.4)	C38–C5–O6	123.8 (0.4)
C7–O6–C5	119.6 (0.4)	C8–C7–O6	108.7 (0.4)
O9–C8–C7	108.8 (0.5)	C10–O9–C8	115.2 (0.5)
C11–C10–O9	113.4 (0.5)	O12–C11–C10	111.6 (0.5)
C13–O12–C11	116.8 (0.5)	C14–C13–O12	135.2 (0.6)
O15–C14–C13	121.4 (0.6)	C16–O15–C14	119.7 (0.5)
C17–C16–O15	116.6 (0.5)	C39–C16–O15	122.5 (0.5)
C39–C16–C17	120.8 (0.5)	N18–C17–C16	118.4 (0.4)
C42–C17–C16	121.2 (0.5)	C42–C17–N18	120.4 (0.4)
C17–N18–P2	129.7 (0.3)	P19–N18–P2	96.8 (0.2)
P19–N18–C17	129.6 (0.3)	N18–P19–N1	82.9 (0.2)
N20–P19–N1	103.5 (0.2)	S52–P19–N18	115.8 (0.1)
N20–P19–N18	112.2 (0.2)	S52–P19–N1	121.1 (0.2)
S52–P19–N20	116.5 (0.2)	C21–N20–P19	130.2 (0.3)
C22–C21–N20	116.3 (0.4)	C43–C21–N20	124.9 (0.4)
C43–C21–C22	118.8 (0.4)	O23–C22–C21	114.7 (0.4)
C46–C22–C21	121.5 (0.4)	C46–C22–O23	123.8 (0.4)
C24–O23–C22	116.7 (0.4)	C25–C24–O23	106.4 (0.4)
O26–C25–C24	107.9 (0.5)	C27–O26–C25	113.9 (0.5)
C28–C27–O26	113.9 (0.5)	O29–C28–C27	108.9 (0.5)
C30–O29–C28	119.4 (0.5)	C31–C30–O29	115.0 (0.6)
O32–C31–C30	107.5 (0.5)	C33–O32–C31	117.4 (0.4)
C34–C33–O32	116.3 (0.4)	C47–C33–O32	123.6 (0.4)
C47–C33–C34	120.1 (0.4)	C33–C34–N1	118.6 (0.4)
C50–C34–N1	120.8 (0.4)	C50–C34–C33	120.7 (0.4)
C36–C35–C4	119.3 (0.4)	C37–C36–C35	118.9 (0.4)
C38–C37–C36	122.4 (0.4)	C37–C38–C5	119.4 (0.4)
C40–C39–C16	116.8 (0.5)	C41–C40–C39	123.5 (0.5)
C42–C41–C40	119.7 (0.5)	C41–C42–C17	117.9 (0.5)
C44–C43–C21	119.5 (0.4)	C45–C44–C43	120.4 (0.4)
C46–C45–C44	120.6 (0.4)	C45–C46–C22	119.1 (0.4)
C48–C47–C33	119.1 (0.5)	C49–C48–C47	121.7 (0.5)
C50–C49–C48	120.1 (0.5)	C49–C50–C34	118.2 (0.5)

Table V. Bond Lengths and Angles for *trans*-1·$2CH_2Cl_2$[a]

	Bond Lengths, Å		
P2–N1	1.684 (0.002)	C17–N1	1.428 (0.004)
N3–P2	1.630 (0.003)	S26–P2	1.914 (0.001)
N1–P2*	1.706 (0.003)	C4–N3	1.419 (0.004)
C5–C4	1.414 (0.005)	C18–C4	1.388 (0.005)
O6–C5	1.363 (0.005)	C21–C5	1.385 (0.006)
C7–O6	1.425 (0.005)	C8–C7	1.470 (0.008)
O9–C8	1.404 (0.006)	C10–O9	1.420 (0.006)
C11–C10	1.501 (0.007)	O12–C11	1.435 (0.005)
C13–O12	1.402 (0.005)	C14–C13	1.489 (0.006)
O15–C14	1.438 (0.004)	C16–O15	1.363 (0.004)
C17–C16	1.407 (0.004)	C22–C16	1.390 (0.004)
C25–C17	1.383 (0.004)	C19–C18	1.392 (0.006)
C20–C19	1.376 (0.007)	C21–C20	1.372 (0.007)
C23–C22	1.386 (0.005)	C24–C23	1.355 (0.006)
C25–C24	1.393 (0.005)	Cl28–C27	1.692 (0.008)
Cl29–C27	1.791 (0.009)		
	Bond Angles, deg		
C17–N1–P2	135.9 (0.2)	N3–P2–N1	112.4 (0.1)
S26–P2–N1	121.2 (0.1)	S26–P2–N3	111.9 (0.1)
C4–N3–P2	127.9 (0.2)	C5–C4–N3	118.5 (0.3)
C18–C4–N3	122.0 (0.3)	C18–C4–C5	119.6 (0.3)
O6–C5–C4	117.1 (0.3)	C21–C5–C4	119.4 (0.4)
C21–C5–O6	123.5 (0.4)	C7–O6–C5	117.3 (0.3)
C8–C7–O6	112.4 (0.4)	O9–C8–C7	109.2 (0.4)
C10–O9–C8	112.9 (0.4)	C11–C10–O9	107.9 (0.4)
O12–C11–C10	108.6 (0.4)	C13–O12–C11	112.2 (0.3)
C14–C13–O12	110.0 (0.3)	O15–C14–C13	108.1 (0.3)
C16–O15–C14	117.3 (0.3)	C17–C16–O15	116.1 (0.3)
C22–C16–O15	124.4 (0.3)	C22–C16–C17	119.5 (0.3)
C16–C17–N1	120.9 (0.3)	C25–C17–N1	119.7 (0.3)
C25–C17–C16	119.4 (0.3)	C19–C18–C4	119.3 (0.4)
C20–C19–C18	121.1 (0.4)	C21–C20–C19	120.0 (0.4)
C20–C21–C5	120.7 (0.4)	C23–C22–C16	120.2 (0.3)
C24–C23–C22	120.1 (0.3)	C25–C24–C23	121.2 (0.3)
C24–C25–C17	119.7 (0.3)	Cl29–C27–Cl28	108.5 (0.4)
P2–N1–P2*	98.1 (0.1)	N1–P2–N1*	81.9 (0.2)
S26–P2–N1*	117.4 (0.1)	N3–P2–N1*	108.3 (0.2)
C17–N1–P2*	126.0 (0.2)		

[a] Atoms marked with an asterisk have been generated by the symmetry operation $1-x, 1-y, -z$.

investigated further. They are mainly made up of mixtures of oligomeric materials of particularly low solubility. **8** might be obtained from the hydrolysis of the tervalent parent compound of **4**, a macrocycle present in the solution all during the reaction, according to a process already reported for anilinophosphine derivatives.[20] However, it is probably the water-induced cleavage of the phosphazane ring that leads to **8**, although the cleavage of an exocyclic P–N bond seems to prevail in the case of aminocyclodiphosph(III)azanes.[21] The macrocyclic phosphine oxide **8** is a new potential ligand containing one phosphoryl group in a crown ether like structure, and its preparation and properties studies are under way.

Cis–Trans Isomerism. After completion of the reaction but prior to the sulfurization step, a sample of the solution was submitted to ^{31}P NMR analysis. Both cis and trans isomers of the phosphorus(III) derivatives could be detected and identified. The phosphorus-31 NMR spectra showed clearly two resonances at 112.8 and 164.4 ppm (toluene, 80 °C), characteristic of the ^{31}P chemical shifts of, respectively, the cis and trans isomers of the P_2N_2 diphosphazane ring.[22,23] Typically, the cis isomer was first formed from the parent P(III) compound of **4**, followed by the trans one. In the course of the reaction, other minor products were formed but were not clearly identified, and the ^{31}P NMR signal of the tervalent precursor of **5** was not assigned.

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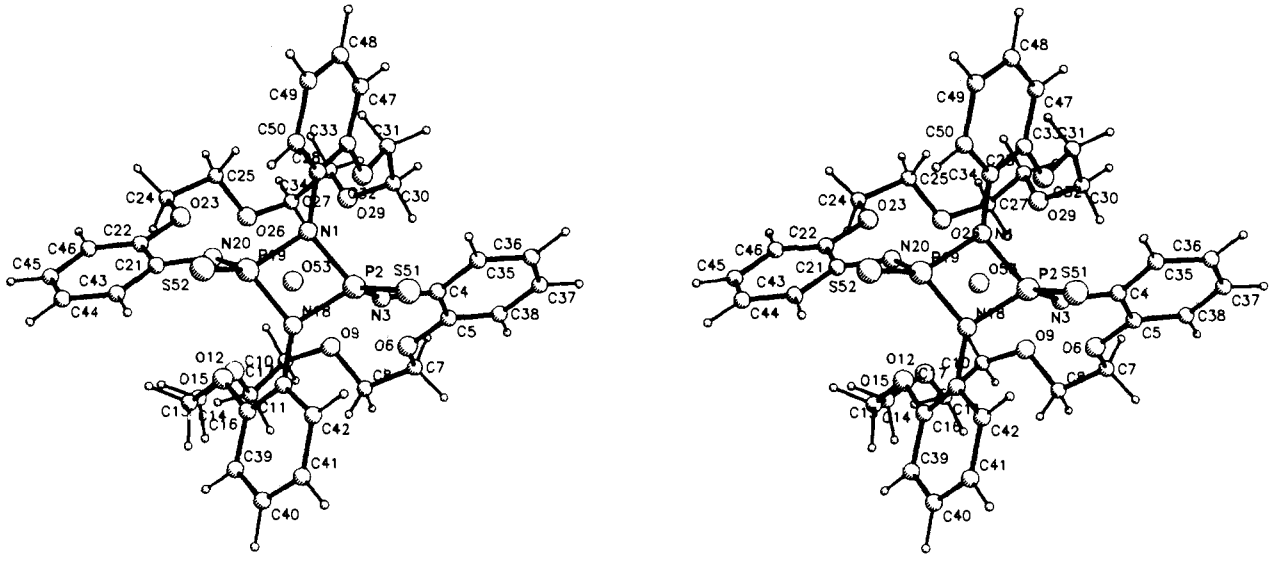

Figure 1. Stereoview and numbering scheme for *cis*-**1**·H_2O.

It is noteworthy that cis and trans isomers are the preferentially formed compounds. The cis to trans ratio observed is highly dependent on the experimental conditions. The trans isomer is easily recovered after the sulfurization of the reaction mixture and is the major product obtained. The cis to trans ratio thus measured is approximately 1:9. However, when the crude solution of the P(III) species is heated at higher temperature in a sealed tube for several hours (135 °C for 3 days), the ^{31}P NMR spectrum does evolve with formation of new species. The cis to trans ratio is modified, but the presence of other compounds and the low solubility of the two isomers do not allow one to conclude the relative stability of the cis and trans isomers. The presence of dimethylamine in the solution probably leads, at high temperature, to a new equilibrium involving dimethylamino phosphorus derivatives.

Circumstances under which cis or trans isomers of N(ring)-aryl-substituted diazadiphosphetidines are either kinetically or thermodynamically favored are not clear.[23] However, it seems that the cis form becomes more stable when at least one *exo*-amino group is a primary amino (RNH) substituent. For examle, the $1,3,2\lambda^3,4\lambda^3$-diazadiphosphetidine **6** is reported as exclusively the cis isomer. The existence of the corresponding *trans*-**6** isomer has not been established from the PCl_3–$C_6H_5NH_2$ reaction.[22] The corresponding disulfide *trans*-**7**, obtained from the thermolysis of $(C_6H_5NH)_3PS$ or from the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction, has been characterized by single-crystal X-ray analysis.[15] According to other authors, **6** was also formed by the reaction of aniline with Cl_2PNR_2 (R = CH_3, C_2H_5)[19] or $P[N(C_2H_5)_2]_3$[14] and by the thermal decomposition of phosphorus trianilide.[24] **6** has been converted to **7** by reacting with sulfur,[19] but no indications are given on the stereochemistry of the compound thus obtained, as well as on that of the starting material. A melting point identical with that of *trans*-**7** suggests that the product from this reaction is also the trans isomer. It would be interesting to know if the stereochemistry of the P_2N_2 diphosphazane ring remains unchanged by reaction with sulfur, although it might be possible that the sulfurization is not a simple reaction.[22] The oxydation of cyclodiphosph(III)azane by dimethyl sulfoxide has been shown to be stereospecific and involved both inversion and retention of configuration at phosphorus.[25] Our studies indicate that the cis to trans ratio is roughly maintained during the sulfurization step. This would be indicative of a single process for the oxidation of phosphorus by elemental sulfur.[26] In addition to **1** and **4**, the ^{31}P NMR spectra showed that during the sulfurization step, two 1:1 signals ($\delta(^{31}P)$ 92.0 and 51.4, toluene, 50 °C) appeared and were attributed to an intermediate $P(S)P^{III}N_2$ species with a J_{PP} value of 0 Hz. It slowly disappeared within a few hours to give **1**. A minor product ($\delta(^{31}P)$ 47.9 and 39.9, J_{PP} = 19.1 Hz, toluene, 70 °C) was also detected and could be probably a higher condensation product containing an asymmetric diphosphazane structure. In any case we were unable to detect any intermediate aminoiminophosphane.

Crystal Structures. Recrystallization of *trans*-**1** from CH_2Cl_2 affords crystals of the *trans*-**1**·$2CH_2Cl_2$ solvate suitable for X-ray analysis. Crystals of the *cis*-**1**·H_2O solvate were obtained from the same solvent. The crystal structures of *cis*-**1** and *trans*-**1** are illustrated in Figures 1 and 2, respectively.[27] Bond distances and angles are given in Tables IV and V. The cis isomer ($\delta(^{31}P)$ 47.5) and the trans isomer ($\delta(^{31}P)$ 44.9) differ mainly by the relative orientations of their crown ether units. The most striking feature of *cis*-**1** is the "face-to-face" relationship of the two macrocyclic moieties. A single water molecule is encapsulated within the so-formed cavity, and the two P–S bonds are directed outward, on the opposite face of the plane defined by the P_2N_2 diphosphazane ring. The molecule adopts a pseudo-C_2 molecular symmetry; in the crystal, right- and left-handed isomers are related by a crystallographic center of symmetry. *trans*-**1** adopts a centrosymmetrical conformation. It lies on a crystallographic center of symmetry located in the center of the P_2N_2 ring. Therefore, only one-half of the molecule is defined in the asymmetric unit. This imposes a macrocyclic unit on each side of the plane defined by the diphosphazane ring. Each of the P–S bonds lies in a close proximity of the adjacent crown ether moiety. Finally, dichloromethane solvent molecules are also incorporated in the lattice, though there are no close interactions of the solvent with the *trans*-**1** molecule.

Common to *cis*-**1** and *trans*-**1** are the bond distances and angles of the four-membered rings (Tables IV and V), which are closely similar to the ones reported for the dianilino derivative **7**.[15] Mean intracyclic P–N distances for *cis*-**1** and *trans*-**1** of 1.694 and 1.695 Å, respectively, are in the range of the previously observed values of 1.680–1.698 Å. The same remark can be made for the extracyclic P–N and P–S bonds.[15,28] Intracyclic N–P–N and P–N–P angles values (respectively, 82.7° and 96.5° average values for *cis*-**1**; 81.9° and 98.1° for *trans*-**1**) agree well with the values reported in the literature.[15,28]

In the trans isomer, the four-membered ring is planar. The ring nitrogen atoms environment is planar, the angles around N1

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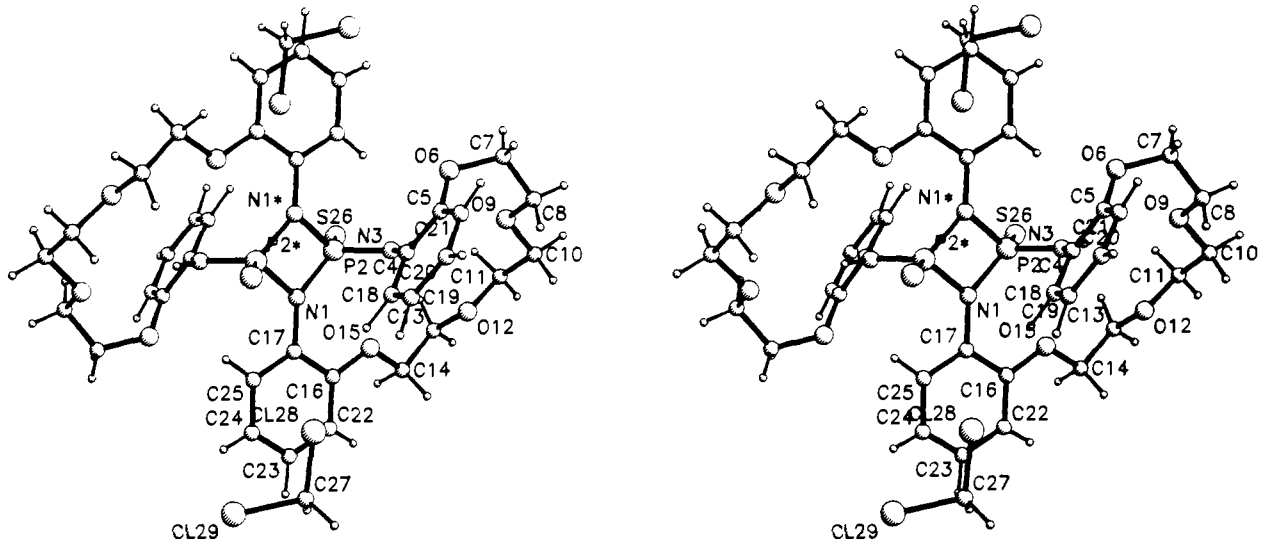

Figure 2. Stereoveiw and numbering scheme for *trans*-**1**·$2CH_2Cl_2$. Atoms marked with an asterisk have been generated by the symmetry operation $1-x, 1-y, -z$.

summing to 360°. The phenyl rings bonded to the P_2N_2 ring approach coplanarity with the P_2N_2 ring, since the phenyl rings plane is twisted by only 7° from the P_2N_2 plane. The conformation around the exocyclic P2–N3 bond results in the near-eclipsing of P-S and N–H bonds and the trans relationship between the P–S and N–C exocyclic bonds. The dihedral S26–P2–N3–C4 and S26–P2–N3–H(N3) angles are 171° and 4°, respectively. The short S- - -H distance of 2.78 Å may indicate the existence of hydrogen bonding between the sulfur and the anilino hydrogen atoms in the molecule,[15] though it is probably not an important factor in determining the structure of *trans*-**1**.[28] The angle defined by the planes of the P_2N_2 ring and the anilinophenyl group is 70°. This results in an endo orientation of the phenyl substituent relatively to the diphosphazane ring.

In *cis*-**1**, the geometry around the nitrogen atoms of the P_2N_2 ring is distorted from planarity. The sum of the bond angles around N1 and N18 atoms is 356.3° and 356.1°, respectively. The P_2N_2 ring is slightly puckered, with the nitrogen and phosphorus atoms lying 0.067 Å from the mean plane calculated from the position of the phosphorus–nitrogen atoms. The average internal torsion angle about the P–N ring bonds is 9.1°. This was expected with the cis isomer, to relieve steric interactions of the aminophenyl substituents. Moreover, steric repulsions are alleviated by the exoorientation of the anilino groups relative to the P_2N_2 ring. This results in a syn relationship between the P–S bond and the exocyclic N–C bond with an averaged $S-P-N_{exo}-C_{exo}$ dihedral angle of 24.9°. The phenyl rings which are bonded to the diphosphazane ring are much more twisted with respect to the four-membered ring than those reported for compound **7**[15] and other N-alkylated parent compounds.[28] The average angle between the planes defined by the P_2N_2 and phenyl rings is 55.6° and is mainly due to severe constraints imposed by the cyclic polyether linkages in the "face-to-face" rearrangement. For the same reason the anilino substituents are rejected outward as compared to *trans*-**1** and **7**.

In considering the conformation of the macrocyclic parts, inspection of the bond lengths and angles (Tables IV and V) reveals no unusual values. In the structural data of *cis*-**1**·H_2O, the thermal vibrations are particularly important around carbon C13. Inspection of the torsion angles around C13–C14 reveals that this group adopts an eclipsed conformation. This can explain the apparently abnormal distances and torsion angles observed around these agitated atoms. Oxygen atoms are directed toward the center of the cavity. Selected bond distances with the encapsulated water molecule are reported in Table IV. The conformation observed for *cis*-**1** is also evidently the result of the steric requirements for water complexation within the cavity (Figure 1). It is noteworthy that the two cavities of *trans*-**1** formed by the two crown ether units are occupied by the corresponding N–H hydrogen atoms. Figure 2 clearly shows that oxygen atoms face inward toward the cavity, whereas no CH_2 group turns inside the cavity. This conformational organization of the macrocyclic moieties is also greatly responsible for the structure oberved for *trans*-**1**.

Table VI. Phosphorus-31 NMR Chemical Shifts for *cis*- and *trans*-$[RP(S)NR']_2$

R	R'	$\delta(^{31}P)$ cis	$\delta(^{31}P)$ trans	ref
t-Bu	CH_3	120.1	105.9	26
$N(CH_3)_2$	*t*-Bu	48.8	53.8	29
$N(CH_3)C_6H_5$	$Si(CH_3)_3$	41.6	44.1	30
OCH_3	*t*-Bu	51.6	56.6	31
NHC_6H_5·CE[a]	CE·C_6H_5[a]	47.5	44.9	this work

[a] CE stands for the crown ether substituent.

Concluding Remarks

Novel ditopic receptors based on the P_2N_2 diphosphazane ring were obtained as *cis*- and *trans*-1,3,2λ^5,4λ^5-diazadiphosphetidine 2,4-disulfides. Under the given experimental conditions the macrocyclic phosphoramide **4** and the new bis(crown ether) **5** were also characterized. The diphosph(III)azane compounds are very sensitive to moisture, and the new macrocyclic **8** containing the P(O)H fragment was isolated from the degradation mixture.

Less than 3 ppm differentiates the phosphorus NMR chemical shifts of *cis*-**1** and *trans*-**1**. Few examples of ^{31}P chemical shifts have been reported in the literature for both cis and trans isomers of 1,3,2λ^5,4λ^5-diazadiphosphetidine 2,4-disulfides $[RP(S)NR']_2$. Examples given in Table VI show that ^{31}P chemical shifts are almost independent of the configuration of the diphosphazane ring. It must be pointed out that the geometry around the phosphorus atoms exhibits very similar bond distances and angles for both isomers. This situation is quite different from that observed with the phosphorus(III) isomers where chemical shift differences of up to 80–90 ppm are observed ($\Delta\delta$ = 51.6 in our case).[8d]

Water complexes of crown type ligands have been reported,[32] but only few cases exist where water is encircled by an uncharged host molecule.[16,33] The molecular structure of *cis*-**1**·H_2O exam-

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plifies the ability of neutral host to complex water via crown ether ligands. Furthermore, *cis*-**1** is most likely to form intramolecular sandwich-type complexes with particular mono- and dicationic species by cooperative action of the two adjacent crown rings. The intrinsic chirality of the cis isomer may be of particular importance in selective complexation of enantiomeric cationic guests. The *trans*-**1** isomer, which possesses two crown ether moieties, has the possibility of forming dinuclear complexes by placing two cations in close proximity. The characterization of such entities and the design of other ligands based on the disphosphazane ring are currently under investigation.

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Registry No. *cis*-**1**, 121754-78-7; *cis*-**1**·H_2O, 121730-72-1; *trans*-**1**, 121754-80-1; *trans*-**1**·$2CH_2Cl_2$, 121754-81-2; **2**, 73776-01-9; **3**, 72583-76-7; **4**, 121730-70-9; **5**, 121730-71-0; **8**, 121754-79-8; $TsO(CH_2)_2O(CH_2)_2O(CH_2)OTs$, 19249-03-7; 2-nitrophenol, 88-75-5.

Supplementary Material Available: Listing of observed and calculated structure factors for *cis*-**1**·H_2O and *trans*-**1**·$2CH_2Cl_2$ (53 pages). Ordering information is given on any current masthead page.

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Functionalization of Saturated Hydrocarbons. 14. Further Studies on the Mechanism of Gif-Type Systems

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Abstract: The photolysis (W light) of acyl derivatives of *N*-hydroxy-2-thiopyridone in pyridine–acetic acid permits a study of the partitioning of secondary radicals between oxygen, pyridine, and the thione function. Comparison with the Gif^{IV} oxidation system for saturated hydrocarbons confirms that radicals are not involved in oxidation at secondary positions. On the contrary, radical behavior at the tertiary position in adamantane is again established. The two recently introduced Gif-type systems, $GoAgg^{I}$ and $GoAgg^{II}$, have been shown to give the same overall selectivity in attack on adamantane with the usual coupling of the tertiary radical with pyridine.

The selective functionalization of saturated hydrocarbons is a subject of great topical concern.[2] Amongst the many approaches to the problem, we have developed several systems that oxidize and substitute saturated hydrocarbons with an unusual regioselectivity.[3a] The system Gif^{III} consists of Fe^0–O_2 in pyridine–acetic acid; Gif^{IV} is similar, with Zn^0–O_2–Fe^{II} catalyst in the same solvent mixture. The Gif-Orsay system[3b] is the same as Gif^{IV}, but the Zn^0 is replaced by the cathode of an electrochemical cell. These systems attack saturated hydrocarbons in the order secondary > tertiary ≥ primary. This contrasts with the normal order of radical attack, such as is seen with P450 porphyrin models,[4,5] of tertiary > secondary > primary. It is quite unlike the selectivity seen in cobalt catalyzed autoxidation reactions.[6] In addition, ketones are the principal reaction product, not secondary alcohols as in other oxidation systems.[2,7]

When the reaction is run in the presence of a large excess of hydrocarbon to a conversion of 10–15%, the yield of ketone is nearly quantitative. In the Gif-Orsay system,[3b,8] the Coulombic yield is high (about 50% for cyclohexane). The electrochemical system does not involve the reduction of pyridine as does the $Gif^{IV}(Zn^0)$ procedure. Recent work[9] has shown that $FeCl_2$–KO_2 ($GoAgg^{I}$) or $FeCl_3$–H_2O_2 ($GoAgg^{II}$) give the same selectivity as the earlier Gif and Gif-Orsay systems in the same solvent mixture. Hence, the reduction of pyridine has nothing to do with the mechanism of the oxidation. However, pyridine is an essential ligand, and acetic acid (or other acid) has to be present to buffer the system.

We have expended much effort on trying to establish the mechanism of this unusual oxidation process. An early obser-

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