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ARTICLE TYPE

Synthesis and unique reversible splitting of 14-membered cyclic aminomethylphosphines on to 7-membered heterocycles.

Elvira I. Musina,[a]* Tatiana I. Fesenko,[a] Igor D. Strelnik,[a] Fedor M. Polyancev,[a] Shamil K. Latypov,[a] Peter Lönnecke[b], Evamarie Hey-Hawkins[b], Andrey A. Karasik,[a] Oleg G. Sinyashin[a]

The novel type of 14-membered cyclic polyphosphines, namely 1,8-diaza-3,6,10,13-tetraphosphacyclotetradecanes $\mathbf{2_a}$-$\mathbf{4_a}$ have been synthesized by the condensation of 1,2-bis(phenylphosphino)ethane, formaldehyde and alkylamines (isopropylamine, ethylamine and cyclohexylamine) as a *RRRR/SSSS*-stereoisomer. The structure of macrocycle $\mathbf{2_a}$ was investigated by NMR-spectroscopy and X-ray crystal structure analysis. The unique reversible processes of macrocycles $\mathbf{2_a}$-$\mathbf{4_a}$ splitting onto corresponding *rac*- ($\mathbf{2_b}$-$\mathbf{4_b}$) and *meso*- ($\mathbf{2_c}$-$\mathbf{4_c}$) stereoisomers of 1-aza-3,6-diphosphacycloheptanes were discovered.

Introduction

The development of phosphorus-containing macrocyclic mixed-donor ligands has emerged as an important subject in coordination chemistry, because they provide characteristic chelating sites that are difficult to construct with their acyclic analogues.[1,2,3] Such hybrid macrocyclic donors are highly promising for designing reactive and multifunctional transition metal catalysts, as, firstly, the metal center can be supported and stabilized by multidentate macrocyclic platforms, secondly, various coordination properties, such as coordination numbers, oxidation state, geometry of the metal center are available by changing of the components of the heteroatom donors, and thirdly, a conformational mobility of the ligands is controllable by suitable choice of the bridging atoms/groups between donor atoms. The macrocyclic multidentate phosphine ligands as formal analogues of the crown ethers hold promise as incredibly stable ligands for applications requiring robust complexes, such as radioactive metal complexes for use as radiopharmaceuticals,[4] for the stable Ni(II) complexes with direct metal-borohydride coordination as potential hydrogenation catalysts,[5] and Cr(II) complexes as reducing agents for the catalytic production of hydrazine and/or ammonia from nitrogen.[6]

It has been over 35 years since the first macrocyclic phosphine ligands were synthesized and few strategies have been designed for their synthesis. However, macrocyclic phosphine ligands have been difficult to synthesize stereoselectively in a good yield and only a handful of synthetic methods have shown broad applicability in terms of the ring sizes, functional groups, and metal complexes that can be obtained.[1,3]

The convenient route to macrocyclic polydentate P,N-ligands by the condensation of primary phosphines or secondary bisphosphines with formaldehyde and primary amines or diamines was developed in our laboratory. This method of the design of macrocyclic polyphosphines was based on the principles of covalent self-assembly and was successfully used for the stereoselective synthesis of macrocyclic aminomethylphosphines: 16-, 18-, 20- membered corands and 28-, 36- and 38-membered cyclophanes.[7] The distinctive feature of the covalent self-assemble processes is their ability of the self-correction, when the "incorrect" intermediate is able to decomposite into starting compounds due to the reversibility of the reaction. These compounds react further to give more thermodynamically stable "correct" product. The P-CH_2-N fragments of aminomethylphosphines are enough labile for the realizing of self-assemble processes. It was shown that lability of aminomethylphosphines plays a key role for the stereoconversion between *RS*- and *RR/SS* isomers of 1-aza-3,6-diphosphacycloheptanes[8] and 16-membered macrocycles as well as alternative formation of only *RSSR* or *RRRR/SSSS* isomer in the row of 16-, 18- and 20-membered cyclic aminomethylphosphines.[7, 9]

The interaction of 1,2-bis(hydroxymethylphenylphospino)ethane with primary aryl- and benzylamines gives only 7-membered 1-aza-3,6-diphosphacycloheptanes as termodinamically more stable products[8] in contrast to hydroxymethyl derivatives of 1,3-, 1,4- and 1,5-bisphosphines giving 16-, 18- and 20-membered cyclic tetraphosphines.[7] However the formation of 14-membered macrocycle was suggested as an intermediate of interconversion of *rac*- and *meso*-isomers of 1-aza-3,6-diphosphacycloheptanes.[8b]

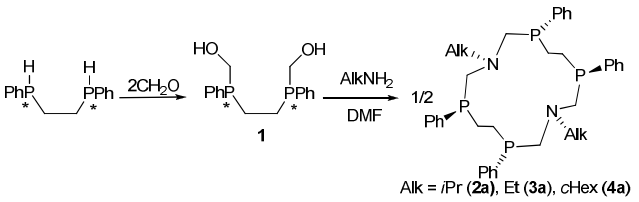
Here we reported the synthesis and crystal structure of novel 14-membered aminomethylphosphines and their unique ability to undergo a reversible splitting on to two 7-membered 1-aza-3,6-diphosphacycloheptanes in solutions.

Results and discussion

Synthesis. It has been shown that sufficient basicity of primary amines is a one of the key requirements for the realization of the self-assembly during Mannich type condensation. The macrocycles $\mathbf{2_a}$-$\mathbf{4_a}$ were obtained by Mannich-like condensation of equimolar mixture of racemic *RR/SS*- and *RS*–isomers of 1,2-bis(hydroxymethylphenylphosphino)ethane **1** with highly basic isopropylamine, ethylamine, and cyclohexylamine respectively in

DMF (Scheme 1). It should be underlined that less basic aryl- or benzylamines in ethanol gave only 7-membered cycles as a result of analogous condensations.[8]

In all cases ^{31}P NMR spectra of the reaction mixtures in DMF (after ca. 1 - 2 hours) show three main signals in the region -27 - -37 ppm which were assigned to the macrocyclic corandes **2a - 4a** and to *rac*- (**2b – 4b**) and *meso*- (**2c – 4c**) isomers of corresponding 1-aza-3,6- diphosphacycloheptanes. However the signals of a few acyclic half-products were registered also.



Scheme 1 Synthesis of macrocycles **2a** - **4a.**

After the heating of the reaction mixture at 60 - 70 °C and following cooling white crystalline products in the yields of 59%, 26% and 20% for $\mathbf{2}_\mathbf{a}$, $\mathbf{3}_\mathbf{a}$ and $\mathbf{4}_\mathbf{a}$ respectively were isolated. The isolated macrocycles $\mathbf{2}_\mathbf{a}$-$\mathbf{4}_\mathbf{a}$ are insoluble in DMF and acetone, but are soluble in benzene, toluene and chloroform. The ESI-MS spectra of these compounds display the picks, the m/z values and isotopic patterns fitted completely with the stoichiometry of macrocycles $\mathbf{2}_\mathbf{a}$-$\mathbf{4}_\mathbf{a}$. In the ^{1}H and ^{31}P NMR spectra of $\mathbf{2}_\mathbf{a}$ - $\mathbf{4}_\mathbf{a}$ measured immediately after the dissolution in C_6D_6 only one set of signals was registered evidencing the formation of only one isomer.

NMR data. Complete structure elucidation of the title compounds was accomplished by a variety of 1D/2D correlation NMR experiments (COSY, HSQC, ^{1}H-^{13}C/^{1}H-^{15}N/^{1}H-^{31}P HMBC).[10,11] 2D DOSY[12,13] and 1D DPFGNOE[14] techniques were used to measure self-diffusion coefficients and NOEs, respectively. The efficiency of NMR approach for total macrocyclic tetraphosphines structure elucidation has been demonstrated recently[15]. Related 1D/2D NMR spectra can be obtained in the Electronic Supplementary Information (ESI, Figures S1 – S29).

Chemical structure of the title 14-membered macrocycles can be established practically "directly" through a variety of internuclear NMR connectivitys starting from P- and N-substituents (e.g. for $\mathbf{2}_\mathbf{a}$ Figure 1). Characteristic NOE's between CH (*i*-Pr) and NCH$^{ax}_2$P, Me^{in} (i-Pr) and NCH$^{ax}_2$P, Me^{out} (i-Pr) and NCH$^{eq}_2$P allow unequivocal assignment of *in*- and *out*-oriented towards macrocycle methyl groups of isopropyl substituent.

One singlet in ^{31}P spectra and only one set of signals for each type of protons in ^{1}H spectra of $\mathbf{2}_\mathbf{a}$-$\mathbf{4}_\mathbf{a}$ suggest high overall symmetry of their 3D structure, *viz* there are four magnetically equivalent fragments that can be superimposed by symmetry operations (Figure 1c). Such high symmetry can be well explained by the fast exchange (in NMR time scale) between two degenerate conformations that occurs through intramolecular rotations around P-CH$_2$-N-CH$_2$-P bonds with synchronous inversions of both nitrogen's LP's (Figure 1c). It is interesting to note that the magnetic environments of each *i*-Pr's methyl groups do not changed during this process, e.g. one methyl (*in*) is always oriented inside while another (*out*) is always outside in respect to macrocycle cavity. Thus configurations of phosphorus atoms of both P-CH$_2$-N-CH$_2$-P fragments have to be the same otherwise *i*-Pr's methyls would be dynamically equivalent and resonate as single doublet. On the other hand P-CH$_2$-CH$_2$-P moiety resonates in ^{1}H spectra as AA'BB'MM' spin system with large vicinal spin-spin couplings ($J_{AB'}$ = ca. 14 Hz, $J_{A'B}$ = ca.15 Hz) that suggests *trans* orientation of two ending phosphorus and opposite directions of their LP's in respect to the macrocycle plane. Thus, NMR spectra of **2a** corresponds to $S_PS_PS_PS_P$ ($R_PR_PR_PR_P$) isomer with three symmetry C_2 axis (passing through two nitrogens, through middles of CH$_2$-CH$_2$ bonds of P-CH$_2$-CH$_2$-P moiety and orthogonal to the macrocycle plane, Figure 1c).

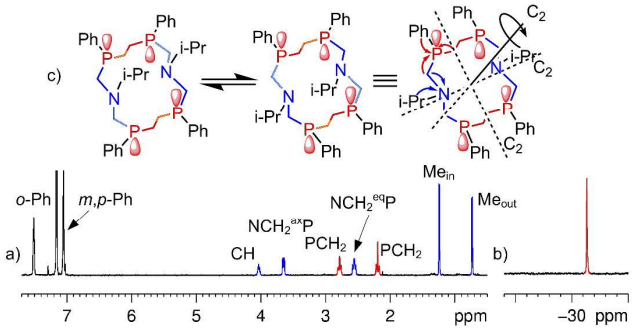


Figure 1 ^{1}H (a) and ^{31}P (b) NMR spectra of 2_a in C_6D_6 at T=303K; c) Schematic representation of the macrocycle conformations in exchange and the main ^{1}H–^{15}N (blue)/^{1}H–^{31}P (red) HMBC correlations.

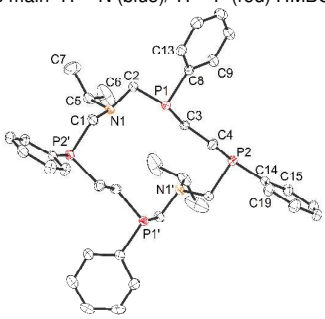


Figure 2 Molecular structure of 2a.

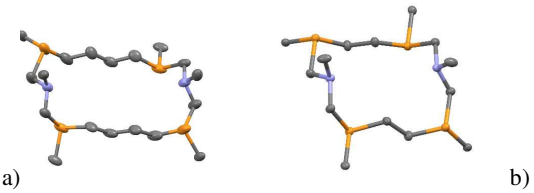


Figure 3 Conformation of 18-membered (a) and 14-membered (b) macrocycles.

Similarity of NMR characteristics of **2a**, **3a** and **4a** (ESI, Figures S1 – S29) let us to conclude that other macrocycles (**3a**, **4a**) were also isolated as one enantiomeric paar *rac*- ($S_PS_PS_PS_P$ ($R_PR_PR_PR_P$)) isomers. The formation of $S_PS_PS_PS_P/R_PR_PR_PR_P$ isomers obeys the recently formulated rule – "If the phosphorus atoms in the macrocycle are linked by an aliphatic chain consisting of an even number of methylene groups, the $S_PS_PS_PS_P/R_PR_PR_PR_P$ isomer is formed".[9]

X-Ray Structure. X-ray analysis of the isolated product $\mathbf{2}_\mathbf{a}$ indicates that the $S_PS_PS_PS_P/R_PR_PR_PR_P$ isomer of the 14-membered corand was formed in the course of the reaction (Figure 2).

Two enantiomers of $\mathbf{2}_\mathbf{a}$, being arranged as separate columns, form a true racemic mixture. Conformation of the cycle is similar to that of $S_PS_PS_PS_P/R_PR_PR_PR_P$ isomer of 18-membered 1,10-diaza-3,8,12,17-tetraphosphacyclooctadecane[9] and differs only by the length of hydrocarbon bridge between phosphorus atoms (4.477Å

and 6.928 Å for 14- and 18-membered macrocycles respectively) (Figure 3). The P…P-distances between phosphorus atoms bridged by CH_2-N-CH_2 fragment have a similar values (4.738 and 4.525 Å) for 14- and 18-membered macrocycles respectively.

According to Dale's nomenclature the conformation of the macrocycle **2a** can be designated as the non-diamond lattice biangular [77]. In the biangular [77] conformations as well as in the [99] conformations for the 18-membered macrocycle, one half of a macrocycle, -$CH_2P(CH_2)_nPCH_2N$-, is the rotated analogue (by $2\pi/2$ radians) of the other with the same configurations at the asymmetric phosphorus atoms (*SSSS* or *RRRR*) and opposing orientations of their lone pairs of electrons relative to each other. The substituents at the nitrogen atoms in **2a** are located on one side of the macrocyclic plane. The nitrogen atoms are trigonal pyramidal (the sum of angles is 335.75°). The phenyl substituents on the phosphorus atoms are located equatorial and alternating relative to macrocycle plane.

Reversible splitting of 2a – 4a in solutions. The lability of the P-CH_2-N-fragment is a key property causing the self-assembly and stereoconversion processes of the cyclic aminomethylphosphines. Recently were reported the interconversions between the stereoisomers of 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes[7] and *rac*- and *meso*-isomers of seven-membered 1-aza-3,7-diphosphacycloheptanes[8] in solutions. The 14-membered heterocycle was supposed to be intermediate of the conversion of seven-membered heterocycles.[8b]

It has been shown that the title 14-membered macrocycles (**2a**–**4a**) are not stable in the solution. After one half of hour two additional sets of signals appeared in the NMR spectra (e.g. Figure 4). Intensities of new sets of signals increased with time while the signals ascribed to 14-membered macrocycle diminished. Finally, after ca. 14 days the system changed significantly. ^{1}H and ^{31}P spectra (Figures 4a, b) corresponded to the mixture of three compounds with integral intensities as ca. 75 (**2b – 4b**) : 22 (**2c – 4c**) : 3 (**2a – 4a**). The quantity of macrocycles **2a - 4a** in the equilibrium mixture is only 2 - 6 %. The isomer **2b – 4b** noticeably prevailed in the equilibrium (73 - 83 %), amount of **2c – 4c** isomer is 15 - 25 %.

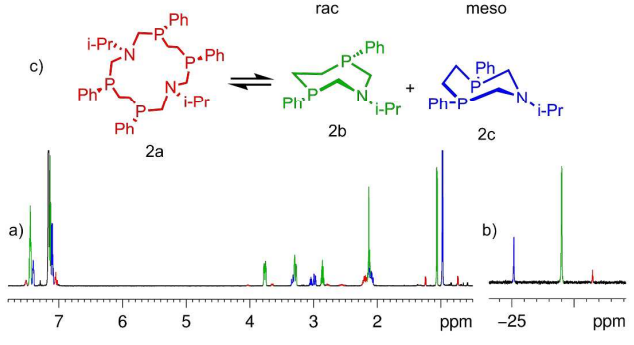


Figure 4 ^{1}H (a) and ^{31}P (b) NMR spectra of 2_a, 2_b and 2_c (correspondingly colored) in C_6D_6 at T=303 K after ca. 14 days. c) Schematic representation of the macrocycle and structures of the 7-membered isomers. The signals on the spectra are colored respectively.

The signals of two new components in ^{1}H and ^{31}P spectra are situated in the same regions and have the same intensity and multiplicity relationships as in described 7-membered heterocycles[8] suggesting that they have chemically close structure. So, it can be well hypothesed that in these cases the 14-membered macrocycles are disassembled onto corresponding half's to give two molecules of 1-aza-3,6-diphosphacycloheptanes in solution (Figure 4c).

^{1}H-^{13}C/^{1}H-^{15}N/^{1}H-^{31}P HMBC correlation experiments allows unequivocally to ascribe signals in NMR spectra to each of component of the mixture (ESI, Figures S7 – S29).

Indeed, according to 2D DOSY spectra for **2** self-diffusion coefficients' (SDC) of new species in solution are ca. equal and notable higher ($1.78*10^{-9}$ m^2/s) than that for initial 14-membered macrocycle ($1.42*10^{-9}$ m^2/s) (ESI, Figure S13). Thus with taking into account Einstein-Stocks relationship between SDC and effective molecular volume,[16] it can be figured out that weight (or volume) of new products are ca. two times less than that of initial 14-membered macrocycle. Thus upon these data we can conclude that new signals correspond to the 7-membered heterocycles. Similar relationships for SDC of different isomers were also observed for **3** (ESI, Figure S21).

Unequivocal assignment of *rac*- and *meso*-isomers can be done on symmetry consideration. For example, two *i*-Pr's methyls of **2** are equivalent in *meso*-form but they should resonate separately in *rac*-isomer like in 14-membered macrocycle. Thus in C_6D_6 solution dominates the *rac*-isomer (δ_P= -28.7 ppm), the *meso*-form (δ_P= -24.8 ppm) being less populated. In similar manner for **3** and **4** equivalence/non-equivalence of N-$C\underline{H}_2$-CH_3 and N-cyclohexyl protons were used to differentiate *meso- versus rac*-isomers

This assignment is also strongly supported by GIAO ^{31}P chemical shift (CS) data. According to calculations (Table 1) for **2** and **4** macrocycles (**2a**, **4a**) should resonate at higher field while the *meso*-isomers (**2c, 4c**) expected to be at lower field than *rac*-isomers (**2b, 4b**). In the case of **3** reverse relationship is expected due to slightly different conformational preference around the N-R bond. All this is in full agreement with experimental findings (Table 1).

Table 1. Calculated and experimental ^{31}P CS's.

	Compound		
	2	**3**	**4**
	δ_{calc}/ δ_{exp} [a]	δ_{calc} [b] / δ_{exp}	δ_{calc}/ δ_{exp}
14-memb. (**a**)	-33.5/ -31.5	-33.7/ -31.5	-33.3 /-31.7
rac (**b**)	-32.3/ -29.0	-43.7/ -36.5	-32.3/-30.0
meso (**c**)	-22.8/ -25.2	-36.9/ -33.5	-23.1/-26.2

[a] Experimental ^{31}P NMR CSs of **2a,b,c** – **4a,b,c** in C_6D_6 at 303 K; [b] for **3** in *rac*- and *meso*-isomers CSs are averaged between two almost isoenergetical conformations around N-R bond.

The NMR monitoring of the interconversion showed that two processes take place: the splitting of the macrocycle onto *RR/SS*- and *RS*-isomers of 7-membered heterocycle and the stereoconversion between those isomers (Figure 5).

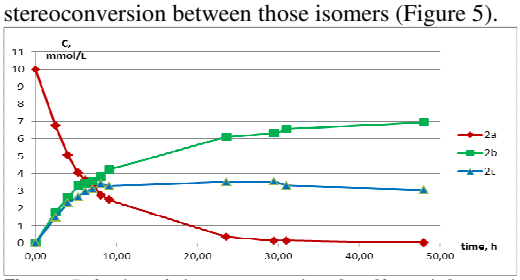


Figure 5 A plot of the concentration **2a**, **2b** and **2c** on the time of the standing in the solution (initial concentration of 2a is 10 mmol/L, T = 343 K, solvent – C_6D_6)

The rate of the both processes is increased by the increase of initial concentration of the macrocycle (from 10mmol/l to 40 mmol/l, ESI, Tables S4, S5) and temperature (295.5K or 343K) (ESI, Tables S5, S6). Moreover, the presence of 10% of p-toluenesulfonic acid as a proton source accelerates the dissociation and the stereoconversion processes (ESI, Table S7). The equilibrium is established during ca. 30 h in contrast to ca. 340 h for acid free mixtures with the same initial concentration and temperature (ESI, Tables S5, S7). The relative content of the products **a**, **b** and **c** in the final equilibrium mixtures does not changed in all cases. So, we suppose, that found interconversion processes are catalyzed by protons from acid or water traces.

Unexpectedly, in spite of prevalence of **2b** – **4b** (73 - 83 %) only crystals of macrocycles **2a** - **4a** were obtained in nearly quantitative yields after the slow evaporation of solvent from equilibrium mixtures. Moreover, only the signal of 14-membered cycle was registered in the NMR spectra of the sample that was obtained after the solvent removal from the equilibrated mixture predominantly containing 7-membered cycles and the subsequent addition of the fresh solvent. These results indicate that the splitting processes are reversible and the difference between formation energies of the 14-membered and 7-membered heterocycles is not significant and crystal packing energy could cause the back formation of 14-membered heterocycle, whereas the stabilization of seven-membered forms in solution may be well explained by the impact of solvent effects and entropic contribution.

Conclusions

In summary, we have demonstrated the effectiveness of the covalent self-assembly approach for the stereoselective synthesis of 14-membered macrocyclic tetrakisphosphines as $S_PS_PS_PS_P/R_PR_PR_PR_P$ stereoisomer thereby expanding the row of 16-, 18- and 20-membered macrocyclic aminomethylphosphines and showing the versatility of Mannich-like condensation reaction between α,ω-bis(arylphosphino)alkanes, formaldehyde and primary amines. In contrast to the higher macrocycles the 14-membered aminomethylphosphines undergo the unusual process of the reversible cycle splitting onto two molecules of 1-aza-3,6-diphosphacycloheptanes. The splitting ability of 14-membered cycles should be taken into account for further design of transition metal complexes and catalytic active systems on their basis, e.g. catalysts for electrochemical hydrogen transformations[17].

Acknowledgements

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Experimental

All manipulations were carried out with standard high-vacuum and dry-nitrogen techniques. Solvents were dried and degased prior to use and stored under nitrogen atmosphere.

NMR Spectroscopy. All NMR experiments were performed with a Bruker AVANCE-600 spectrometer (14.1 T) equipped with a 5 mm diameter gradient inverse broad band probehead and a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5 G·cm^{-1}. Frequencies are 600.13 MHz in ^{1}H NMR, 242.94 MHz in ^{31}P NMR, 150.90 MHz in ^{13}C NMR, and 60.81 MHz in ^{15}N NMR experiments. For 1H-13C correlations HSQC experiment optimized for J = 165 Hz. For 1H-13C long range correlations HMBC experiment optimized for J = 8 Hz. For 1H-31P long range correlations HMBC experiment optimized for J = 8 Hz. For 1H-15N long range correlations HMBC experiment optimized for J = 6 Hz. DOSY experiments were performed with ledbpgp2s, using stimulated echo sequence and two spoil gradients. NOE experiments were performed with 1D DPFGNOE techniques. Samples (ca. 1 mg) were prepared by dissolving in 0.6 mL of the corresponding solvent (C_6D_6 99.5% D (Sigma-Aldrich, Germany)) in an inert atmosphere (Ar) and were placed in standard NMR tubes (Norell, USA). Chemical shifts are reported in the δ (ppm) scale relative to the ^{1}H and ^{13}C signals of tetramethylsilane (TMS) (0.00 ppm). ^{15}N and ^{31}P chemical shifts were referenced to the ^{15}N signal of CH_3CN (235.5 ppm) and ^{31}P signal of 85% H_3PO_4 (0.00 ppm), respectively.

The Fourier transform pulsed-gradient spin–echo (FTPGSE) 13-14 experiments were performed by BPP-STE-LED (bipolar pulse pair–stimulated echo–longitudinal eddy current delay) sequence. Data were acquired with a 50.0 or 120.0 ms diffusion delay, with bipolar gradient pulse duration from 2.2 to 6.0 ms (depending on the system under investigation), 1.1 ms spoil gradient pulse (30%) and a 5.0 ms eddy current delay. The bipolar pulse gradient strength was varied incrementally from 0.01 to 0.32 T/m in 16 steps.

Calculations.

The quantum chemical calculations were performed on the Gaussian 03 software package.[20] Full geometry optimizations have been carried out within the framework of DFT (PBE1PBE) method using 6-31+G(d) basis sets. As recommended[21] ^{31}P CSs were calculated at the PBE1PBE/6-311G(2d,2p) level of theory. ^{31}P CSs were referred at H_3PO_4. Linear scaling procedure was applied for correcting systematic errors.[21]

The ESI mass spectra were obtained on a Bruker Esquire 3000 Plus. The melting points were determined on a Boetius apparatus and are uncorrected.

Synthesis of starting 1,2-bis(phenylphosphino)ethane was carried by described method. All other reagents were purchased from commercial sources and used as received.

Compound **1** was synthesised by described method from corresponded 1,2-bis(phenylphosphino)ethane and formaldehyde.[8]

1,8-diisopropyl-3,6,10,13-tetraphenyl-1,8-diaza-3,6,10,13-tetraphosphacyclotetradecane (2)

To the solution of **1** (from 0.84 g (3.4 mmol) 1,2-bis(phenylphosphino)ethane and 0.20 g (6.7 mmol) paraform) in 5 ml DMF isopropylamine (0.20 g, 3.4 mmol) in 2 ml DMF was added. Reaction mixture was warmed at 50 °C for 7 hours. After cooling the precipitated white crystals were filtered off and washed 2 times with 5 ml of ethanol. Yield: 0.66 g, 59%, mp 159-160 °C. ^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.51 (8 H, br, *o*-Ph), 7.02 - 7.08 (12 H, m, *m,p*-Ph), 4.03 (2 H, p, $^3J_{HH}$ 6.6, CH_3CH), 3.65 (4 H, dd, $^2J_{HH}$ 12.5, $^2J_{PH}$ 4.3, PCH_2N_{ax}), 2.78 (4 H, dd, $^2J_{PH}$ 14.7, $^2J_{HH}$ 11.6, PCH_2), 2.56 (4 H, dd, $^2J_{HH}$ 12.5, $^2J_{PH}$ 8.3, PCH_2N_{eq}), 2.19 (4 H, dd, $^2J_{PH}$ 14.7, $^2J_{HH}$ 12.2, PCH_2), 1.24 (6 H, d, $^3J_{HH}$ 6.9, CH_3CH - *in*), 0.73 (6 H, d, $^3J_{HH}$ 6.6, CH_3CH - *out*). ^{13}C{^{1}H} NMR (150.90 MHz, C_6D_6; ppm): 138.9 (dd, $^1J_{PC}$ 24.0, J_{PC} 5.0, *i*-Ph), 133.7 (ddd, $^2J_{PC}$ 12.5, $^5J_{PC}$ 9.7, $^6J_{PC}$ 9.1, *o*-Ph), 129.7 (s, *m*-Ph), 129.5 (s, *p*-Ph), 57.1 (br, AA'X spin system, $^1J_{PC}$ -10.2, $^3J_{PC}$ 5.9, $^3J_{PP}$ 22.0, $^4J_{PP}$ 11.1, PCH_2N), 51.1 (s, CH_3CH), 27.1 (br, AA'X spin system, $^1J_{PC}$ -19.9, $^2J_{PC}$ 13.2, $^3J_{PP}$ 22.0, $^4J_{PP}$ 11.1, P-CH_2), 22.7 (s, CH_3CH - *in*), 12.7 (s, CH_3CH - *out*). ^{31}P{^{1}H} NMR (242.94 MHz; C_6D_6; ppm): -31.3. ^{15}N (60.81

MHz, C_6D_6, ppm): 41.1, 40.3. MS (ESI+), *m/z*, (I_{rel}, %): 675 (73 $[M+O+H]^+$, 681 (73) $[M+Na]^+$, 697 (100) $[M+K]^+$. Anal. calc. for $C_{38}H_{50}N_2P_4$: C, 69.29; H, 7.65; N, 4.25; P, 18.81. Found: C, 69.27; H, 7.67; N, 4.24; P, 18.76 %.

After 14 days of standing of **2**$_a$ in C_6D_6 the signals of dissociation products - *rac*- (**2**$_b$) and *meso*– (**2**$_c$) isomers of **1-isopropyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane** are prevailed.

Rac- isomer of **1-isopropyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane** (**2**$_b$). ^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.45 (4 H, dd, $^3J_{HH}$ 7.0, $^3J_{PH}$ 6.7, *o*-Ph), 7.13 (6 H, t, $^3J_{HH}$ 7.0, *m,p*-Ph), 3.77 (2 H, ddd, $^2J_{HH}$ 13.6, $^2J_{PH}$ 4.4, $^4J_{HH}$ 4.4, PCH_2N), 3.28 (2 H, dd, $^2J_{HH}$ 13.6, $^4J_{PH}$ 3.1, PCH_2N), 2.86 (1 H, o, $^3J_{HH}$ 6.7, $^3J_{HH}$ 6.4, CH_3CH), 2.04 - 2.25 (4 H, m, PCH_2), 1.06 (3 H, d, $^3J_{HH}$ 6.4, CH_3CH), 0.97 (3 H, d, $^3J_{HH}$ 6.7, CH_3CH). ^{13}C{^{1}H} NMR (150.90 MHz, C_6D_6; ppm): 140.7 (dd, $^1J_{PC}$ 10.7, $^4J_{PC}$ 2.9, *i*-Ph), 133.1 (dd, $^2J_{PC}$ 9.1, $^5J_{PC}$ 5.7, *o*-Ph), 129.4 (m, *m*-Ph), 129.3 (m, *p*-Ph), 57.7 (m, AA'X spin system, $^1J_{PC}$ -15.1, $^3J_{PC}$ 10.5, $^3J_{PP}$ 11.5, PCH_2N), 57.4 (t, $^3J_{PC}$ 3.6, CH_3CH), 27.7 (m, AA'X spin system, $^1J_{PC}$ -15.9, $^2J_{PC}$ 14.1, $^3J_{PP}$ 11.5, PCH_2), 20.4 (s, CH_3CH). ^{31}P{^{1}H} NMR (242.94 MHz; C_6D_6; ppm): -29.0. ^{15}N (60.81 MHz, C_6D_6, ppm): 42.3.

Meso- isomer of **1-isopropyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane** (**2**$_c$).

^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.40 (4 H, dd, $^3J_{HH}$ 7.4, $^3J_{PH}$ 6.3, *o*-Ph), 7.11 (6 H, t, $^3J_{HH}$ 7.4, *m,p*-Ph), 3.26 - 3.35 (2 H, m, PCH_2N), 3.04 (1 H, p, $^3J_{HH}$ 6.6, CH_3CH), 2.98 (2 H, dd, $^2J_{HH}$ 14.0, $^2J_{PH}$ 4.2, PCH_2N), 2.04 - 2.25 (4 H, m, PCH_2), 0.97 (6 H, d, $^3J_{HH}$ 6.7, CH_3CH). ^{13}C{^{1}H} NMR (150.90 MHz, C_6D_6; ppm): 141.1 (dd, $^1J_{PC}$ 10.7, $^4J_{PC}$ 5.3, *i*-Ph), 132.7 (dd, $^2J_{PC}$ 9.0, $^5J_{PC}$ 8.0, *o*-Ph), 129.4 (m, *m*-Ph), 129.3 (m, *p*-Ph), 56.9 (m, AA'X spin system, $^1J_{PC}$ -9.3, $^3J_{PC}$ 2.1, $^3J_{PP}$ 19.5, PCH_2N), 56.4 (t, $^3J_{PC}$ 5.9, CH_3CH), 23.1 (br, AA'X spin system, $^1J_{PC}$ -23.0, $^3J_{PC}$ 15.1, $^3J_{PP}$ 19.5, PCH_2), 20.1 (s, CH_3CH). ^{31}P{^{1}H} NMR (242.94 MHz; C_6D_6; ppm): -25.2. ^{15}N (60.81 MHz, C_6D_6, ppm): 41.3.

1,8-diethyl-3,6,10,13-tetraphenyl-1,8-diaza-3,6,10,13-tetraphosphacyclotetradecane (3)

To the solution of **1** (from 1.6 g (6.5 mmol) 1,2-bis(phenylphosphino)ethane and 0.39 g (13.0 mmol) paraform) in 5 ml DMF 0.2 M solution of ethylamine in methanol (3.3 ml, 6.6 mmol) was added. Reaction mixture was warmed at 50 ^{o}C for 1 hours. After cooling the precipitated white crystals were filtered off and washed 2 times with 5ml of diethyl ether. Yield: 0.54 g, 26%, mp 129-130 °C. ^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.47 (8 H, br, *o*-Ph), 7.05 (12 H, br, *m,p*-Ph), 3.67 (4 H, d, $^2J_{HH}$ 12.1, P-CH_2-N$_{ax}$), 3.45 (2 H, dq, $^2J_{HH}$ 14.0, $^3J_{HH}$ 6.4, NCH_2CH$_3$), 2.74 (4 H, ddm, $^2J_{HH}$ 14.8, $^2J_{PH}$ 12.0, PCH_2), 2.44 (6 H, m, PCH_2N$_{eq}$ + NCH_2CH$_3$), 2.16 (4 H, dd, $^2J_{HH}$ 14.8, $^2J_{PH}$ 12.7, PCH_2), 1.10 (6 H, t, $^3J_{HH}$ 7.1, CH$_2$CH_3). ^{13}C{^{1}H} NMR (150.90 MHz, C_6D_6; ppm): 138.8 (br, *i*-Ph), 133.6 (br, *o*-Ph), 129.5 (br, *m,p*-Ph), 61.4 (m, PCH_2N), 51.3 (m, NCH_2CH$_3$), 26.8 (s, P-CH_2), 12.6 (s, CH$_2$CH_3). ^{31}P{^{1}H} NMR (242.94 MHz; C_6D_6; ppm): -31.5. MS (ESI+), *m/z*, (I_{rel}, %): 647 (100 $[M+O+H]^+$, 663 (29) $[M+2O+H]^+$, 693 (15) $M+4O]^+$. Anal. calc. for $C_{36}H_{46}N_2P_4$: C, 68.56; H, 7.35; N, 4.44; P, 19.65. Found: C, 68.52; H, 7.36; N, 4.45; P, 19.70 %.

After 7 days of standing of **3**$_a$ in C_6D_6 the signals of dissociation products - *rac*- (**3**$_b$) and *meso* – (**3**$_c$) isomers of **1-ethyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane 3** are prevailed.

Rac- isomer of **1-ethyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane** (**3**$_b$). ^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.34 - 7.42 (4 H, br, *o*-Ph), 7.08-7.15 (6 H, m, *m,p*-Ph), 3.83 (2 H, ddd, $^2J_{HH}$ 13.7, $^4J_{HH}$ 4.5, $^2J_{PH}$ 4.5, PCH_2N), 3.20-3.32 (2 H, m, PCH_2N), 2.60-2.79 (2 H, m, NCH_2CH$_3$), 2.00 - 2.20 (4 H, m, PCH_2), 0.98 (3 H, t, $^3J_{HH}$ 7.1, CH$_2$CH_3). ^{13}C{^{1}H} NMR (150.90 MHz, C_6D_6; ppm): 140.2 (dd, $^1J_{CP}$ 8.2, $^4J_{CP}$ 3.9, *i*-Ph), 133.0 (dd, $^2J_{CP}$ 15.8, $^5J_{CP}$ 6.1, *o*-Ph), 129.4 (m, *m*-Ph), 129.0 (s, *p*-Ph), 61.4 (m, AA'X spin system, $^1J_{PC}$ -14.1, $^3J_{PC}$ 11.0, $^3J_{PP}$ 13.5, PCH_2N), 53.9 (t, $^3J_{CP}$ 6.0, NCH_2CH$_3$), 28.8 (m, AA'X spin system, $^1J_{PC}$ -13.8, $^2J_{PC}$ 11.9, $^3J_{PP}$ 13.5, PCH_2), 13.9 (s, CH$_2$CH_3). ^{31}P{^{1}H} NMR (242.94 MHz; C_6D_6; ppm): -36.5.

Meso- isomer of **1-ethyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane** (**3**$_c$). ^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.34 - 7.42 (4 H, br, *o*-Ph), 7.08-7.15 (6 H, m, *m,p*-Ph), 3.20-3.32 (4 H, m, PCH_2N), 2.94 (2 H, q, $^3J_{HH}$ 7.1, NCH_2CH$_3$), 2.00 - 2.20 (4 H, m, PCH_2), 1.03 (3 H, t, $^3J_{HH}$ 7.1, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (150.90 MHz, C_6D_6; ppm): 140.9 (dd, $^1J_{CP}$ 8.5, J_{CP} 5.5, *i*-Ph), 132.8 (dd, $^2J_{CP}$ 18.3, $^5J_{CP}$ 9.2, *o*-Ph), 129.4 (m, *m*-Ph), 129.1 (s, *p*-Ph), 60.8 (dd, $^1J_{CP}$ 11.7, $^3J_{CP}$ 8.9, P-CH_2-N), 51.3 (t, $^3J_{CP}$ 10.2, NCH_2CH$_3$), 24.2 (m, AA'X spin system, $^1J_{PC}$ -22.1, $^2J_{PC}$ 17.9, $^3J_{PP}$ 19.5, PCH_2), 13.8 (s, CH$_2$CH_3). ^{31}P{^{1}H} NMR (242.94 MHz; C_6D_6; ppm): -33.5. MS (ESI+), *m/z*, (I_{rel}, %): 316 (100 $[M+H]^+$, 332 (203) $[M + O + H]^+$.

1,8-dicyclohexyl-3,6,10,13-tetraphenyl-1,8-diaza-3,6,10,13-tetraphosphacyclotetradecane (4)

To the solution of **1** (from 1.1 g (4.5 mmol) 1,2-bis(phenylphosphino)ethane and 0.27 g (9.0 mmol) paraform) in 5 ml DMF cyclohexylamine (0.44 g, 4.4 mmol) in 3 ml DMF was added. Reaction mixture was warmed at 50 ^{o}C for 1 hour. After cooling the precipitated white crystals were filtered off and washed 2 times with 5 ml of ethanol. Yield: 0.33 g, 20%, mp 157-159 °C. ^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.53 (8 H, br, *o*-Ph), 7.04-7.07 (12 H, m, *m,p*-Ph), 3.68 (4 H, dd, $^2J_{HH}$ 12.4, $^2J_{PH}$ 5.4, PCH_2N), 3.61 (2 H, t, $^3J_{HH}$ 9.0, 1-H (*c*Hex)), 2.82 (4 H, br m, PCH_2), 2.68 (4 H, dd, $^2J_{HH}$ 12.4, $^2J_{PH}$ 19.5 Hz, PCH_2N), 2.22 (4 H, br m, PCH_2), 2.04 (2 H, br, 2-H (*c*Hex)), 1.88 (2 H, br, 3-H (*c*Hex)), 1.74 (2 H, d, $^2J_{HH}$ 11.6, 2'-H (*c*Hex)), 1.68 (2 H, d, $^2J_{HH}$ 13.1, 3'-H (*c*Hex)), 1.61 (2 H, d, $^2J_{HH}$ 12.6, 3-H (*c*Hex)), 1.47 (4 H, br, 2,4-H (*c*Hex)), 1.21 (2 H, dt, $^2J_{HH}$ 13.1, $^3J_{HH}$ 12.4, 3'-H (*c*Hex)), 1.02 (2 H, dt, $^2J_{HH}$ 12.8, $^3J_{HH}$ 9.3, 4-H (*c*Hex)), 0.79 (2 H, dt, $^2J_{HH}$ 12.4, $^3J_{HH}$ 11.9 Hz, 2'-H (*c*Hex)). ^{13}C{^{1}H} NMR (150.90 MHz, C_6D_6; ppm): 138.9 (s, *i*-Ph), 133.7 (dd, $^1J_{CP}$ 10.0, J_{CP} 8.0, *o*-Ph), 129.6 (s, *m*-Ph), 129.4 (s, *p*-Ph), 60.4 (s, C-1 (*c*Hex)), 57.8 (s, PCH_2N), 33.4 (s, C-2 (*c*Hex)), 27.6 (s, C-3 (*c*Hex)), 27.4 (s, C-4 (*c*Hex)), 27.1 (br, PCH_2), 26.9 (s, C-3' (*c*Hex)), 24.2 (br, C-2' (*c*Hex)). ^{31}P{^{1}H} NMR (242.94 MHz; C_6D_6; ppm): -31.7. MS (ESI+), *m/z*, (I_{rel}, %): 370 (100 [1/2M + H]$^+$, 755 (36 $[M+O+H]^+$. Anal. calc. for $C_{44}H_{58}N_2P_4$: C, 71.53; H, 7.91; N, 3.79; P, 16.77 %. Found: C, 71.51; H, 7.92; N, 3.75; P, 16.70.

After 5 days of standing of **4**$_a$ in C_6D_6 the signals of dissociation products - *rac*- (**4**$_b$) and *meso* – (**4**$_c$) isomers of **1-cyclohexyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane 4** are prevailed.

Rac- isomer of **1-cyclohexyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane** (**4**$_b$). ^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.47 (4 H, br, *o*-Ph), 7.07-7.14 (6 H, *m, p*-Ph), 3.87 (2 H, ddd, $^2J_{HH}$ 13.7, $^2J_{PH}$ 4.2, $^4J_{HH}$ 4.2, PCH_2N), 3.38 (2 H, d, $^2J_{HH}$ 13.7, PCH_2N), 2.52 (1 H, m, 1-H (*c*Hex)), 2.08 - 2.24 (4 H, m, P-CH_2), 2.00 – 2.08 (1 H, m, 2-H (*c*Hex)), 1.85 – 1.98 (1 H, m, 2'-H (*c*Hex)), 1.57-1.71 (2 H, m, 3, 3'-H (*c*Hex)), 1.45 (1 H, br, 4-H (*c*Hex)), 1.04 – 1.32 (4 H, m, 2, 2', 3, 3'-H (*c*Hex)), 0.90 – 1.02 (1 H, m, 4-H (*c*Hex)). ^{13}C{^{1}H} NMR (150.90 MHz, C_6D_6; ppm): 140.6 (dd, $^1J_{CP}$ 9.7, $^4J_{CP}$ 4.3, *i*-Ph), 133.1 (ddd, $^2J_{CP}$ 18.7, $^5J_{CP}$ 9.8, $^6J_{CP}$ 6.2, *o*-Ph), 129.4 (m, *m*-Ph), 129.0 (m, *p*-Ph), 66.0 (s, C-1 (*c*Hex)), 58.1 (m, AA'X spin system, $^1J_{PC}$ -14.2, $^3J_{PC}$ 10.8, $^3J_{PP}$ 12.9, PCH_2N), 31.19 (s, C-2 (*c*Hex)), 31.14 (s, C-2' (*c*Hex)), 28.0 (m, AA'X spin system, $^1J_{PC}$ -14.2, $^2J_{PC}$ 12.2, $^3J_{PP}$ 12.9, PCH_2),

27.1 (s, C-4 (*c*Hex), 26.7 (s, C-3 (*c*Hex)), 26.6 (s, C-3' (*c*Hex)). $^{31}P\{^{1}H\}$ NMR (242.94 MHz; C_6D_6; ppm): -30.0.

Meso-isomer of **1-cyclohexyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane** (**4$_c$**).

^{1}H NMR (600.13 MHz; C_6D_6; ppm): 7.41 (4 H, br, *o*-Ph), 7.07-7.14 (6 H, *m, p*-Ph), 3.45 (2 H, m, PCH_2N), 3.05 (2 H, d, $^{2}J_{HH}$ 14.2, PCH_2N), 2.78 (1 H, m, 1-H (*c*Hex)), 2.08 - 2.24 (4 H, m, PCH_2), 1.85 – 1.98 (2 H, m, 2-H (*c*Hex)), 1.57-1.71 (2 H, m, 3-H (*c*Hex)), 1.45 (1 H, br, 4-H (*c*Hex)), 1.04 – 1.32 (2 H, m, 3-H (*c*Hex)), 0.90 – 1.02 (1 H, m, 4-H (*c*Hex)). $^{13}C\{^{1}H\}$ NMR (150.90 MHz, C_6D_6; ppm): 141.2 (dd, $^{1}J_{CP}$ 10.7, $^{4}J_{CP}$ 6.5, *i*-Ph), 132.7 (dd, $^{2}J_{CP}$ 8.7, $^{5}J_{CP}$ 5.5, *o*-Ph), 129.4 (m, *m*-Ph), 129.0 (m, *p*-Ph), 64.0 (s, C-1 (*c*Hex)), 57.5 (dd, $^{1}J_{CP}$ -8.7, $^{3}J_{CP}$ 5.1, PCH_2N), 30.8 (s, C-2 (*c*Hex)), 27.0 (s, C-4 (*c*Hex)), 26.5 (s, C-3 (*c*Hex)), 23.4 (m, AA'X spin system, $^{1}J_{PC}$ -22.2, $^{2}J_{PC}$ 15.2, $^{3}J_{PP}$ 20.1, PCH_2). $^{31}P\{^{1}H\}$ NMR (242.94 MHz; C_6D_6; ppm): -26.2. MS (ESI+), *m/z*, (I_{rel}, %): 370 (100 $[M+H]^+$.

X-ray crystallography data. The crystals of **2a** suitable for X-ray diffraction were hand selected from precipitates that separated from the reaction mixtures. The data of **2a** were collected on a Gemini diffractometer (Agilent Technologies) using MoKα radiation (λ = 0.71073 Å) and ω-scan rotation. Data reduction was performed with CrysAlis-Pro[22] including the program SCALE3 ABSPACK for empirical absorption correction. The structure was solved by direct methods (SIR92)[23] and the refinement was performed with SHELXL-2014.[24] The molecule is located on a special position (C_2 axis). All non-hydrogen atoms were refined with anisotropic thermal parameters. A difference-density Fourier map was used to locate all hydrogen atoms in the final stage of the structure refinement. Figure 2 was generated with Diamond.[25] CCDC 1060031 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

Notes and references

a *A.E.Arbuzov Institute of Organic and Physical Chemistry of KSC RAS, Arbuzov str.8, Kazan, 420088,Russian Federation. Fax: +(007)8432732253; Tel: +(007)8432734893; E-mail: elli@iopc.ru*

b *Institute of Inorganic Chemistry, Leipzig University, Johannisallee 29, 04103 Leipzig, Germany. Fax: +(0049)341973319; Tel: +(0049)3419736151; E-mail: hey@uni-leipzig.de*

† Electronic Supplementary Information (ESI) available:. 1D/2D NMR spectra of macrocycle **2a**; ^{1}H - ^{13}C/ ^{1}H - ^{15}N / ^{1}H - ^{31}P HMBC correlation experiments; kinetics of splitting of **2a**; X-Ray Crystallography. See DOI: 10.1039/b000000x/

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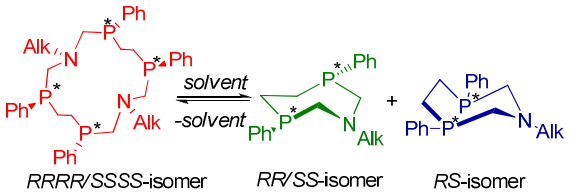
Graphycal abstract.



14-membered cyclic polyphosphines as only *RRRR/SSSS*-stereoisomers have been synthesized by the Mannich-like condensation. The unique reversible processes of macrocycles splitting onto corresponding *rac*- and *meso*- stereoisomers of 1-aza-3,6-diphosphacycloheptanes were discovered.