Synthesis of novel paracyclophanes with linear P,N-containing spacers*

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Condensation of bis(hydroxymethyl)mesityl- and bis(hydroxymethyl)phenylphosphines with *N*,*N*´-disubstituted bis(4-aminophenyl)methanes and bis(4-amino-3-carboxyphenyl)methane occurred as covalent self-assembly spontaneously giving a mixture of *trans*- and *cis*-diastereomers of 1,5,19,23-tetra-R´-3,21-di-R-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophanes as the major products. The *trans*-isomer (R is mesityl; R´ is methyl) was isolated in the individual state and structurally characterized by X-ray diffraction analysis. Sulfurization of macrocyclic diphosphines (R = Ph; R´ is 3-pyridylmethyl or 4-pyridylmethyl) gave the corresponding diphosphine disulfides, the *trans*-stereoisomer being isolated in the individual state.

Key words: phosphorus-containing cyclophanes, bis(hydroxymethyl)phenylphosphine, bis(hydroxymethyl)mesitylphosphine, *N*,*N*´-disubstituted bis(4-aminophenyl)methanes, bis(4-amino-3-carboxyphenyl)methane, condensation, covalent self-assembly.

Macrocycles containing soft electron-donating sites (in particular, tricoordinate phosphorus atoms) are of constant interest primarily as a basis for development of catalytic systems with reactive sites inside or adjacent to the macrocyclic cavity.[1,2] In such macrocycles, secondary interactions of the cavity with substrates and reagents become possible, thus making catalytic processes more efficient and selective. Specific catalytic properties have been discovered with both macrocycles containing phosphine sites at the periphery of the cavity (such as phosphinocyclodextrins,[3,4] phosphinocalixarenes,[5] and cyclophanes with exocyclic phosphino groups (*e.g.*, PhanePhos[6]) and compounds with P atoms in the macrocycle itself.[1,2] In addition, phosphorus-containing macrocycles are of interest for design of supramolecular systems: receptors and sensors with specific properties.[7,8] From either point of view, cyclophanes with tricoordinate phosphorus atoms in the macrocycles composed of aromatic building blocks (*e.g.*, *m*- and *p*-arylene fragments capable of forming deep hydrophobic cavities) are attractive. However, despite a great number of known P-containing macrocycles, described[9—11] cyclophanes of this type are relatively few, mostly including macrocyclic diphosphites, diphosphonites, and bis(phosphoramidites).[11—16] Recently, we have developed an efficient approach to the synthesis of cage-type cyclophanes containing four phosphine sites, namely, 1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphanes. The approach involves condensation of bis(hydroxymethyl)organylphosphines with primary diamines containing spacers formed by two *p*-phenylene fragments linked by various monoatomic bridges.[17,18] At high concentrations of the reagents and in the absence of templates, those reactions mainly yielded macrocycles *via* covalent self-assembly.[18] The goal of the present work was to further develop this approach and use it for the synthesis of more flexible cyclophanes with two tricoordinate P atoms in the macrocycle. To solve this problem, here we studied reactions of bis(hydroxymethyl)phenyl- and bis(hydroxymethyl)mesitylphosphines with a number of secondary diamines containing di(*p*-phenylene)methane spacers: bis(4-methylaminophenyl)methane **1** (see Ref. 19), bis[4-(3-pyridylmethyl)aminophenyl]methane (**2**), and bis[4-(4-pyridylmethyl)aminophenyl]methane (**3**). The use of functionalized diamines made it possible to construct cyclophanes with additional peripheral donating sites. Bis(4-amino-3-carboxyphenyl)me-

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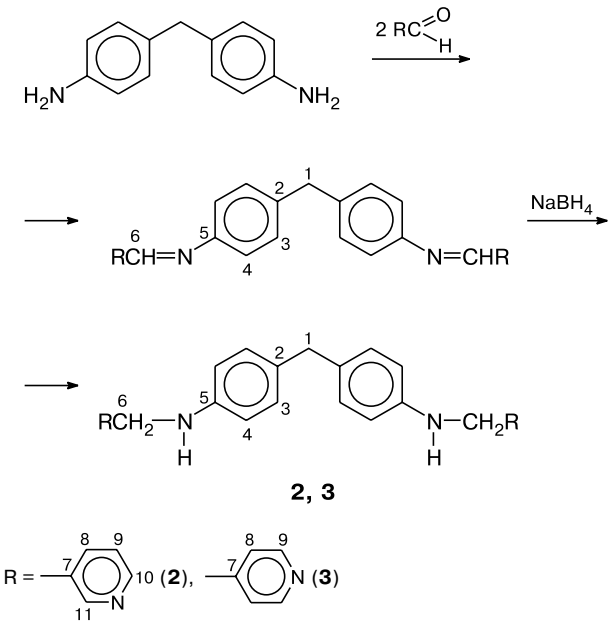
Scheme 1



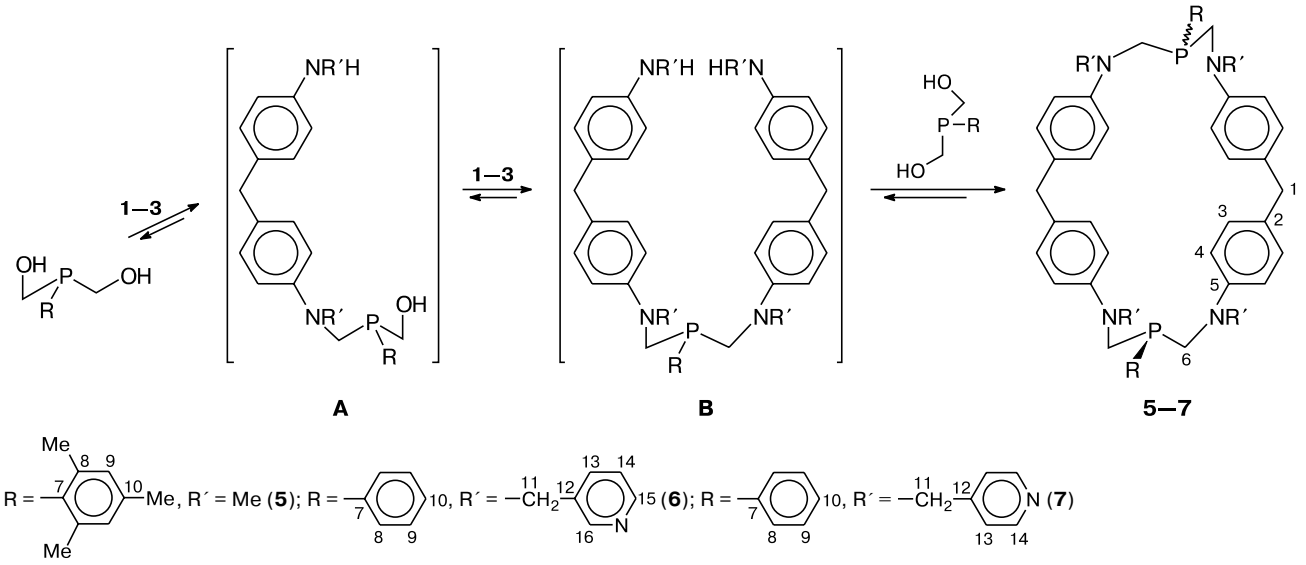
thane **4** (see Ref. 20) was also employed as a starting reagent since structurally similar anthranilic acid reacts with hydroxymethylphosphines as a secondary amine because of strong intramolecular hydrogen bonding between the carboxy and amino groups.[21]

The starting diamines **1** and **4** were prepared by acid-promoted reactions of formaldehyde with *N*-methylaniline and anthranilic acid, respectively (see Refs 19, 20). Earlier unknown bis[4-(3-pyridylmethyl)aminophenyl]methane (**2**) and bis[4-(4-pyridylmethyl)aminophenyl]methane (**3**) were synthesized by reduction of appropriate diimines with $NaBH_4$ in ethanol as described for bis[4-(2-pyridylmethyl)aminophenyl]methane[22] (Scheme 1).

Condensation of bis(hydroxymethyl)phenyl- and bis(hydroxymethyl)mesitylphosphines with secondary diamines **1**—**3** was carried out in DMF at 100—110 °C (for **1**) or room temperature (**2**, **3**); the concentrations of the starting reagents were 0.1—0.3 mol L^{-1}. The room-temperature conditions were found to be optimum for diamines **2** and **3**, though the reaction time in the case of compound **2** was substantially longer (22 days). The long reaction time allowed monitoring of its course by ^{31}P NMR spectroscopy. At early reaction steps (after 1—2 days), the ^{31}P NMR spectra of the reaction mixture contained, along with a signal at δ −19.70 for the starting bis(hydroxymethyl)phenylphosphine, a signal at δ −28.50, probably due to the corresponding (aminomethyl)(hydroxymethyl)phenylphosphine (**A**).[18] Later, the spectra showed a signal at δ −33.50 for the corresponding bis(aminomethyl)phenylphosphine (**B**)[18] and a signal at δ −38.25 that became dominant at the final reaction step and related to the target macrocyclic aminomethylphosphine (Scheme 2).

It should be noted that the reaction steps were poorly distinguishable. In the spectra of the final reaction mixtures, one or two closely spaced signals at δ −37 to −42 were vastly dominant. The relative contents of the corresponding reaction products were 70—85%; in addition, the spectra contained low-intensity signals in the same range and, in the case of bis(hydroxymethyl)mesitylphosphine, signals at δ −95 to −105 due to unidentified secondary phosphines resulting from successive dissociation and amination of the starting P-containing diol. The contents of these by-products were 20—30% and we had

Scheme 2



much difficulty in removing them. As the result, only macrocyclic products **5** and **6** were isolated in the individual state. Their yields were 21 and 67%, respectively. Compound **7** was obtained as a very viscous oil containing the target product (~85%) and unidentified oligomeric aminomethylphosphines.

The positive-ion MALDI TOF mass spectrum of compound **5** showed a molecular ion peak with *m/z* 804 corresponding to the condensation product 3,21-dimesityl-1,5,19,23-tetramethyl-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophane and peaks with *m/z* 827 and 843 due to the ions $[M + Na]^+$ and $[M + K]^+$ respectively; no peaks with higher *m/z* values were detected. Like the spectrum of the reaction mixture, the ^{31}P NMR spectrum of compound **5** contained two closely spaced signals at δ −41.25 and −41.30. They suggest that cyclophane **5** is a mixture of the *cis*- and *trans*-stereoisomers. The ^1H NMR spectrum of compound **5** exhibited a double set of signals almost for all types of protons; the ratio of the major and minor isomers was 1.3 : 1.

The major *trans*-stereoisomer of the macrocyclic diphosphine **5** was isolated in the individual state by second fractional recrystallization of a mixture of its isomers from DMF. The structure of compound **5** was determined by 1D and 2D NMR correlation experiments ($^1H—^1H$ COSY, $^1H—^{13}C$ HSQC, and $^1H—^{13}C/^1H—^{15}N$ HMBC).[23]

First, the protons of separate spin systems were distinguished from 2D COSY data. Then, the carbon atoms attached to these protons were located from the 2D HSQC spectrum. Finally, the $^1H—^{13}C$ and $^1H—^{15}N$ 2D HMBC data (Fig. 1) were used to integrate the fragments. Thus,

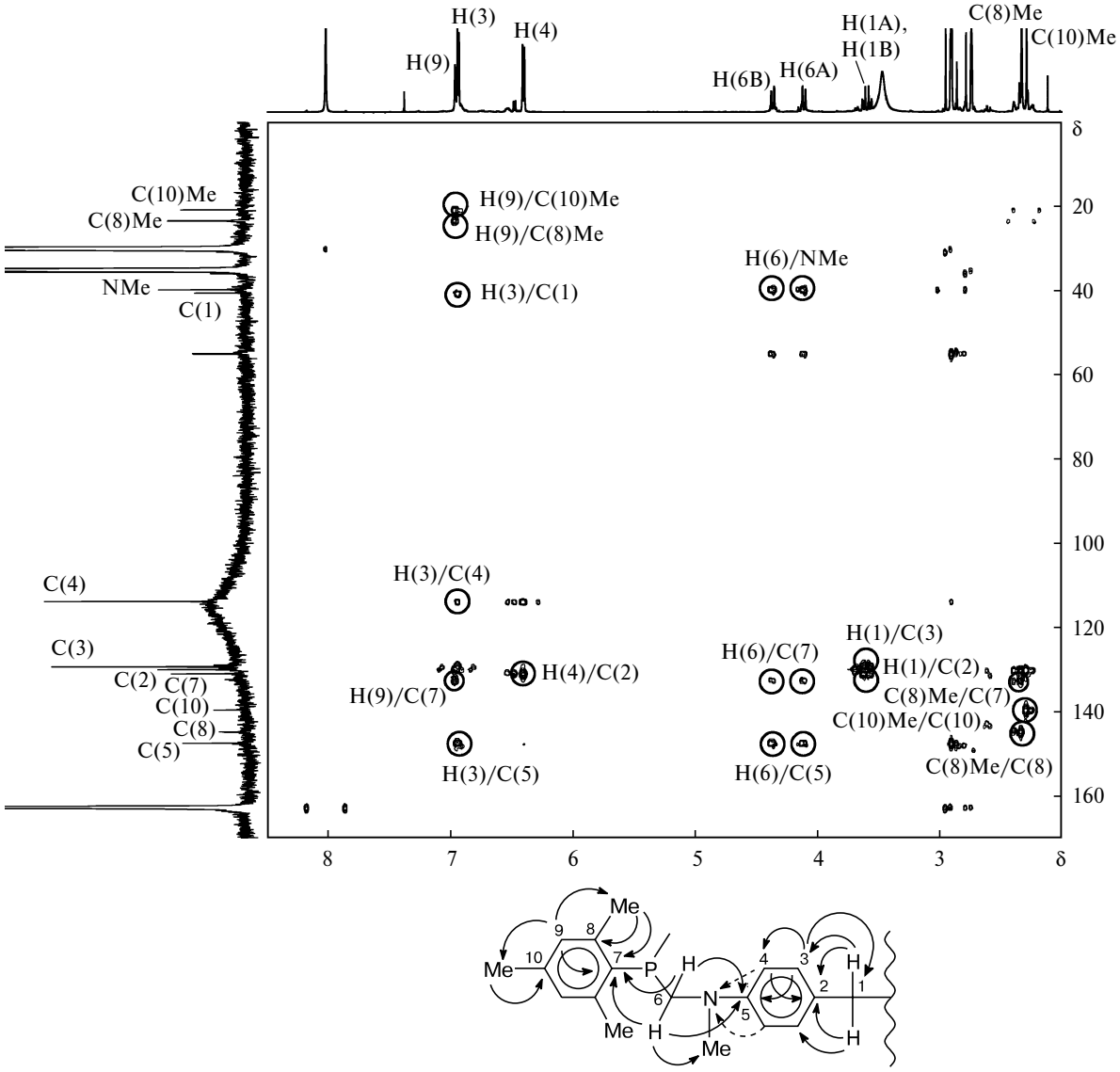


Fig. 1. ^1H —^{13}C 2D HMBC NMR spectrum and a scheme of key correlations for the *trans*-isomer of compound **5**; $^1H \rightarrow ^{13}C$ and $^1H \rightarrow ^{15}N$ cross-correlations are indicated with solid and dashed arrows, respectively.

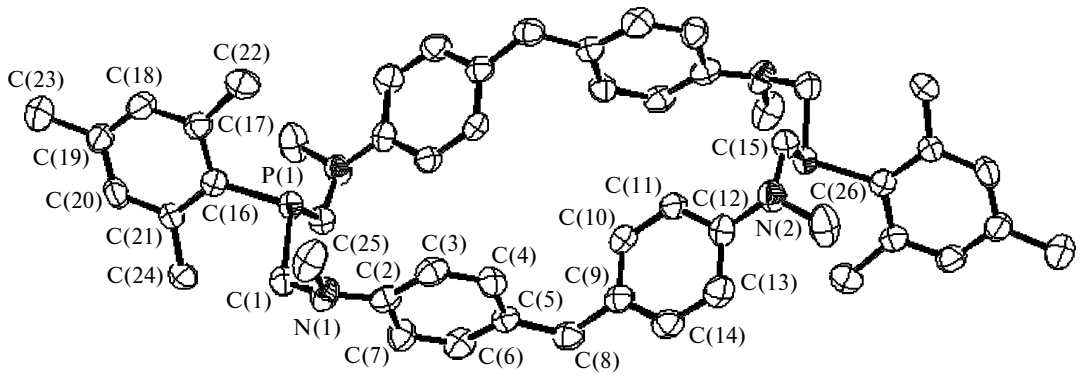


Fig. 2. Molecular geometry of the *trans*-isomer of cyclophane **5** in the crystal. The hydrogen atoms are omitted for clarity. The thermal displacement ellipsoids are shown at 50% probability.

Table 1. Selected geometrical parameters in structure **5**

Bond	*d*/Å	Bond angle	ω/deg	Torsion angle	τ/deg
P(1)—C(16)	1.849(4)	C(16)—P(1)—C(1)	103.7(2)	C(15′)—P(1)—C(1)—N(1)	111.4(4)
P(1)—C(1)	1.868(4)	C(16)—P(1)—C(15′)	104.5(2)	P(1)—C(1)—N(1)—C(25)	68.9(4)
P(1)—C(15′)	1.871(4)	C(1)—P(1)—C(15′)	101.4(2)	P(1)—C(1)—N(1)—C(2)	−70.5(4)
N(1)—C(2)	1.410(5)	C(2)—N(1)—C(25)	117.0(4)	C(1)—N(1)—C(2)—C(7)	−50.5(4)
N(1)—C(25)	1.456(6)	C(2)—N(1)—C(1)	116.9(3)	N(1)—C(2)—C(7)—C(6)	−175.0(4)
N(1)—C(1)	1.458(5)	C(25)—N(1)—C(1)	112.3(4)	C(7)—C(6)—C(5)—C(8)	174.3(4)
N(2)—C(12)	1.394(5)	C(12)—N(2)—C(15)	119.8(4)	C(6)—C(5)—C(8)—C(9)	166.4(4)
N(2)—C(15)	1.440(5)	C(12)—N(2)—C(26)	118.8(4)	C(5)—C(8)—C(9)—C(10)	−60.4(3)
N(2)—C(26)	1.451(5)	C(15)—N(2)—C(26)	115.4(4)	C(8)—C(9)—C(10)—C(11)	−174.6(3)
C(2)—C(3)	1.382(6)	N(1)—C(1)—P(1)	112.7(3)	C(10)—C(11)—C(12)—N(2)	−177.7(3)
C(3)—C(4)	1.401(6)	C(3)—C(2)—N(1)	123.0(4)	C(11)—C(12)—N(2)—C(15)	−25.2(4)
C(4)—C(5)	1.374(6)	C(4)—C(5)—C(8)	123.9(4)	C(12)—N(2)—C(15)—P(1′)	−66.3(4)
C(5)—C(8)	1.512(6)	C(9)—C(8)—C(5)	118.8(4)	C(26)—N(2)—C(15)—P(1′)	86.3(43)
C(8)—C(9)	1.505(6)	N(2)—C(12)—C(11)	121.6(4)	N(2)—C(15)—P(1′)—C(1′)	172.6(4)
C(9)—C(10)	1.388(6)	N(2)—C(15)—P(1′)	113.5(3)	C(1)—P(1)—C(16)—C(17)	133.5(5)
C(10)—C(11)	1.381(6)	C(21)—C(16)—P(1)	126.2(3)	P(1)—C(16)—C(17)—C(22)	−3.5(5)
C(11)—C(12)	1.395(6)	C(17)—C(16)—P(1)	115.6(3)	C(15′)—P(1)—C(16)—C(17)	−120.6(5)
C(16)—C(17)	1.410(6)	C(16)—C(17)—C(22)	122.3(4)	P(1)—C(16)—C(21)—C(24)	−1.3(4)
C(17)—C(18)	1.384(6)	C(18)—C(17)—C(22)	118.4(4)		
C(18)—C(19)	1.365(6)	C(20)—C(19)—C(23)	120.8(5)		
C(17)—C(22)	1.508(6)	C(18)—C(19)—C(23)	121.7(5)		
C(19)—C(23)	1.507(6)	C(20)—C(21)—C(24)	117.0(4)		
		C(16)—C(21)—C(24)	123.8(4)		

we determined the structure of the key fragment of the macrocycle.

To confirm our assignments of the signals for the atoms of the macrocycle, we additionally carried out *ab initio* calculations of the ^{13}C chemical shifts (GIAO RB3LYP/6-31G(d)//RHF/6-31G[24])*. The calculated data were in full agreement with the experiment ($R^2 = 0.9986$, RMS = 5.9, MAD = 5.2, $a = 0.934$), which verified the conclusions about the chemical structure.

Single-crystal X-ray diffraction analysis of the individual stereoisomer of compound **5** provided cogent evidence for its centrosymmetric structure of the *trans*-isomer. The *trans*-**5** (Fig. 2; Table 1) contrasts with earlier reported cage-type cyclophanes in molecular structure.[17,18] 1,5(1,5)-Di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphanes possess a cavity like a truncated prism; the phenylene rings forming its lateral walls are nearly perpendicular to the basal plane of the macrocycle defined by the N atoms; *i.e.*, the diphenylenemethane fragments are in the "open book" conformation.[17,18] Structure **5** is centrosymmetric; all the N atoms are also coplanar, while the P atoms with the attached mesityl substituents lie on each side of the plane. In the spacer N—C—P—C—N, one methyl group has a pseudoaxial orientation, while the other has a pseudoequatorial one.

* The chemical shifts were calculated for the key fragment of the molecule with additional terminal substituents modeling the substituents in the macrocycle.

In contrast to the aforementioned cage-type cyclophanes, in which the N atoms are strongly conjugated with the π systems of the phenylene rings,[17,18] the configuration of two N atoms bearing the pseudoaxial substituents in structure **5** is intermediate between planar and tetrahedral (the sum of the bond angles at these atoms is 346.2°). This suggests a lower degree of conjugation. The torsion angle between the planes of the adjacent phenylene rings is 69.7°. One pair of the opposite phenylene fragments makes an angle of 73.1° with the planes of the four N atoms, while the analogous angle for the other pair is 138.6°. This conformation of the macrocycle is typical of [n.1.n.1]paracyclophanes;[25—27] *e.g.*, a close structure with nearly perpendicular adjacent aromatic rings and a virtually collapsed cavity of the macrocycle has been found for 2,18-bis(diethylamino)-10,10,26,26-tetramethyl-1,3,17,19-tetraoxa-2,18-diphospha[3.1.3.1]paracyclophane, in which similar diphenylenemethane fragments are linked by O—P—O spacers.[16] Structure **5** is elongated: the distance between the P atoms is 11.80 Å, while the distance between the planes of the opposite aromatic rings C(2)—C(3)—C(4)—C(5)—C(6)—C(7) and C(2´)—C(3´)—C(4´)—C(5´)—C(6´)—C(7´), which give the cavity walls, is only 5.85 Å. (For the aforementioned macrocyclic bis(phosphoramidite)[16] and the cage-type 1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphanes,[18] the latter distance is 7.7 and 8.7 Å, respectively.) It should be noted that the equivalence of all the phenylene rings and the methyl groups at the N atoms in the ^{1}H NMR spectra of cyclophane **5** suggests possible rapid dynamic equilibrium between its conformers in solutions.

The ^{31}P NMR spectra of compounds **6** and **7** show a signal at δ –40.31 ($CDCl_3$) and –37.66 (DMF), respectively. Their ^{1}H NMR spectra contain a double set of signals almost for all proton types and, consequently, part of the signals are complex multiplets. The integral intensity ratio of different groups of the ^{1}H NMR signals suggests that compounds **6** and **7** are mixtures of the *trans*- and *cis*-stereoisomers 3,21-diphenyl-1,5,19,23-tetrakis(3-pyridylmethyl)- and -1,5,19,23-tetrakis(4-pyridylmethyl)-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophanes, respectively. The ratio of the major and minor stereoisomers was estimated from the intensities of the best resolved doublets for the protons of the phenylene groups that are *ortho* to the N atoms. This ratio was 3 : 1 for compound **6** and 1.5 : 1 for compound **7**. Analogous *cis—trans* stereoisomerism has been found in macrocyclic diphosphites obtained from various bisphenols.[16] However, compounds **6** and **7** were unstable for mass spectrometric analysis.

For more reliable determination of the structure and the ring size, diphosphines **6** and **7** were converted into the corresponding diphosphine disulfides **8** and **9** *via* treatment with elemental sulfur in DMF (Scheme 3).

The MALDI TOF mass spectra of compounds **8** and **9** contain peaks with *m/z* 1093 corresponding to the $[M + H]^+$ ions of the [2+2] adducts 3,21-diphenyl-1,5,19,23-tetrakis(3-pyridylmethyl)- and -1,5,19,23-tetrakis(4-pyridylmethyl)-3,21-dithio-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophanes.

No peaks with higher *m/z* values were observed. The ^{31}P NMR spectra of compounds **8** and **9** show a narrow signal at δ 40.76 and 40.10, respectively. However, a double set of signals in the ^{1}H NMR spectrum of disulfide **9** suggests the presence of the *trans*- and *cis*-diastereomers in the ratio 2.6 : 1; some signals for the minor isomer are noticeably broadened. In contrast, disulfide **8** was

Scheme 3

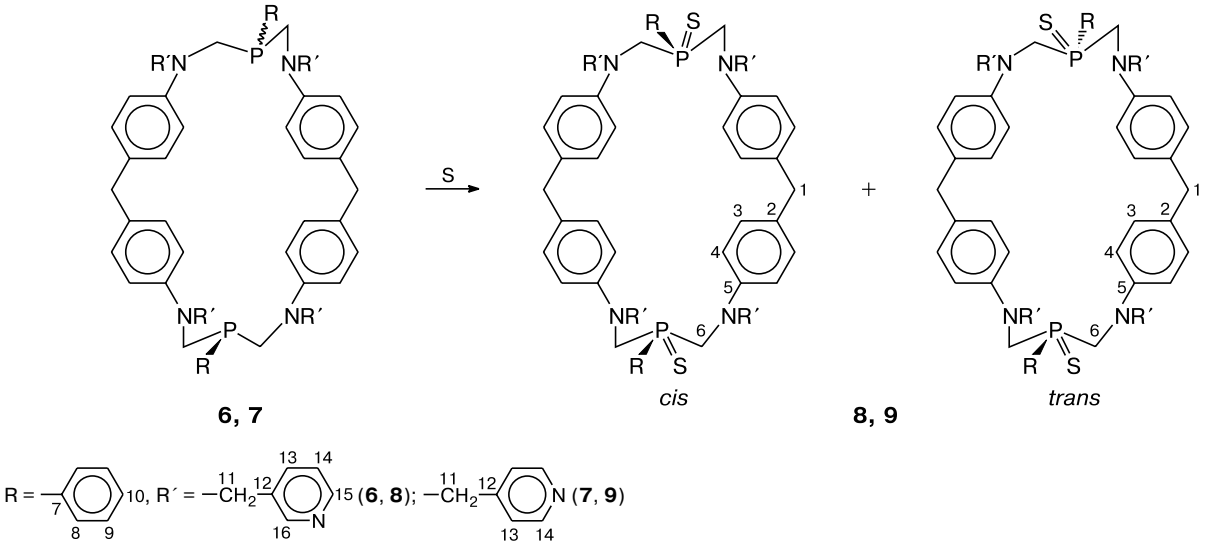
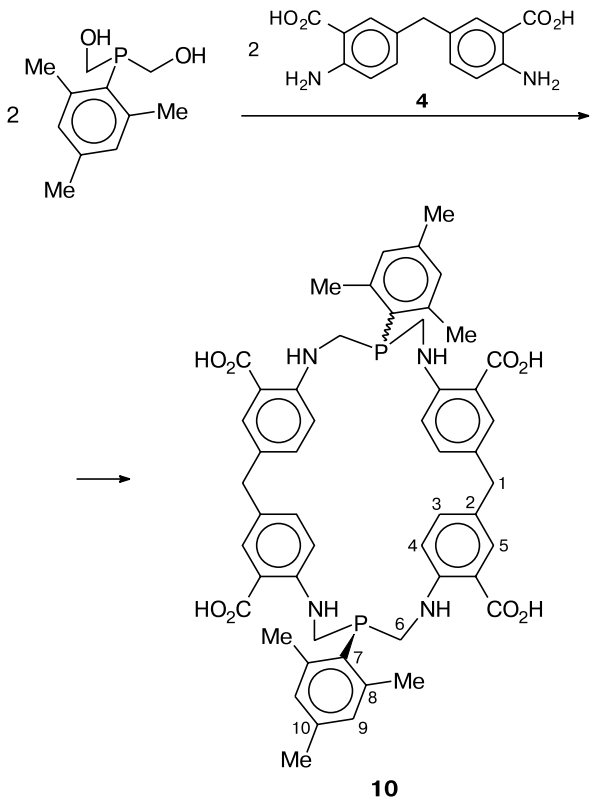


Table 2. Bond lengths in the *trans*-isomer of compound **5**

Bond	*d*/Å	Bond	*d*/Å
P(1)—C(16)	1.849(4)	C(9)—C(14)	1.370(6)
P(1)—C(1)	1.868(4)	C(9)—C(10)	1.388(6)
P(1)—C(15´)	1.871(4)	C(10)—C(11)	1.381(6)
N(1)—C(2)	1.410(5)	C(11)—C(12)	1.395(6)
N(1)—C(25)	1.456(6)	C(12)—C(13)	1.396(6)
N(1)—C(1)	1.458(5)	C(13)—C(14)	1.386(6)
N(2)—C(12)	1.394(5)	C(15)—P(1´)	1.871(4)
N(2)—C(15)	1.440(5)	C(16)—C(21)	1.408(6)
N(2)—C(26)	1.451(5)	C(16)—C(17)	1.410(6)
C(2)—C(3)	1.382(6)	C(17)—C(18)	1.384(6)
C(2)—C(7)	1.396(6)	C(17)—C(22)	1.508(6)
C(3)—C(4)	1.401(6)	C(18)—C(19)	1.365(6)
C(4)—C(5)	1.374(6)	C(19)—C(20)	1.373(6)
C(5)—C(6)	1.380(6)	C(19)—C(23)	1.507(6)
C(5)—C(8)	1.512(6)	C(20)—C(21)	1.389(6)
C(6)—C(7)	1.373(6)	C(21)—C(24)	1.510(6)
C(8)—C(9)	1.505(6)		

isolated as one stereoisomer (^{1}H NMR data). The corresponding protons of the phenylene, methylene, and pyridyl fragments are equivalent and their signals are not broadened, which suggests a symmetrical *trans*-structure of this isomer. Most likely, the stereoisomers of diphosphines **6** and **7** we isolated are also *trans*-diastereomers. Apparently, the predominant formation of [2+2] adducts is due to spatial complementarity of their constituent di(*p*-phenylene)methane spacers and bis(aminomethyl)phosphine fragments. It should be noted that reactions of bisphenols containing analogous spacers with various bifunctional phosphorus-containing reagents also occurs mainly as [2+2] macrocyclization, although under high or pseudo-high dilution.[12,13,15,16]

Scheme 4



10

As expected, the major product of condensation of bis(hydroxymethyl)mesitylphosphine with bis(4-amino-3-carboxyphenyl)methane was also the corresponding 1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophane **10** (Scheme 4). The yield of compound **10** was 72%; it is resistant to oxidation in the solid state and in solu-

Table 3. Bond angles in the *trans*-isomer of compound **5**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(16)—P(1)—C(1)	103.7(2)	C(4)—C(5)—C(8)	123.9(4)	N(2)—C(15)—P(1´)#	113.5(3)
C(16)—P(1)—C(15´)#	104.5(2)	C(6)—C(5)—C(8)	119.0(4)	C(21)—C(16)—C(17)	118.2(4)
C(1)—P(1)—C(15´)#	101.4(2)	C(7)—C(6)—C(5)	122.3(4)	C(21)—C(16)—P(1)	126.2(3)
C(2)—N(1)—C(25)	117.0(4)	C(6)—C(7)—C(2)	121.0(4)	C(17)—C(16)—P(1)	115.6(3)
C(2)—N(1)—C(1)	116.9(3)	C(9)—C(8)—C(5)	118.8(4)	C(18)—C(17)—C(16)	119.3(4)
C(25)—N(1)—C(1)	112.3(4)	C(14)—C(9)—C(10)	117.2(4)	C(18)—C(17)—C(22)	118.4(4)
C(12)—N(2)—C(15)	119.8(4)	C(14)—C(9)—C(8)	121.5(4)	C(16)—C(17)—C(22)	122.3(4)
C(12)—N(2)—C(26)	118.8(4)	C(10)—C(9)—C(8)	121.1(4)	C(19)—C(18)—C(17)	123.0(4)
C(15)—N(2)—C(26)	115.4(4)	C(11)—C(10)—C(9)	121.5(4)	C(18)—C(19)—C(20)	117.5(4)
N(1)—C(1)—P(1)	112.7(3)	C(10)—C(11)—C(12)	121.4(4)	C(18)—C(19)—C(23)	121.7(5)
C(3)—C(2)—C(7)	117.2(4)	N(2)—C(12)—C(11)	121.6(4)	C(20)—C(19)—C(23)	120.8(5)
C(3)—C(2)—N(1)	123.0(4)	N(2)—C(12)—C(13)	121.4(4)	C(19)—C(20)—C(21)	122.7(4)
C(7)—C(2)—N(1)	119.6(4)	C(11)—C(12)—C(13)	117.0(4)	C(20)—C(21)—C(16)	119.2(4)
C(2)—C(3)—C(4)	120.7(4)	C(14)—C(13)—C(12)	120.6(4)	C(20)—C(21)—C(24)	117.0(4)
C(5)—C(4)—C(3)	121.7(4)	C(9)—C(14)—C(13)	122.4(5)	C(16)—C(21)—C(24)	123.8(4)
C(4)—C(5)—C(6)	117.0(4)				

The symmetry operation code used to generate the equivalent atoms is $-x + 1, -y, -z + 1$.

tions. This diphosphine was oxidized only under the conditions of the MALDI TOF experiment; the mass spectrum contains two peaks with *m/z* 1057 and 1073 due to the ions $[M + O + 3 K]^+$ and $[M + 2 O + 3 K]^+$; no peaks with higher *m/z* values were observed. Like macrocyclic compounds **5**—**7**, cyclophane **10** was isolated as a mixture of the *cis*- and *trans*-diastereomers, which is evident from a double set of signals in its ^{1}H NMR spectrum. Part of the signals appear as superimposed singlets or complex multiplets resulting from stereoisomerism; the ratio of the major (*trans*) and minor (*cis*) stereoisomers was 1.4 : 1. The ^{31}P NMR spectrum of compound **10** exhibits a signal at δ −29.00. Its IR spectrum shows a wide band (ν_{max} = 3360 cm^{-1}) due to the amino group and wide bands due to the carboxy group (ν_{max} = 1660 (C=O) and 3100 cm^{-1} (OH)). The band character and positions suggest that the amino and carboxy groups are linked by strong hydrogen bonds. The presence of four carboxy groups makes compound **10** soluble in aqueous NaOH. The formation of macrocyclic structure **10** rather than a cage-type cyclophane, as in the condensation of other primary diamines with bis(hydroxymethyl)organylphosphines,[17,18] can be explained by deactivation of the amino groups with strong hydrogen bonds.

Spontaneous closure of macrocycles from four building blocks at relatively high concentrations of the starting reagents and in the absence of templates allows these reactions to be considered covalent self-assembly processes leading to selective formation of the thermodynamically most stable reaction products.[28] This was additionally confirmed by the fact that macrocyclization proceeds through a great number of coexisting intermediates that gradually transform themselves into the most stable dimeric macrocycle. According to the data obtained, the formation of 1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophanes as major products in reactions of bis(hydroxymethyl)organylphosphines with secondary diamines containing di(*p*-phenylene)methane spacers is of general character and can be considered a route to this novel class of macrocyclic compounds.

Experimental

All NMR experiments were carried out at 303 K. ^{31}P NMR spectra were recorded on Bruker MSL 400 (161.98 MHz) and CXP-100 spectrometers (36.47 MHz). ^{1}H NMR spectra were recorded on Bruker AVANCE 600 (600.13 MHz, wide-line 5-mm probe) and Bruker MSL 400 spectrometers (400.13 MHz). ^{13}C and ^{15}N NMR spectra were recorded on a Bruker AVANCE 600 spectrometer (150.90 (^{13}C) and 60.81 MHz (^{15}N)). Chemical shifts are given on the δ scale with reference to $SiMe_4$ (δ 0.0 (^{1}H) and 0.0 (^{13}C)), CH_3CN (δ 239.5 (^{15}N)), and H_3PO_4 (δ 0.0 (^{31}P)). The 2D HMBC experiment was optimized for the coupling constants $J_{H,C}$ = 9.0 Hz and $J_{H,N}$ = 8.0 Hz. IR spectra were recorded on a Bruker Vector-22 spectrometer (Nujol) in the 400—4000 cm^{-1} range. MALDI TOF mass spectra were recorded on a MALDI TOF-DYNAMO spectrometer with the tetrahydroxyanthracene (THA) matrix. The starting phenyl-[29] and mesitylphosphines[30] were prepared according to known procedures. All manipulations with phosphines were carried out in an inert atmosphere. Dimethylformamide was dried and twice distilled *in vacuo* over P_2O_5; other solvents were purified in common ways.

X-ray diffraction data for compound 5. Single crystals of compound **5** were obtained by crystallization from DMF. Crystals are monoclinic, $C_{52}H_{62}N_4P_2$, M = 805.00. At 210(2) K, a = 19.047(8) Å, b = 10.336(5) Å, c = 11.533(5) Å, α = 90°, β = 99.861(8)°, γ = 90°, V = 2236.9 Å^3, d_{calc} = 1.195 g cm^{-1}, Z = 2, space group $P2(1)/c$ (special position of the molecule in the center of symmetry). The unit cell parameters and the intensities of 7946 reflections (2535 reflections with $I \geq 2\sigma$) were measured on a Siemens CCD SMART diffractometer (λMo-Kα radiation (λ = 0.71073 Å), graphite monochromator, ω scan mode, 2.25 ≤ θ ≤ 23.15°). The data obtained were processed with the SAINT program.[31] Absorption correction was empirically applied with the SADABS program[32] (μMo = 1.37 cm^{-1}). The structure was solved by the direct method and refined in the anisotropic approximation with the SHELX-97 programs.[33] Hydrogen atoms were located in the calculated positions. The image of molecular structure **5** was depicted with the ORTEP program.[34] Final residuals were $R_1(I \geq 2\sigma(I))$ = 0.0877 and $wR_2(I \geq 2\sigma(I))$ = 0.1442 for 2535 independent reflections with $I^2 \geq 2\sigma$ and R_1 = 0.1214 and wR_2 = 0.1540 for all reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Center (CCDC).

Bis[4-(3-pyridylmethyl)aminophenyl]methane (2). A solution of pyridine-3-carbaldehyde (2.16 g, 20.18 mmol) in anhydrous ethanol (10 mL) was added to a solution of bis(4-aminophenyl)methane (2 g, 10.1 mmol) in anhydrous ethanol (20 mL). The reaction mixture was stirred at room temperature for 20 h. The precipitate that formed was filtered off, washed with ethanol, and dried *in vacuo*. The yield of bis[4-(3-pyridylmethylidene)aminophenyl]methane was 3.37 g (81%), m.p. 120 °C. IR, ν/cm^{-1}: 1628 (C=N). ^{1}H NMR (acetone-d_6), δ: 4.09 (s, 2 H, H(1)); 7.26 (d, 4 H, H(3), $^3J_{H(4),H(3)}$ = 8.7 Hz); 7.33 (d, 4 H, H(4), $^3J_{H(3),H(4)}$ = 8.7 Hz); 7.50 (dd, 2 H, H(9), $^3J_{H(10).H(9)}$ = 8.0 Hz, $^3J_{H(8),H(9)}$ = 4.6 Hz); 8.35 (ddd, 2 H, H(10), $^3J_{H(9),H(10)}$ = 8.0 Hz, $^4J_{H(8),H(10)} \approx {}^4J_{H(11),H(10)} \approx$ 2.0 Hz); 8.66—8.71 (m, 4 H, H(6) + H(8)); 9.08 (d, 2 H, H(11), $^4J_{H(10),H(11)}$ = 2.0 Hz).

A solution of bis[4-(3-pyridylmethylidene)aminophenyl]methane (2.73 g, 7.28 mmol) in anhydrous ethanol (50 mL) was added to a suspension of $NaBH_4$ (0.41 g, 10.78 mmol) in anhydrous ethanol (20 mL). The reaction mixture was stirred at 60 °C for 5 h and left for 16 h. The solvent was removed *in vacuo* and the solid residue was washed with diethyl ether and recrystallized from acetonitrile. The yield of compound **2** was 1.85 g (67%), m.p. 116 °C. Found (%): C, 78.47; H, 6.54; N, 14.28. $C_{25}H_{24}N_4$. Calculated (%): C, 78.95; H, 6.31; N, 14.74. IR, ν/cm^{-1}: 3264 (N—H). ^{1}H NMR (CD_3CN), δ: 3.64 (s, 2 H, H(1)); 4.29 (br.s, 2 H, $H(6)_A$); 4.31 (br.s, 2 H, $H(6)_B$); 4.83 (br.s, 2 H, N<u>H</u>); 6.53 (d, 4 H, H(4), $^3J_{H(3),H(4)}$ = 8.3 Hz); 6.92 (d, 4 H, H(3), $^3J_{H(4),H(3)}$ = 8.3 Hz); 7.27 (dd, 2 H, H(9), $^3J_{H(8),H(9)}$ = 7.3 Hz, $^3J_{H(10),H(9)}$ = 4.7 Hz); 7.69 (br.d, 2 H, H(8), $^3J_{H(9),H(8)}$ = 7.3 Hz); 8.43 (dd, 4 H, H(10),

$^3J_{H(9),H(10)}$ = 4.7 Hz, $^4J_{H(11),H(10)}$ = 1.3 Hz); 8.56 (d, 2 H, H(11), $^4J_{H(10),H(11)}$ = 1.3 Hz).

Bis[4-(4-pyridylmethylidene)aminophenyl]methane was obtained as described above from bis(4-aminophenyl)methane (5 g, 25.2 mmol) and pyridine-4-carbaldehyde (5.4 g, 50.5 mmol). The yield was 8.2 g (86%), m.p. 133 °C. IR, ν/cm^{-1}: 1629 (C=N). ^{1}H NMR (acetone-d_6), δ: 4.05 (s, 2 H, H(1)); 7.29 (d, 4 H, H(3), $^3J_{H(4),H(3)}$ = 8.2 Hz); 7.34 (d, 4 H, H(4), $^3J_{H(3),H(4)}$ = 8.2 Hz); 7.83 (d, 4 H, H(8), $^3J_{H(9),H(8)}$ = 5.8 Hz); 8.65 (s, 2 H, H(6)); 8.73 (d, 4 H, H(9), $^3J_{H(8),H(9)}$ = 5.8 Hz).

Bis[4-(4-pyridylmethyl)aminophenyl]methane (3) was obtained analogously from $NaBH_4$ (0.61 g, 16.05 mmol) and bis[4-(4-pyridylmethylidene)aminophenyl]methane (4 g, 10.63 mmol). The reaction time was 10 h. The yield of compound **3** recrystallized from acetone was 3.6 g (89%), m.p. 63 °C. Found (%): C, 78.55; H, 6.61; N, 14.32. $C_{25}H_{24}N_4$. Calculated (%): C, 78.95; H, 6.31; N, 14.74. IR, ν/cm^{-1}: 3285 (N—H_{bound}); 3415 (N—H_{free}). ^{1}H NMR ($CDCl_3$), δ: 3.73 (s, 2 H, H(1)); 4.23 (br.s, 2 H, N<u>H</u>); 4.29—4.33 (m, 4 H, H(6)); 6.47 (d, 4 H, H(4), $^3J_{H(3),H(4)}$ = 8.2 Hz); 6.95 (d, 4 H, H(3), $^3J_{H(4),H(3)}$ = 8.2 Hz); 7.26 (d, 4 H, H(8), $^3J_{H(9),H(8)}$ = 5.5 Hz); 8.51 (d, 4 H, H(9), $^3J_{H(8),H(9)}$ = 5.5 Hz).

3,21-Dimesityl-1,5,19,23-tetramethyl-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophane (5). A mixture of mesitylphosphine (1.13 g, 7.43 mm) and paraformaldehyde (0.45 g, 15 mmol) was stirred at 100—115 °C to homogenization, cooled, and dissolved in dry degassed DMF (15 mL). Then a solution of diamine **1** (1.68 g, 7.43 mmol) in DMF (9 mL) was added. The reaction mixture was stirred at 110 °C for 48 h and concentrated *in vacuo* to one third of its volume. Acetonitrile (20 mL) was added. The liquid over the resulting viscous colorless resin was decanted and volatile components were removed *in vacuo*. The residue was dissolved in a minimum amount of DMF and again reprecipitated. The resulting glassy residue was stirred with ethanol (30 mL) at room temperature for a day. The white powdery precipitate that formed was filtered off, washed with ethanol, dried *in vacuo* (0.1 Torr) for 3 h, and recrystallized from DMF. The resulting fine crystalline precipitate was filtered off, washed with DMF and ethanol, and dried *in vacuo* (0.1 Torr) for 4 h. The yield of compound **5** as a 1.3 : 1 mixture of the *trans*- and *cis*-isomers was 0.63 g (21%), m.p. 165—169 °C. Found (%): C, 77.14; H, 7.89; N, 6.65; P, 7.52. $C_{52}H_{62}N_4P_2$. Calculated (%): C, 77.61; H, 7.71; N, 6.97; P, 7.71. ^{1}H NMR (DMF-d_7), δ: 2.28 (s, C(10)—C<u>H</u>$_3$-*cis*); 2.29 (s, C(10)—C<u>H</u>$_3$-*trans*) (total intensity 6 H); 2.33 (s, C(8)—C<u>H</u>$_3$-*trans*); 2.35 (s, C(8)—C<u>H</u>$_3$-*cis*) (total intensity 12 H); 2.86 (s, N—C<u>H</u>$_3$-*cis*); 2.90 (s, N—C<u>H</u>$_3$-*trans*) (total intensity 12 H); 3.57 (d, H(1)$_A$-*trans*, $^2J_{H,H}$ = 14.1 Hz); 3.62 (m, H(1)$_B$-*trans* + H(1)$_A$-*cis*); 3.68 (d, H(1)$_B$-*cis*, $^2J_{H,H}$ = 10.7 Hz) (total intensity 4 H); 4.11 (dd, H(6)$_A$-*trans*, $^2J_{H,H}$ = 15.0 Hz, $^2J_{H,P}$ = 1.5 Hz); 4.14 (br.d, H(6)$_A$-*cis*, $^2J_{H,H}$ = 15.4 Hz) (total intensity 4 H); 4.35 (dd, H(6)$_B$-*cis*, $^2J_{H,H}$ = 15.4 Hz, $^2J_{H,P}$ = 3.7 Hz); 4.37 (dd, H(6)$_B$-*trans*, $^2J_{H,H}$ = 15.0 Hz, $^2J_{H,P}$ = 2.2 Hz) (total intensity 4 H); 6.40 (d, H(4)-*trans*, $^3J_{H(3)H(4)}$ = 8.7 Hz); 6.48 (d, H(4)-*cis*, $^3J_{H(3),H(4)}$ = 8.5 Hz) (total intensity 8 H); 6.94 (d, 8 H, H(3)-*cis* + H(3)-*trans*, $^3J_{H(4),H(3)} \approx$ 8.7 Hz); 6.96 (s, 4 H, H(9)-*cis* + H(9)-*trans*). ^{31}P{^{1}H} NMR (DMF-d_7), δ: –41.25 (*trans*-**5**), –41.30 (*cis*-**5**). MALDI TOF MS (THA), *m/z* (I_{rel} (%)): 804 $[M]^+$ (45), 827 $[M + Na]^+$ (100), 843 $[M + K]^+$ (67).

The mixture of stereoisomers **5** (0.08 g) was recrystallized from DMF under slow cooling. The precipitate was filtered off, washed with ethanol, and dried *in vacuo* (0.1 Torr) for 4 h. The yield of *trans*-**5** was 0.02 g, m.p. 167—170 °C. ^{1}H NMR (DMF-d_7), δ: 2.29 (s, 6 H, C(10)—C<u>H</u>$_3$); 2.33 (s, 12 H, C(8)—C<u>H</u>$_3$); 2.90 (s, 12 H, N—C<u>H</u>$_3$); 3.57 (d, 2 H, H(1)$_A$, $^2J_{H,H}$ = 14.1 Hz); 3.62 (d, 2 H, H(1)$_B$, $^2J_{H,H}$ = 14.1 Hz); 4.11 (dd, 4 H, H(6)$_A$, $^2J_{H,H}$ = 15.0 Hz, $^2J_{H,P}$ = 1.5 Hz); 4.37 (dd, 4 H, H(6)$_B$, $^2J_{H,H}$ = 15.0 Hz, $^2J_{H,P}$ = 2.2 Hz); 6.40 (d, 8 H, H(4), $^3J_{H(3),H(4)}$ = 8.7 Hz); 6.94 (d, 8 H, H(3), $^3J_{H(4),H(3)}$ = 8.7 Hz); 6.96 (s, 4 H, H(9)). ^{13}C{^{1}H} NMR (DMF-d_7), δ: 20.93 (s, C(10)—<u>C</u>H$_3$); 23.53 (d, C(8)—<u>C</u>H$_3$, $^3J_{C,P}$ = 16.3 Hz); 39.90 (s, N—<u>C</u>H$_3$); 40.68 (s, C(1)); 55.11 (d, C(6), $^1J_{C,P}$ = 18.3 Hz); 113.91 (s, C(4)); 129.36 (s, C(3)); 130.09 (s, C(9)); 131.02 (s, C(2)); 132.50 (d, C(7), $^1J_{C,P}$ = 25.9 Hz); 139.68 (s, C(10)); 144.85 (d, C(8), $^2J_{C,P}$ = 13.7 Hz); 147.50 (s, C(5)). ^{31}P{^{1}H} NMR (DMF-d_7), δ: –41.25. ^{15}N NMR (DMF-d_7), δ: 49.00.

3,21-Diphenyl-1,5,19,23-tetra(3-pyridylmethyl)-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophane (6). A mixture of phenylphosphine (0.8 g, 7.27 mmol) and paraformaldehyde (0.43 g, 14.33 mmol) was stirred at 90—100 °C to homogenization, cooled, and dissolved in dry degassed DMF (5 mL). Then a solution of diamine **2** (2.74 g, 7.21 mmol) in DMF (22 mL) was added. The reaction mixture was stirred at room temperature for 22 days. Volatile components were removed *in vacuo* and the residue was stirred with diethyl ether. The resulting powdery precipitate was filtered off, washed with ether, and dried *in vacuo* (0.1 Torr) for 4 h. The yield of compound **6** as a 3 : 1 mixture of the *trans*- and *cis*-stereoisomers was 2.5 g (67%), m.p. 117—120 °C. Found (%): C, 76.74; H, 6.31; N, 10.61; P, 5.91. $C_{66}H_{62}N_8P_2$. Calculated (%): C, 77.04; H, 6.03; N, 10.90; P, 6.03. ^{1}H NMR ($CDCl_3$), δ: 3.66—3.83 (m, 8 H, H(6)-*cis* + H(6)-*trans*)); 3.86 (br.s, 4 H, H(1)-*cis* + H(1)-*trans*)); 4.29—4.43 (m, 8 H, H(11)-*cis* + H(11)-*trans*)); 6.54 (br.d, H(4)-*cis*, $^3J_{H(3),H(4)}$ = 8.0 Hz); 6.62 (d, H(4)-*trans*, $^3J_{H(3),H(4)}$ = 7.6 Hz) (total intensity 8 H); 6.94 (br.s, 8 H, H(3)-*cis* + H(3)-*trans*); 7.06 (br.s, 4 H, H(14)-*cis* + + H(14)-*trans*), 7.20—7.39 (m, 10 H, H(8) + H(10) + H(13) (*cis* + *trans*)); 7.47 (br.s, 4 H, H(9)-*cis* + H(9)-*trans*); 8.30 (br.s, 4 H, H(16)-*cis* + H(16)-*trans*)); 8.40 (br.s, 4 H, H(15)-*cis* + + H(15)-*trans*)). ^{31}P{^{1}H} NMR ($CHCl_3$), δ: –40.31.

3,21-Diphenyl-1,5,19,23-tetra(4-pyridylmethyl)-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophane (7). A mixture of phenylphosphine (0.45 g, 4.09 mmol) and paraformaldehyde (0.25 g, 8.16 mmol) was stirred at 90—100 °C to homogenization, cooled, and dissolved in dry degassed DMF (15 mL). A solution of diamine **3** (1.55 g, 4.07 mmol) in DMF (15 mL) was added and the reaction mixture was stirred at room temperature for a day. Volatile components were thoroughly removed *in vacuo*. The resulting very viscous oil (2.03 g) was a 1.5 : 1 mixture of *trans*- and *cis*-**7** (85% purity). The yield of compound **7** was 82%.

^{1}H NMR (DMF-d_7), δ: 3.60 (s, H(1)-*cis*)); 3.62 (s, H(1)-*trans*)) (total intensity 4 H); 4.08—4.23 (m, 8 H, H(6)-*cis* + H(6)-*trans*); 4.35 (br.d, H(11)$_A$-*cis*, $^2J_{H,H}$ = 14.0 Hz); 4.45 (d, H(11)$_A$-*trans*, $^2J_{H,H}$ = 17.8 Hz) (total intensity 4 H); 4.57 (d, H(11)$_B$-*trans*, $^2J_{H,H}$ = 17.8 Hz); 4.67 (br.d, H(11)$_B$-*cis*, $^2J_{H,H}$ = 14.0 Hz) (total intensity 4 H); 6.53 (br.d, H(4)-*cis*, $^3J_{H(3),H(4)}$ = 8.2 Hz); 6.64 (d, H(4)-*trans*, $^3J_{H(3),H(4)}$ = 7.6 Hz)

(total intensity 8 H); 6.86—6.95 (m, 8 H, H(3)-*cis* + H(3)-*trans*); 7.08 (br.s, 6 H, H(8) + H(10) (*cis* + *trans*)); 7.37 (br.s, 8 H, H(13)-*cis* + H(13)-*trans*)); 7.73—7.83 (m, 4 H, H(9)-*cis* + + H(9)-*trans*); 8.38 (br.s, H(14)-*trans*); 8.47 (br.s, H(14)-*cis*) (total intensity 8 H). $^{31}P\{^1H\}$ NMR (DMF), δ: −37.66.

3,21-Diphenyl-1,5,19,23-tetra(3-pyridylmethyl)-3,21-dithio-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophane (8). Sulfur (0.022 g, 0.68 mmol) was added to a solution of diphosphine **6** (0.3 g, 0.29 mmol) in DMF (10 mL). The reaction mixture was heated to homogenization and kept for 16 h. The solvent was partially removed *in vacuo* and the precipitate that formed was filtered off, washed with diethyl ether, and dried *in vacuo* (0.1 Torr) for 2 h. The yield of *trans*-**8** was 0.12 g (40%), m.p. 246 °C. Found (%): C, 72.09; H, 6.01; N, 9.97; P, 5.93; S, 6.04. $C_{66}H_{62}N_8P_2S_2$. Calculated (%): C, 72.53; H, 5.68; N, 10.25; P, 5.67; S, 5.86. ^1H NMR ($CDCl_3$), δ: 3.76 (s, 4 H, H(1)); 4.18 (d, 4 H, $H(11)_A$, $^2J_{H,H}$ = 15.5 Hz); 4.27 (d, 4 H, $H(11)_B$, $^2J_{H,H}$ = 15.5 Hz); 4.43 (d, 4 H, $H(6)_A$, $^2J_{H,H}$ = 17.0 Hz); 4.64 (d, 4 H, $H(6)_B$, $^2J_{H,H}$ = 17.0 Hz); 6.65 (d, 8 H, H(4), $^3J_{H(3),H(4)}$ = 8.4 Hz); 6.92 (d, 8 H, H(3), $^3J_{H(4),H(3)}$ = 8.4 Hz); 7.09 (dd, 4 H, H(14), $^3J_{H(13),H(14)}$ = 7.8 Hz, $^3J_{H(15),H(14)}$ = 4.8 Hz); 7.35 (br.d, 4 H, H(13), $^3J_{H(14),H(13)}$ = 7.8 Hz); 7.40 (ddd, 4 H, H(9), $^3J_{H(8),H(9)}$ = 8.0 Hz, $^3J_{H(10),H(9)}$ = 7.2 Hz, $^4J_{P,H}$ = 2.4 Hz); 7.51 (t, 2 H, H(10), $^3J_{H(9),H(10)}$ = 7.2 Hz); 7.79 (dd, 4 H, H(8), $^3J_{P,H}$ = 11.4 Hz, $^3J_{H(9),H(8)}$ = 8.0 Hz); 8.19 (d, 4 H, H(16), $^4J_{H(15),H(16)}$ = 1.2 Hz); 8.39 (br.d, 4 H, H(15), $^3J_{H(14),H(15)}$ = 4.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 40.75. MALDI TOF MS (THA), *m/z* (I_{rel} (%)): 1093 $[M + H]^+$ (100).

3,21-Diphenyl-1,5,19,23-tetra(4-pyridylmethyl)-3,21-dithio-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]paracyclophane (9). Sulfur (0.04 g, 1.25 mmol) was added to a solution of diphosphine **7** (0.65 g, 0.63 mmol) in DMF (10 mL). The reaction mixture was heated to homogenization and kept for 16 h. The solvent was removed *in vacuo* and the residue was stirred with diethyl ether at room temperature. The resulting powdery precipitate was filtered off, washed with ether, and dried *in vacuo* (0.1 Torr) for 3 h. The yield of compound **9** as a 2.6 : 1 mixture of the *trans*- and *cis*-stereoisomers was 0.45 g (65%), m.p. 122—124 °C. Found (%): C, 72.04; H, 5.92; N, 10.31; P, 5.55; S, 6.21. $C_{66}H_{62}N_8P_2S_2$. Calculated (%): C, 72.53; H, 5.68; N, 10.25; P, 5.67; S, 5.86. ^1H NMR (DMF-d_7), δ: 3.55—4.10 (m, 12 H, H(1) + H(11) (*cis* + *trans*)); 4.60—4.92 (m, 8 H, H(6)-*cis* + + H(6)-*trans*); 6.52 (br.d, H(4)-*cis*, $^3J_{H(3),H(4)}$ = 8.2 Hz); 6.69 (d, H(4)-*trans*, $^3J_{H,H}$ = 8.2 Hz) (total intensity 8 H); 6.78—6.88 (m, 8 H, H(3)-*cis* + H(3)-*trans*); 6.91 (br.d, H(13)-*cis*, $^3J_{H,H}$ = 5.5 Hz); 7.12 (br.s, H(13)-*trans*) (total intensity 8 H); 7.30—7.60 (m, 6 H, H(8) + H(10) (*cis* + *trans*)), 8.14—8.22 (m, 4 H, H(9)-*cis* + H(9)-*trans*); 8.39 (br.s, H(14)-*trans*); 8.50 (br.d, H(14)-*cis*, $^3J_{H,H}$ = 5.5 Hz) (total intensity 8 H). $^{31}P\{^1H\}$ NMR (DMF), δ: 40.10. MALDI TOF MS (THA), *m/z* (I_{rel} (%)): 1093 $[M + H]^+$(100).

3,21-Dimesityl-1,5,19,23-tetraaza-3,21-diphospha[5.1.5.1]-paracyclophane-7,15,25,33-tetracarboxylic acid (10). Diamine **4** (0.6 g) in dry degassed DMF (20 mL) was added to a solution of bis(hydroxymethyl)mesitylphosphine (0.45 g, 2.12 mmol) (prepared as described for compound **5**) in dry degassed DMF (10 mL). The reaction mixture was stirred at 100 °C for a day and then at room temperature for two days. Volatile components were removed *in vacuo*. Acetonitrile was added to the residue and the resulting precipitate was filtered off, washed with acetonitrile, and dried *in vacuo* (0.1 Torr) for 3 h. The yield of compound **10** as a 1.3 : 1 mixture of the *trans*- and *cis*-stereoisomers was 0.71 g (72%), m.p. 169 °C. Found (%): C, 67.23; H, 6.08; N, 5.87; P, 7.02. $C_{52}H_{54}N_4O_8P_2$. Calculated (%): C, 67.53; H, 5.84; N, 6.06; P, 6.71. IR, ν/cm^{-1}: 1660 br (C=O), 3100 br (OH), 3360 br (N—H). ^1H NMR (DMF-d_7), δ: 2.17 (br.s, C(8)—C$\underline{H}_3$-*trans*); 2.21 (br.s, C(8)—C$\underline{H}_3$-*cis*) (total intensity 12 H); 2.48 (br.s, 6 H, C(10)—C$\underline{H}_3$(*cis* + *trans*)); 3.69 (s, H(1)-*cis*); 3.71 (s, H(1)-*trans*) (total intensity 4 H); 3.85—4.28 (m, 8 H, H(6)-*cis* + H(6)-*trans*); 6.70—6.75 (m, 8 H, H(4)-*cis* + + H(4)-*trans*)); 6.80—6.89 (m, 8 H, H(3)-*cis* + H(3)-*trans*); 7.15 (s, H(9)-*cis*); 7.17 (s, H(9)-*trans*) (total intensity 4 H); 7.69 (br.s, 4 H, H(5)-*cis* + H(5)-*trans*). $^{31}P\{^1H\}$ NMR (DMF), δ: −30.51. MALDI TOF MS (THA), *m/z* (I_{rel} (%)): 1057 $[M + O + 3 K]^+$ (100), 1073 $[M + 2 O + 3 K]^+$ (74).

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