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Self-assembly of novel macrocyclic aminomethylphosphines with hydrophobic intramolecular cavities

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Novel macroheterocyclic tetraphosphines, namely, 1,1′,5,5′-bis(arylene)-bis(1,5-diaza-3,7-diphosphacyclooctanes) **2**–**6**, were obtained without the use of high-dilution techniques or any matrix by the reaction of bis(hydroxymethyl)-organylphosphines with primary aromatic diamines containing two *p*-phenylene fragments linked by various one-atom bridges in a molecular self-assembly process. The structures of **4**, **5** and **6** were investigated by X-ray crystal structure analyses. The macrocyclic cavities can be described as a truncated rhombohedral prism with side faces formed by phenylene rings and 1,5-diaza-3,7-diphosphacyclooctanes in the truncated acute angles. In the crystals of these macrocycles, solvating DMF molecules are present, and a methyl group from each of two DMF molecules penetrates the macrocyclic cavities of **4** and **5** from either side, whereas only one disordered molecule of DMF penetrates the cavity of macrocycle **6**. Different types of crystal packing are observed for the P-benzyl-substituted compounds **4** and **5** and for the P-mesityl-substituted compound **6**: for **4** and **5** the formation of alternating layers containing the macrocycles and the DMF molecules is observed, in which the cavities of the macrocyclic molecules form channels and the DMF molecules are located in the centers of the channels; in the crystal of **6**, six molecules are arranged around the $\bar{3}$ axis in the fashion of a six-bladed propeller.

Introduction

Phosphines with a large, hollow, basket-like intramolecular cavity have attracted considerable interest during the last decade as a tool for the construction of organized coordination compounds that position catalytic centers, notably transition metals, with hydrophobic host functions in close proximity. Thus, the necessary conditions for effective secondary interaction of the cavity with substrates or reagents in the course of catalytic processes are fulfilled. A number of so-called phosphinocyclodextrins[1,2] and upper-rim phosphinocalixarenes[3–8] were described, and the structures and specific catalytic properties of these unusual ligands were studied. However, no examples of macrocyclic phosphines with sufficiently large basket-like hydrophobic cavities had been described before our preliminary Communication.[9]

Macrocycles containing three-coordinate phosphorus atoms[10–15] are of interest as potential hosts for mono- or polynuclear guests[14] or selective sensors,[16,17] as stabilizing systems for unusual metal-containing species[18] or unusual oxidation states of transition metals,[10,19] and as potential ligands for transition metal catalyzed reactions in organic synthesis, as the geometry and possibly well-defined position of the complexing donor centers could lead to specific catalyst complexes.[20,21] The usual synthetic routes to these macrocycles are reactions under high-dilution conditions or template processes.[10] Nowadays the most promising route to highly organized three-dimensional macrocyclic compounds is a self-assembly process, as was proposed for the spontaneous formation of polynuclear macrocyclic metal complexes.[22–24] The self-assembly approach is now widely used in modern coordination chemistry for the design of well-defined and complex molecular entities by formation of coordinate bonds which can be considered to have properties intermediate between those of covalent bonds and weak and kinetically labile non-covalent interactions in biological systems. Nevertheless, the same principle—a thermodynamic drive to lower energy—generally applies. A characteristic feature of thermodynamic self-assembly processes is that a kinetically rapid and reversible thermodynamic equilibrium exists between the starting materials and the products for all steps of the reaction, so the proportion of each product in the final reaction mixture is determined by its relative thermodynamic stability. As the equilibrium is reversible, the process is self-correcting; a bond which is initially formed "incorrectly" can dissociate and re-associate "correctly". If one of the products is substantially more stable than any of its competitors, the process is highly selective.[22] However this synthetic approach has not yet been practically utilized for the design of organic and organoelement macrocycles. There are only a few examples in the literature of spontaneous closure of phosphorus-containing macrocycles under conditions of relatively high concentration and without any matrix.[10,25–27] Recently we reported the high-yield synthesis and structure of the first representative of a new type of nitrogen-containing macroheterocyclic phosphines, namely, 1,1′,5,5′-bis[methylene-bis(*p*-phenylene)]bis(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (**1**).[9,28] We have now extended this synthetic approach to other macroheterocyclic phosphines **2**–**6**, which are derived from the reaction of bis(hydroxymethyl)phenyl-, bis(hydroxymethyl)benzyl- or bis(hydroxymethyl)mesitylphosphine with 4,4′-diamino-diphenylmethane and its heteroatom analogues 4,4′-thiodianiline and bis(4-aminophenyl)sulfone.

Experimental

General

All manipulations involving primary phosphines and bis(hydroxyalkyl)organylphosphines were carried out under an inert atmosphere. NMR spectra: MSL-400 (Bruker), standards: ^{31}P NMR (161 MHz): external 85% H_3PO_4; WM-250 (Bruker): ^{1}H NMR (250 MHz): internal solvent. ^{13}C NMR spectra were

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Table 1 Reaction conditions and selected spectroscopic data of the macrocycles **2**–**6**

	Concentration of phosphine/M	Reaction time/h	Yield (%)	δ_P/ppm [c]	MS, *m*/*z* ($I_{rel.}$ (%), ion)
2	0.206	4	42	−50.5 (br.)	968 (100, $[M]^+$) [a]
3	0.291	40	18	−47.8	1032 (100, $[M]^+$) [b], 1049 (64, $[M+O+H]^+$)
4	0.25	43	21	−51.7	988 (30, $[M]^+$) [b], 1004 (85, $[M+O]^+$), 1020 (100, $[M+2O]^+$), 1036 (65, $[M+3O]^+$), 1052 (10, $[M+4O]^+$)
5	0.328	41	21	−46.3	1041 (64, $[M+O+H]^+$) [b], 1057 (100, $[M+2O+H]^+$), 1073 (82, $[M+3O+H]^+$)
6	0.084	60	60	−41.5	1136 (100, $[M]^+$) [a]

[a] FAB mass spectrum. [b] MALDI-TOF mass spectrum (matrix: 3-nitroaniline). [c] In DMF.

of only poor quality due to low solubility; the most indicative signals (those of the CH_2 groups) had only very low intensity. The IR spectra were recorded as nujol mulls on a Specord M-80 spectrometer in the range 400–4000 cm^{-1}. The FAB mass spectra were obtained on a ZAB-HSQ-VG Analytical Manchester. The MALDI-TOF mass spectra were obtained on a MALDI-TOF-DYNAMO spectrometer. The melting points were determined on a Boetius apparatus and are uncorrected.

Preparations

General procedure for the synthesis of 2–6. Solid paraformaldehyde (12 mmol) was added to the corresponding primary phosphine (6 mmol) and the reaction mixture was heated at 100–110 °C until the mixture became homogeneous. The resulting bis(hydroxymethyl)organylphosphine was dissolved in dry, degassed DMF (15–35 mL), and then a solution of the corresponding diamine (3 mmol) in DMF (15–35 mL) was added. The reaction mixture was stirred at 100–120 °C for 4–60 h (see Table 1). The precipitate formed was filtered off, washed carefully with DMF and MeCN and dried at 0.1 Torr for 2–4 h. $^{31}P\{^1H\}$ NMR and FAB MS data are given in Table 1.

1,1′,5,5′-Bis[thio-bis(*p*-phenylene)]bis(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (2). Yield: 0.60 g, 42%; mp 220–222 °C. ^1H NMR (DMF-d_7): δ 4.26 (dd, $^2J_{HH}$ = 15.0 Hz, $^2J_{PH}$ = 13.4 Hz, 8H, P–CH_e–N), 4.69 (dd, $^2J_{HH}$ = 15.0 Hz, $^2J_{PH}$ = 4.7 Hz, 8H, P–CH_a–N), 6.73 (d, $^3J_{HH}$ = 8.7 Hz, 8H, *o*-H in N–C_6H_4), 7.53 (d, $^3J_{HH}$ = 8.7 Hz, 8H, *m*-H in N–C_6H_4), 7.55–7.90 (m, 20H, C_6H_5). Anal. calc. for $C_{56}H_{52}N_4P_4S_2$ [968]: C 69.42, H 5.37, N 5.79, P 12.81, S 6.61. Found: C 68.96, H 5.61, N 5.66, P 12.33, S 6.30%.

1,1′,5,5′-Bis[sulfo-bis(*p*-phenylene)]bis(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (3). Yield: 0.28 g, 18%; mp 254–257 °C. ^1H NMR (DMF-d_7,): δ 4.37 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{PH}$ = 11.6 Hz, 8H, P–CH_e–N), 4.81 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{PH}$ = 4.7 Hz, 8H, P–CH_a–N), 6.96 (d, $^3J_{HH}$ = 9.1 Hz, 8H, *o*-H in N–C_6H_4), 7.50–7.90 (m, 20H, C_6H_5), 7.78 (d, $^3J_{HH}$ = 9.1 Hz, 8H, *m*-H in N–C_6H_4). Anal. calc. for $C_{56}H_{52}N_4O_4P_4S_2$ [1032]: C 65.12, H 5.04, N 5.42, P 12.02, S 6.20. Found: C 64.81, H 5.59, N 5.34, P 11.63, S 6.11%.

1,1′,5,5′-Bis[methylene-bis(*p*-phenylene)]bis(3,7-dibenzyl-1,5-diaza-3,7-diphosphacyclooctane) (4). Yield 0.31 g, 21%; mp 189 °C. ^1H NMR (DMF-d_7): δ 3.58 (s, 4H, CH_2), 4.10 (dd, $^2J_{HH}$ = 15.1 Hz, $^2J_{PH}$ = 10.9 Hz, 8H, P–CH_e–N), 6.10 (d, $^3J_{HH}$ = 8.4 Hz, 8H, *o*-H in N–C_6H_4), 6.87 (d, $^3J_{HH}$ = 8.4 Hz, 8H, *m*-H in N–C_6H_4), 7.24–7.50 (m, 20H, C_6H_5). P–CH_2–Ph and P–CH_a–N are obscured by the solvent. Anal. calc. for $C_{62}H_{64}N_4P_4$ [988]: C 75.30, H 6.48, N 5.67, P 12.55. Found: C 74.92, H 6.79, N 5.16, P 12.23%.

1,1′,5,5′-Bis[thio-bis(*p*-phenylene)]bis(3,7-dibenzyl-1,5-diaza-3,7-diphosphacyclooctane) (5). Yield: 0.32 g, 21%; mp 200 °C. ^1H NMR (DMSO-d_6): δ 2.88 (s, 8H, P–CH_2–Ph), 3.74 (dd, $^2J_{HH}$ = 14.7 Hz, $^2J_{PH}$ = 5.0 Hz, 8H, P–CH_a–N), 3.97 (dd, $^2J_{HH}$ = 14.7 Hz, $^2J_{PH}$ = 11.6 Hz, 8H, P–CH_e–N), 6.08 (d, $^3J_{HH}$ = 8.9 Hz, 8H, *o*-H in N–C_6H_4), 7.11 (d, $^3J_{HH}$ = 8.9 Hz, 8H, *m*-H in N–C_6H_4), 7.20–7.40 (m, 20H, C_6H_5). Anal. calc. for $C_{60}H_{60}N_4P_4S_2$ [1024]: C 70.31, H 5.86, N 5.46, P 12.11, S 6.25. Found: C 69.82, H 6.11, N 5.23, P 11.86, S 6.01%.

1,1′,5,5′-Bis[thio-bis(*p*-phenylene)]bis(3,7-dimesityl-1,5-diaza-3,7-diphosphacyclooctane) (6). Yield: 1.02 g, 60%; mp 220 °C. ^1H NMR (DMF-d_7): δ 2.60 (s, 24H, *o*-CH_3 in Mes), 2.83 (s, 12H, *p*-CH_3 in Mes), 4.25 (dd, $^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 7.8 Hz, 8H, P–CH_e–N), 5.07 (dd, $^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 4.1 Hz, 8H, P–CH_a–N), 6.34 (d, $^3J_{HH}$ = 8.8 Hz, 8H, *o*-H in N–C_6H_4), 7.03 (s, 8H, *m*-H in Mes), 7.43 (d, $^3J_{HH}$ = 8.8 Hz, 8H, *m*-H in N–C_6H_4). Anal. calc. for $C_{68}H_{76}N_4P_4S_2$ [1136]: C 71.83, H 6.69, N 4.92, P 10.92, S 5.63. Found: C 71.19, H 7.01, N 4.65, P 11.14, S 5.87%.

X-ray crystallography

X-ray data collection, structure determination, and refinement.

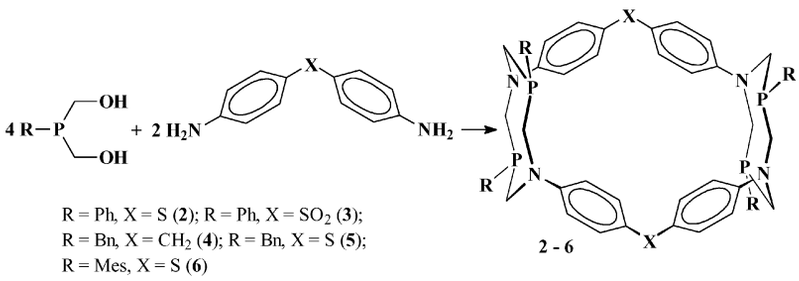
Crystal data: $C_{62}H_{64}N_4P_4{\cdot}4C_3H_7NO$ (**4**); M = 1281.51, monoclinic, space group $P2_1/c$, a = 10.045(1), b = 22.78(1), c = 15.661(3) Å, β = 96.50(1)°, V = 3560(1) Å^3, T = 20 °C; Z = 2, D_{calc} = 1.20 (g cm^{-3}); μ(Cu-Kα) = 1.387 mm^{-1}; 3058 reflections measured, 1691 were observed ($I \geq 2\sigma(I)$). Final R = 0.084, R_w = 0.090 for 1184 reflections with $F^2 \geq 3\sigma(I)$.

$C_{60}H_{60}N_4P_4S_2{\cdot}4C_3H_7NO$ (**5**); M = 1317.58, monoclinic, space group $P2_1/c$, a = 9.983(1), b = 22.972(4), c = 15.777(2) Å, β = 96.94(1)°, V = 3592(1) Å^3, T = 20 °C; Z = 2, D_{calc} = 1.22 (g cm^{-3}); μ(Mo-Kα) = 0.208 mm^{-1}; 7442 reflections measured, 2577 were observed ($I \geq 2\sigma(I)$). Final R = 0.056, R_w = 0.065 for 2543 reflections with $F^2 \geq 3\sigma(I)$. One of the DMF molecules in **5** is disordered between two positions with the equal occupancies 0.5.

Compounds **4** and **5** are isostructural.

$C_{68}H_{76}N_4P_4S_2{\cdot}3C_3H_7NO$ (**6**); M = 1356.62, hexagonal, space group $R\bar{3}$, a = 29.456(3), c = 22.728(5) Å, V = 17078(4) Å^3, T = −50 °C; Z = 9, D_{calc} = 1.19 (g cm^{-3}); μ(Mo-Kα) = 0.205 mm^{-1}; 33048 reflections measured, 7756 independent reflections. Final $R1$ = 0.0552, R_w = 0.1583 for reflections with $I \geq 2\sigma(I)$.

X-ray diffraction data were obtained with an Enraf-Nonius CAD4 four-circle diffractometer [graphite monochromator, Cu-Kα (**4**) and Mo-Kα (**5**) radiation, $\omega/2\theta$ scan method, $\theta \leq$ 74.3° (**4**) or $\theta \leq$ 26.4° (**5**)] or with a SMART CCD diffractometer using ω scan rotation (**6**). Twenty-five centered reflections gave the refined unit cell parameters. The structures of **4** and **5** were solved in the uniquely assignable space group $P2_1/c$ by direct methods using SIR [29] and difference Fourier syntheses. The structure of **6** was solved by direct methods using SHELXS-97 and SHELXL-97 [30] for structure refinement. For **5** and **6**, all non-hydrogen atoms were refined anisotropically; for **4**, only the P and N atoms were refined anisotropically, and all other non-hydrogen atoms were refined isotropically while the thermal and positional parameters of hydrogen atoms were fixed. The calculations for **4** and **5** were carried out on a DEC Alpha Station 200 computer with the MolEN [31] system.



Scheme 1

CCDC reference numbers 218504–218506.

See http://www.rsc.org/suppdata/dt/b3/b311592e/ for crystallographic data in CIF or other electronic format.

Results and discussion

The macrocycle 1,1′,5,5′-bis[methylene-bis(*p*-phenylene)]-bis(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) **1** was the main product of the reaction of bis(hydroxymethyl)phenylphosphine with 4,4′-diaminodiphenylmethane in DMF and was isolated in 50% yield,[9,28] which is unusually high for a one-pot synthesis of such a highly organized structure from six components[12] and may indicate that in the course of the formation of **1** some self-assembly process takes place, similar to that proposed for the formation of polynuclear macrocyclic metal complexes.[22] It was earlier shown that different aminomethylphosphines readily undergo mutual interconversion in the presence of primary and secondary amines or hydroxyalkylphosphines at elevated temperature.[32] So we assumed that the formation of **1** was a particular case of a more general phenomenon. To verify this assumption and to study the influence of the structure of the diamine on the macrocyclization process we carried out the reaction of various bis(hydroxymethyl)organylphosphines with a series of primary aromatic diamines containing different bridging fragments, namely, 4,4′-diaminodiphenylmethane, 4,4′-thiodianiline, 4,4′-oxydianiline, bis(4-aminophenyl)sulfone, 3,3′-diaminodiphenylmethane and benzidine.

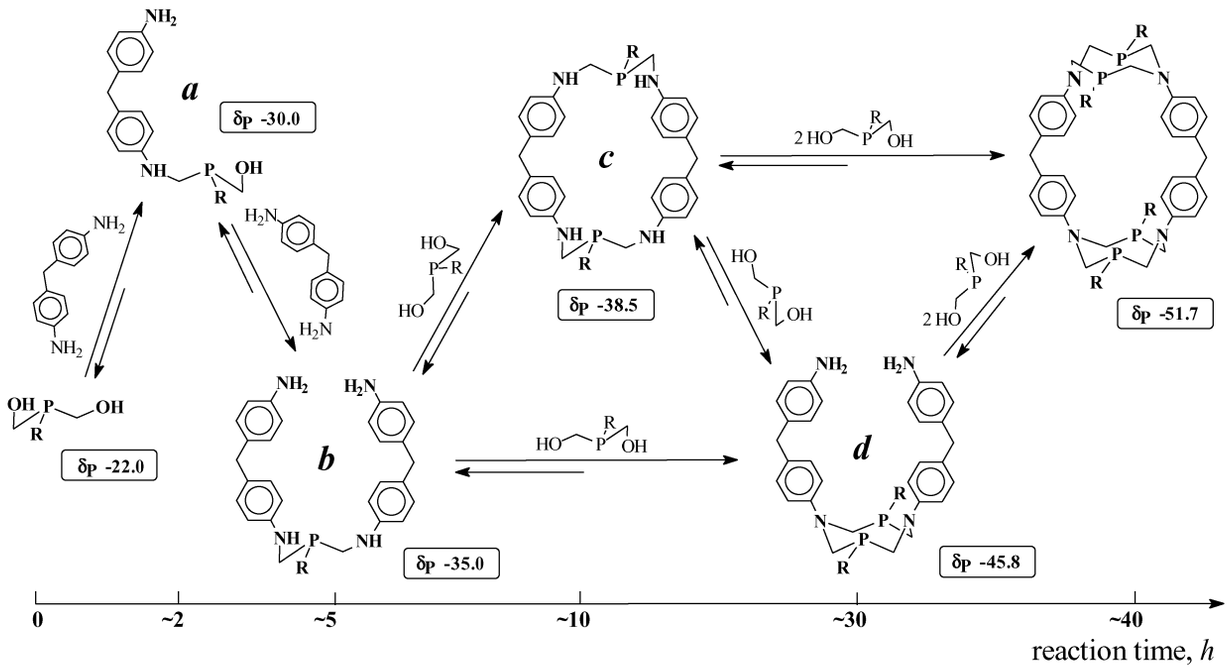
The reactions of bis(hydroxymethyl)phenyl-, bis(hydroxymethyl)benzyl- and bis(hydroxymethyl)mesitylphosphine with 4,4′-diaminodiphenylmethane, 4,4′-thiodianiline and bis(4-aminophenyl)sulfone were performed in DMF at 100–120 °C (Scheme 1). The necessary reaction time depended significantly on both the nature and the concentration of the starting materials (Table 1). Thus, at a phosphine concentration of 0.2–0.3 M the reaction of bis(hydroxymethyl)phenylphosphine with 4,4′-thiodianiline took only 4 h to go to completion, whereas for the less nucleophilic bis(4-aminophenyl)sulfone the necessary reaction time was 40 h. Bis(hydroxymethyl)benzylphosphine unexpectedly appeared to be less reactive than the phenyl derivative, and its reactions with 4,4′-diaminodiphenylmethane and 4,4′-thiodianiline required heating for 41–43 h. The reaction of bis(hydroxymethyl)mesitylphosphine with the above-mentioned diamines was carried out at a phosphine concentration of about 0.08 M and required even longer heating (60–100 h).

In the ^{31}P NMR spectra of the resulting reaction mixtures several peaks in the range δ_P −47 to −52 ppm for the P-phenyl- and the P-benzyl-substituted compounds or in the range δ_P −41.5 to −44.5 ppm for the P-mesityl-substituted compounds were observed, one of which prevailed over the others, and the relative content of the major products in the reaction mixtures was 80–85%. These chemical shifts are similar to those for the monocyclic 1,5-diaza-3,7-diphosphacyclooctanes with the corresponding substituents at the phosphorus atoms.[33,34]

^{31}P NMR monitoring of the relatively slow reaction of bis(hydroxymethyl)benzylphosphine with 4,4′-diaminodiphenylmethane showed that at the very beginning of the reaction a peak at δ_P −30 ppm appeared besides the signal of the phosphine starting material at δ_P −22 ppm. The signal at −30 ppm lies between those observed for bis(hydroxymethyl)organylphosphines and bis(aminomethyl)organylphosphines (δ_P −32 to −35 ppm),[32] which indicates that this signal likely corresponds to the monoaminomethyl derivative **a** (Scheme 2). Further heating (spectrum was obtained after 5 h) led to a predominance of signals in the region −32 to −36 ppm, which is typical for bis(aminomethyl)organylphosphines. Apparently these signals correspond to intermediates including acyclic macrochelate fragments which are similar to the simplest structure **b** shown in Scheme 2. After *ca.* 10 h the intensity of these signals gradually decreased and a peak at δ_P −38.5 ppm became prevalent. The similarity of its chemical shift with that of the monomacrocyclic compound obtained earlier by the reaction of bis(hydroxymethyl)phenylphosphine with bis[4-(methylamino)phenyl]methane (δ_P −39.2 ppm)[28] allows a similar monomacrocyclic structure to be proposed for the corresponding intermediate **c**. Almost at the same time several signals in the 1,5-diaza-3,7-diphosphacyclooctane region (–46 to −52 ppm) appeared, which could correspond both to macrochelate intermediates of type **d** and to different acyclic and cyclic oligo(diazadiphosphacyclooctanes), including the macrocycle **4**. The signal of the latter at −51.7 ppm became the most intense in the final stages of the reaction. It should be mentioned that a clear separation of the reaction steps was not observed, so only the chemical shifts of the prevailing signals of the key intermediates of the self-assembly processes are shown in Scheme 2.

Our attempts to synthesize and isolate the analogous macrocyclic tetraphosphines based on 4,4′-oxydianiline and bis(hydroxymethyl)phenylphosphine or bis(hydroxymethyl)-mesitylphosphine failed. In the ^{31}P NMR spectra of the final reaction mixtures predominant signals were observed at δ_P −52.4 and −44.7 ppm, respectively, which apparently correspond to the macrocyclic products, but we failed to separate these products from other oligomers present as impurities by fractional crystallization or by reprecipitation because of the small difference in the solubility of the macrocyclic aminomethylphosphines and the acyclic oligomeric by-products. Mass spectra showed, besides the peaks of the corresponding 1,1′,5,5′-bis(arylene)-bis(1,5-diaza-3,7-diphosphacyclo-octanes), other peaks at higher and lower masses. Decreasing the concentration of the reagents led only to substantial deceleration of the reactions but did not suppress the formation of undesirable by-products.

Compounds **1**–**6** are high-melting colorless crystalline solids which are sparingly soluble in DMF and DMSO. The structure elucidation of these compounds was based on elemental analysis, ^{31}P and ^{1}H NMR, and mass spectra. Mass spectra (FAB) of compounds **2** and **6** showed only peaks for the molecular ions with *m*/*z* 968 and 1136, respectively, whereas mass spectra (MALDI-TOF) of the macrocycles **3**, **4** and **5** showed several peaks which indicated oxidation of these compounds up to the corresponding mono-, di-, tri- and tetraoxides in a 3-nitroaniline matrix (Table 1). The ^{31}P NMR



Scheme 2 The supposed key intermediates of the macrocyclization process of **4**.

spectra of compounds **2**–**6** showed the absence of oxidation products in solution. The spectra of macrocycles **3**–**6** exibit narrow singlets in the region between −41.5 and −51.7 ppm, which indicate the equivalence of all phosphorus atoms; only the signal of **2** at −50.5 ppm is slightly broadened. The ^{1}H NMR spectra of **2**–**6** also indicate symmetrical structures for all macrocycles in solution. The proton signals of the P–CH_2–N fragments appear as $(AB)_2X$ spin systems. The values of the coupling constants $^{2}J_{HH}$ (14.5–15.6 Hz) and $^{2}J_{PH}$ (7.8–13.4 Hz for the equatorial protons and 4.1 −5.0 Hz for the axial ones) are indicative of a chair–chair conformation of the 1,5-diaza-3,7-diphosphacyclooctane fragments with equatorial orientation of all substituents on the phosphorus atoms.

Whereas the reactions of bis(hydroxymethyl)organylphosphines with diamines with two *p*-phenylene fragments linked by a one-atom bridge X (X = CH_2, S, O, SO_2) afforded the corresponding macrocycles **2**–**6** as major products, even small changes in the spatial structure of the diamine starting material change the direction of these reactions. Thus, the reaction of bis(hydroxymethyl)phenylphosphine with 3,3′-diaminodiphenylmethane gave several unidentified aminomethylphosphines, and the signals of 1,5-diaza-3,7-diphosphacyclooctane-containing species in the region of −45 to −55 ppm were not observed in the ^{31}P NMR spectra of the reaction mixtures. The reaction of bis(hydroxymethyl)phenylphosphine with the linear diamine benzidine led to the formation of a practically insoluble precipitate, which prevented NMR spectroscopic investigations. Its IR spectrum showed weak, broad absorption bands of terminal hydroxyl or amino groups and broad bands in the fingerprint region of the spectrum. Such an IR spectrum is characteristic for oligo(diazadiphosphacyclooctanes) and, in combination with the elemental analysis data, indicates that this product is a mixture of cyclic and linear oligo{1,5-(*p*-phenylene)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctanes.

Strong dependence of the type of product formed on the geometry of the building blocks is typical for the self-assembly of coordination-based supramolecular entities.[23] In these processes the shape of an individual polygon is determined first of all by the values of the turning angles within its angular components. The combination of two 120° bidentate angular components and two 60° angular components yields a molecular parallelogram.[23] In the case of 1,1′,5,5′-bis(arylene)-bis(1,5-diaza-3,7-diphosphacyclooctanes) the values of the turning angles are determined by the bond angles at the bridging atom X between the two *p*-phenylene fragments (103–116°)[35–38] and by the dihedral angle formed by the exocyclic C–N bonds of the diazadiphosphacyclooctane fragment (about 70° according to X-ray analysis data for 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane[39]). Thus, these values are close enough to "ideal" values for the formation of a [2+2] dimer, and the actual shape of the cavity of macrocycle **1** is a hexagonal prism.

The structures of the macrocycles **4**, **5** (Fig. 1) and **6** (Fig. 2) were investigated by X-ray analysis. In all cases the crystals of the macrocycles were obtained as solvates, with four molecules of DMF for **4**, **5** (and **1**) and three for **6**. In **1** (rhombic space group), **4**, **5** (monoclinic space groups) and **6** (hexagonal space group) the macrocyclic molecules are located on crystallographic centers of inversion, and the DMF molecules inside the macrocyclic cavities are disordered. Compounds **4** and **5** are isostructural. In general, the overall structures of the macrocycles **4**–**6** are very similar to each other and to that of compound **1**. Thus, replacement of the substituents on the phosphorus atoms and of the bridging methylene group by a

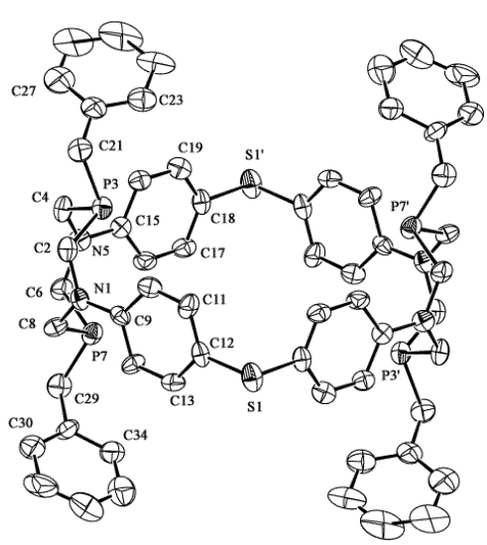


Fig. 1 ORTEP plot of the molecular structure of compound **5**. H atoms and DMF molecules are omitted.

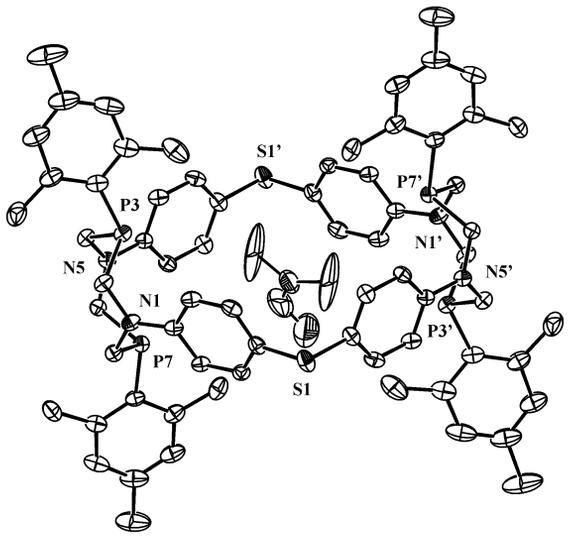


Fig. 2 ORTEP plot of the molecular structure of compound **6** and DMF molecule inside the cavity. H atoms and the other DMF molecules are omitted.

sulfur atom resulted in only minor changes in the geometry of the molecules. The main difference is the conformation of the exocyclic substituents of the phosphorus atoms.

The eight-membered heterocycles adopt a chair–chair conformation, as was also observed for other 1,5-diaza-3,7-diphosphacyclooctanes.[38] The substituents on the phosphorus atoms are in equatorial positions, so that the electron lone pairs of these atoms are directed into the macrocyclic cavity.

The nitrogen atoms are coordinated in a trigonal-planar fashion (the sums of the bond angles are *ca.* 360°) due to conjugation of their electron lone pairs with the π systems of the benzene rings. This conjugation is responsible for the rigid conformation of the macrocycles as a whole.

No noteworthy distortions of the geometrical parameters within experimental errors of the moieties forming the macrocycles are observed. Evidently, the possibility of closure of the macrocycles without appreciable strain favours their formation. The conformations of the macrocycles **4**–**6** are similar, and their overall structures can be described as truncated rhombohedral prisms with the side faces formed by the phenylene rings and 1,5-diaza-3,7-diphosphacyclooctanes in the truncated acute angles. The bridging sulfur atoms in **5** and **6** slightly deviate to opposite sides of the reference plane formed by the four nitrogen atoms. All phenylene fragments forming the cavity are practically orthogonal to this plane (the dihedral angles are about 87°). The two diphenylenesulfide units are oriented face-to-face and generate a cavity with the form of a truncated rhombohedral prism. The cavities of compounds **4**, **5** and **6** are accessible in the observed conformations from the top and the bottom (Fig. 3). For the macrocycles **4** and **5** the diagonal P(3)–P(3′) and P(3)–P(7′) distances are about 9.4 and 8.6 Å, respectively. Due to the bulky mesityl substituents on the phosphorus atoms in compound **6** these distances increase to 9.8 and 10.1 Å. The distances between opposite phenylene rings are in the range of 8.8–9.0 Å. The space-filling model of **5** (Fig. 3) shows the form and size of the cavity. The free volume of the intramolecular cavity is about 100–120 Å^3.

The peculiarity of the crystal structures of the macrocycles **4** and **5** and the previously described macrocycle **1** is the presence of four DMF molecules per molecule of the macrocycle. A methyl group of each of two DMF molecules, which are located on opposite sides of the macrocycle, resides in the macrocyclic cavity (Fig. 4). The position of the methyl groups indicates H-π interaction between these protons and the phenylene fragments of the macrocycles. Two other DMF molecules participate in hydrogen bonding with protons of the exocyclic substituents and form intermolecular contacts with each other.

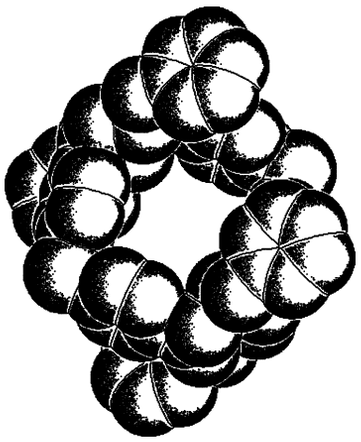


Fig. 3 Space-filling representation of **5** (top view). Solvent molecules are omitted for clarity.

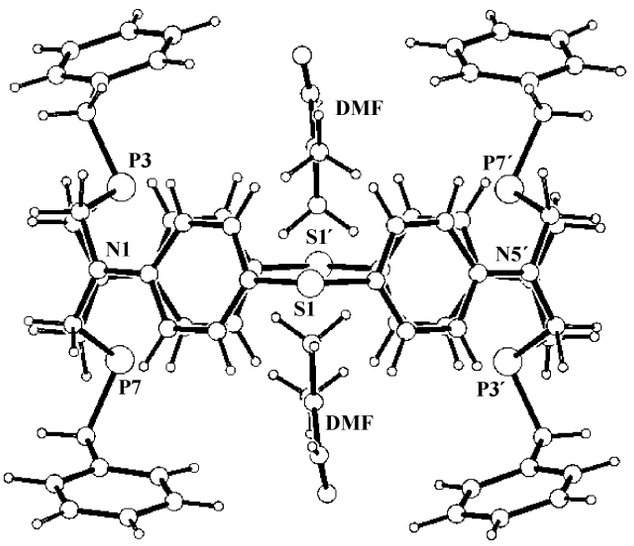


Fig. 4 Side view of **5** with two molecules of DMF inside the cavity.

In the crystal of the macrocycle **6** only one disordered molecule of DMF is located inside the hydrophobic cavity. In the crystal packing of compounds **4** and **5** (Fig. 5) alternating layers containing the macrocycles and the DMF molecules are observed. The exocyclic benzyl substituents of the macrocycles are located in the layers formed by the solvating DMF. Along the *a* axis the macrocyclic molecules form channels, and the DMF molecules are located in the centers of the channels. A very similar crystal packing was observed for the P-phenyl-substituted macrocycle **1**.

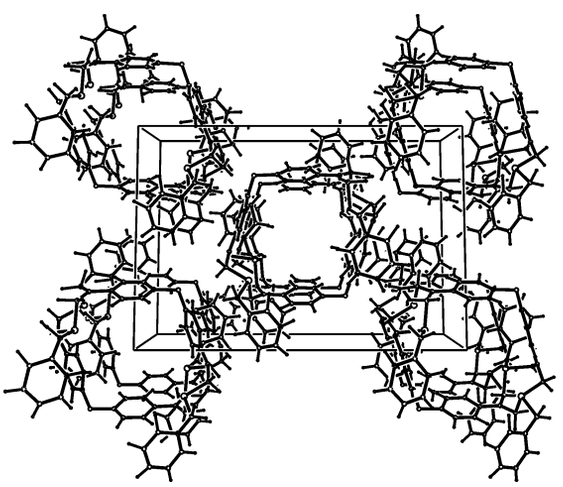


Fig. 5 Five channels of molecules in the crystal structures of **5** viewed along the *a* axis.

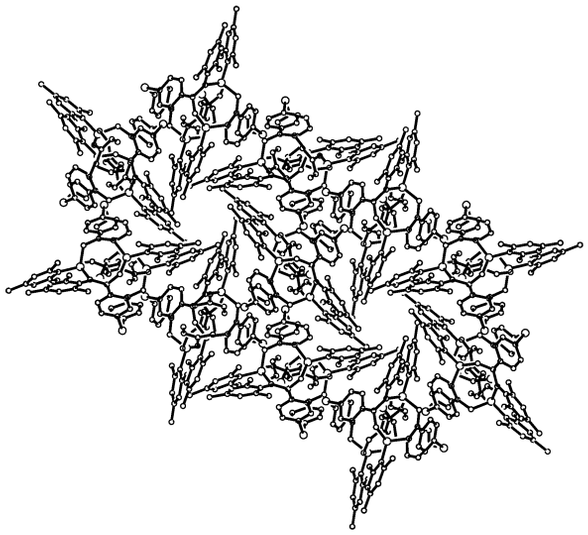


Fig. 6 Crystal packing of **6**.

For the P-mesityl-substituted compound **6** (Fig. 6), six molecules are arranged around an inverted threefold axis in the fashion of a six-bladed propeller. The external and internal parts of the blades are formed by the mesityl groups and are hydrophobic, whereas their middle parts consist of the 28-membered heterocycles and DMF solvate molecules and are relatively more hydrophilic. The external parts of each six-bladed propeller interpenetrate with six other six-bladed propellers. Thus, changes in the substituents on the phosphorus atoms and in the bridging groups do not lead to essential changes in the conformation of the macrocycles, but the nature of the substituents has an influence on the type of crystal packing.

Although the formation of covalent macrocycles based on bis(hydroxymethyl)phosphines and primary aromatic diamines such as 4,4′-diaminodiphenylmethane, 4,4′-thiodianiline and bis(4-aminophenyl)sulfone is less selective than "strict" thermodynamic self-assembly of metal-based supramolecules, it appears to be a general process and may be considered to be a useful method for a simple one-pot synthesis of macroheterocyclic tetraphosphines.

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