Dalton Transactions

PAPER

View Article Online
View Journal | View Issue



Cite this: *Dalton Trans.*, 2014, **43**, 12784

# Alternating stereoselective self-assembly of *SSSS/RRRR* or *RSSR* isomers of tetrakisphosphines in the row of 14-, 16-, 18- and 20-membered macrocycles†

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Received 2nd June 2014,
Accepted 24th June 2014

DOI: 10.1039/c4dt01619j

www.rsc.org/dalton

Novel 18- and 20-membered P,N-macrocycles have been obtained stereoselectively by covalent self-assembly of α,ω-bisphosphines, formaldehyde and benzylamine. Alternating *SSSS/RRRR* or *RSSR* diastereomers were formed in the row of the 14-, 16-, 18- and 20-membered macrocyclic aminomethylphosphines. For the first time it was demonstrated that the stereochemical result of the reaction depends on the even or odd number of the methylene groups between the two chiral phosphorus atoms in the initial α,ω-bisphosphines.



## Introduction

Unlike macrocyclic amines, macrocyclic polyphosphines exist as mixtures of diastereomers[1] due to the higher inversion barrier of phosphines with an $sp^3$-hybridized phosphorus atom (150 kJ $mol^{-1}$) compared to amines (30 kJ $mol^{-1}$).[2] Separation of these mixtures and isolation of individual isomers in a pure state are serious obstacles for the use of macrocyclic phosphines in coordination and supramolecular chemistry, as well as in catalysis. Two approaches that allow overcoming the problem have been developed.[3] In a template synthesis, the central metal ion is coordinated by the phosphorus donor centers of an appropriate macrocyclic ligand in the most sterically favorable mode. Decomplexation yields a single diastereomer, in which the directions of the lone pairs of electrons at phosphorus replicate the direction of the coordinative bonds in the complex.[1a,g] The relatively low inversion barrier at phosphorus in phospholes (approximately 67 kJ $mol^{-1}$) and the impossibility of inversion of an $sp^2$-hybridized phosphorus atom in phosphinines are applied in the second approach which facilitates the utilization of polyphospha-macrocycles.[1a,g] Together with their apparent advantages these approaches have drawbacks that hamper their wide application. Due to the high stability of a M–P bond and the macrocyclic effect, the final demetallation step in template synthesis is rather difficult to achieve. The second approach is limited by derivatives of phosphole and phosphinine. We have proposed a novel solution for the problem concerning stereoselective synthesis of macrocyclic polyphosphines. This original method is based on the covalent self-assembly in Mannich-type condensation reactions of 1,3-bis(arylphosphino)propanes, primary alkylamines, and formaldehyde.[1a,4] The self-assembly process in its classical conception is driven by lability of non-covalent forces or coordination bonds which are equally capable to be formed and dissociate in the course of reaction.[5] It results in reversibility of all steps of the reaction and its error correction when thermodynamically less favorable intermediates, being connected through the chain of reversible interactions, are able to be transformed into a single product with a higher thermodynamic stability. However, in some cases equilibrium between interconnected intermediates, existing under self-assembly conditions, may be affected by kinetics rather than thermodynamic control, which shifts a reaction towards a product with lower solubility.[5] Unlike non-covalent linkages, the number of examples in which covalent bonding is involved in thermodynamically controlled self-assembly is relatively limited.[6] This limitation is mainly caused by the ability of only certain types of covalent bonds to dissociate and to be formed reversibly so that the equilibrium between all intermediates in a reaction mixture would be under thermodynamic control.[6] Among such bonds there are imine, amide, disulfide, disele-

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†CCDC 973340 974210. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01619j

nide, alkene, as well as carboxylate, organophosphorus and borate ester bonds.[4]

In 2004, the first stereoselective self-assembly of the $R_PS_PS_PR_P$ stereoisomer of the 16-membered macrocyclic aminomethylphosphine, namely 1,9-dibenzyl-3,7,11,15-tetramesityl-1,9-diaza-3,7,11,15-tetraphosphacyclohexadecane, was described.[7a] Later, other 16-membered macrocyclic aminomethylphosphines (**1**) were reported: 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes with aryl (phenyl and mesityl) substituents on phosphorus atoms and various substituents on nitrogen atoms (phenethyl, picolyl-2, picolyl-3, picolyl-4 and *etc.*).[7b,c] The stereoselective formation of only the $R_PS_PS_PR_P$ stereoisomers was observed. The $R_PS_PS_PR_P$ stereoisomers of 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes were obtained in good yields despite the fact that the starting material, 1,3-bis(arylphosphino)propanes, was used as equimolar diastereomeric mixtures of *meso* and *rac* isomers. The reaction could have potentially resulted in five macrocyclic isomers. Moreover, in spite of the presence of six asymmetric atoms, chiral derivatives of 1,9-di-(*R*)- or -(*S*)-α-methylbenzyl-3,7,11,15-tetramesityl-1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes were obtained as single diastereomers.[7d]

The first example of covalent self-assembly of the 14-membered 1,8-diisopropyl-3,6,10,13-tetraphenyl-1,8-diaza-3,6,10,13-tetraphosphacyclotetradecane (**2**) has been reported recently.[8] Unlike the 16-membered heterocycles, only the $S_PS_PS_PS_P$/$R_PR_PR_PR_P$ isomer of the 14-membered heterocycle was obtained.

In order to find the dependence of stereoselectivity on the length of the chain between the phosphorus atoms we have extended the borders of the ring sizes.

## Results and discussion

Two novel bis(arylphosphino)alkanes, namely 1,4-bis(mesitylphosphino)butane (**3**) and 1,5-bis(mesitylphosphino)pentane (**4**), with longer aliphatic spacers between two asymmetric secondary phosphine groups, were synthesized in good yields. Similar to 1,4-bis(phenylphosphino)butane and 1,5-bis(phenylphosphino)pentane that exist as a 1 : 1 mixture of diastereomers,[9] the *rac* and *meso* isomers of bisphosphines **3** and **4** have shown almost no difference in their NMR spectra. Only in the $^{31}P\{^1H\}$ spectrum of **4** two close signals were observed ($\Delta\delta$ = 0.03 ppm) that can be attributed to two diastereomers.

The one-pot condensation reaction of bis(mesitylphosphino)alkanes **3** and **4** with benzylamine and formaldehyde was carried out for 28 hours at 80 °C with concentrations of reagents in the range of 0.1–0.3 M and without templating reagents. The NMR monitoring of the reaction mixtures showed that the reactions proceeded with the formation of plenty of intermediates and the reaction mixtures were enriched by the isolated products only at the final stage, as in the case of macrocyclizations described earlier for similar 16-membered macrocycles.[7] In the spectra of final reaction mixtures there were minor signals at −28 to −32 ppm which were assigned to intermediate acyclic aminomethylphosphine products and several intensive signals in the narrow range −40 to −44 ppm. It should be underlined that in both cases one of these signals essentially prevailed and corresponded to the stereoisomer of macrocyclic tetraphosphine which was isolated by the spontaneous crystallization from the reaction mixture. Other close signals probably corresponded to other stereoisomers of the formed macrocycles.

As a result, the 18-membered 1,10-dibenzyl-3,8,12,17-tetramesityl-1,10-diaza-3,8,12,17-tetraphosphacyclooctadecane (**5**) and 20-membered 1,11-dibenzyl-3,9,13,19-tetramesityl-1,11-diaza-3,9,13,19-tetraphosphacycloeicosane (**6**) were isolated as crystalline solids in moderate yield and were fully characterized by ESI-MS, $^1H$, $^{13}C$, $^{31}P$ NMR spectroscopy, elemental and X-ray diffraction studies (Scheme 2).

Only one set of signals corresponding to a single diastereomer was observed in the NMR spectra of the 18- and 20-membered corands **5** and **6** proving the isolation of only one isomer of the macrocycles. It has been shown earlier that unlike the acyclic diphosphines the NMR spectra of the diastereomers of the cyclic polyphosphines have a significant difference.[10] Additionally, the NMR $^1H$ spectra of macrocyclic phosphines **5** and **6** had the characteristic features observed earlier for the wide row of 16-membered macrocycles, namely 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes.[7] For instance, a –$PCH_2N$– group is observed in the $^1H$ NMR spectra of **5** and **6** as an AMX spin system with one proton signal shifted upfield ($\delta$ = 2.63 (**5**) and 2.71 (**6**) ppm) in comparison with signals of the corresponding protons for seven- and eight-membered cyclic aminomethylphosphines (3.2–3.6 ppm).[7,11] The geminal methylene protons of the benzyl fragment are nonequivalent and observed as the AB spin system.

It should be mentioned that after few hours in the NMR spectra of (**5**) and (**6**) appeared low intensive additional signals at −40 to −44 ppm which might potentially be attributed to other diastereomers indeed detectable in $^{31}P\{^1H\}$ spectra. Afterwards the spectra did not change perhaps due to the equilibrium establishing. It should be emphasized that the interconversion of macrocyclic stereoisomers in solution confirms the lability of the covalent bonds in the –$PCH_2N$– fragment that provide the self-assembly of macrocycles in the Mannich-type reaction. Recently we described the similar stereoisomer interconversion for 7-membered 1-aza-3,6-diphosphacycloheptanes.[11b,c]

X-ray diffraction studies of the isolated products indicated that the $S_PS_PS_PS_P$/$R_PR_PR_PR_P$ isomer of the 18-membered corand **5** and the $R_PS_PS_PR_P$ isomer of the 20-membered corand **6** were formed in the course of the reaction (Fig. 1). It should be mentioned that pounding and further drying of the macrocrystalline products lead to substances with NMR data identical to (**5**) and (**6**).

X-ray diffraction studies showed that the two enantiomers of product **5**, being arranged as separate columns, form a true racemic mixture (Fig. 2).

The X-ray data of the synthesized products demonstrate identity of the conformations found for the 14-membered

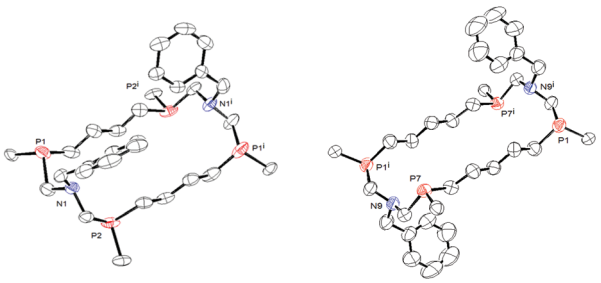


Fig. 1 Molecular structures of macrocycles **5** and **6** in ORTEP view (only the *ipso*-C atoms of the mesityl groups at phosphorus atoms are shown).

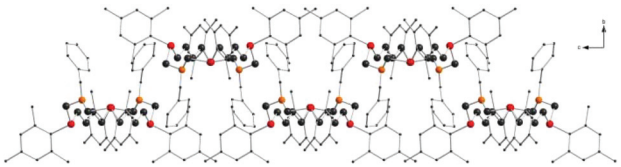


Fig. 2 Packing diagram of macrocycle **5**. The molecules are oriented in an "up-down" fashion.

macrocycles **2** and **5** on the one hand, and the 16-membered derivatives **1** and **6** on the other hand. According to Dale's nomenclature,[12] in which the torsion-angle sequences between *anti* and *gauche* endocyclic bonds were assumed as a basis, the conformations that were found in the solid state of the P,N-containing corands could be designated as the non-diamond lattice biangular [77] (14-membered aminomethylphosphine **2**),[8] [88] (16-membered aminomethylphosphine **1**),[7] [99] (**5**), and [1010] (**6**) (Fig. 3 and 4).

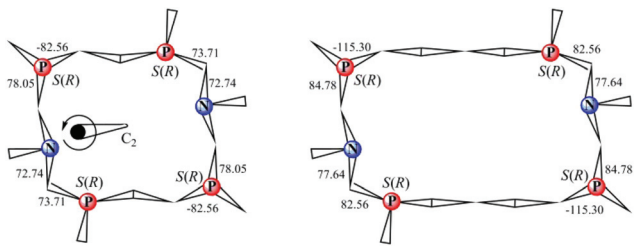


Fig. 3 Dale's wedge representation of the [77] and [99] conformations of the 14- and 18-membered macrocyclic aminomethylphosphines (angles are given in degrees, °).

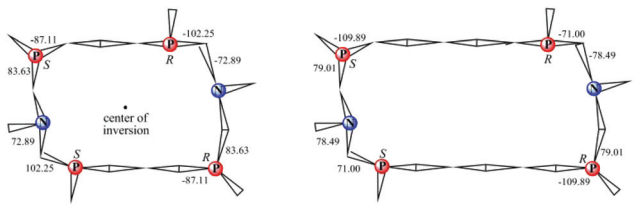



Fig. 4 Dale's wedge representation of the [88] and [1010] conformations of the 16- and 20-membered macrocyclic aminomethylphosphines (angles are given in degrees, °).

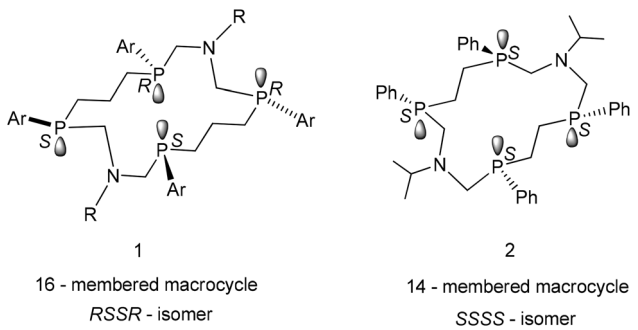
In all the observed conformations there are two "genuine corners" that are composed of an *anti–gauche–gauche–anti* bond sequence with the same sign of torsion angles and two "pseudocorners" in which the signs of torsion angles are opposite (Fig. 3 and 4).

The numbers in square brackets indicate the number of bonds between two "genuine" corners. In spite of the fact that forcefield calculations demonstrated that the biangular [77] conformation of 1,4,8,11-tetraoxacyclotetradecane is more thermodynamically stable than the diamond-lattice quadrangular [3434] conformation,[13] only a few examples of macrocycles existing in this conformation have been reported up to now.[14] The major difference between the biangular [77] and [99] conformations that were found for the $S_PS_PS_PS_P/R_PR_PR_PR_P$ isomers with respect to biangular [88] and [1010] conformations observed for the $R_PS_PS_PR_P$ forms is that the former possess $C_2$ symmetry whereas the latter have a center of inversion. In the biangular [77] and [99] conformations, 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. In the biangular [77] and [99] conformations, the substituents at the nitrogen atoms are located on one side of the macrocyclic plane. In contrast to the $S_PS_PS_PS_P/R_PR_PR_PR_P$ forms, each of two identical fragments $-CH_2P(CH_2)_nPCH_2N-$ in the [88] and [1010] conformations of the $R_PS_PS_PR_P$ isomers is related to the other half by an $S_2$ symmetry operation. The two phosphorus atoms in each half have different configurations (*RS*), and the substituents at the amine units are located on opposite sides of the plane of a macrocycle.

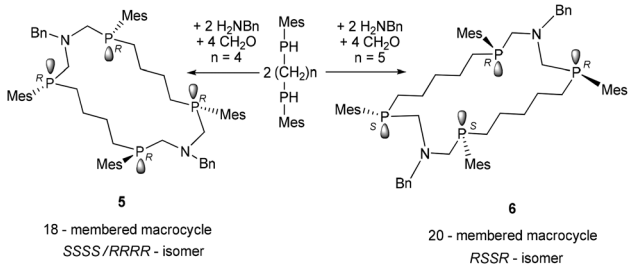
The total number of possible diastereomers for **1**,**2**,**5**,**6** is five: two *rac* forms existing as a pair of enantiomers (II and III, Scheme 3) and three *meso* forms (I, IV, V, Scheme 3).

However, only the stereoisomer with *SSSS*/*RRRR* configuration at phosphorus (type II) in the 14- and 18-membered macrocycles **2** and **5** and the *RSSR* configuration (type I) in the 16- and 20-membered derivatives **1** and **6** was isolated stereoselectively (Schemes 1 and 2).

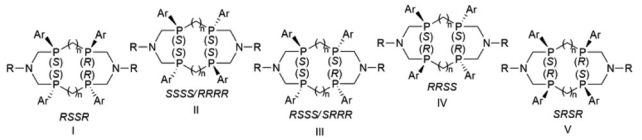
Thus, the configuration at phosphorus in the compounds studied seems to obey a rule: if the two chiral phosphorus centers in the macrocycle are linked by an odd number of




Scheme 1 14- and 16-membered P,N-macrocycles.




Scheme 2 Mannich-type condensation reaction of bis(mesitylphosphino)alkanes, primary amines and formaldehyde.




Scheme 3 Possible diastereomers of macrocyclic tetrakisphosphines **1**,**2**,**5**,**6**.

methylene groups, the $R_PS_PS_PR_P$ (type I) stereoisomer is adopted. If the phosphorus atoms in the macrocycle are linked by an aliphatic chain consisting of an even number of methylene groups, the $S_PS_PS_PS_P/R_PR_PR_PR_P$ (type II) isomer is formed.

## Conclusions

In conclusion, we have demonstrated the effectiveness of the covalent self-assembly approach for the stereoselective synthesis of $S_PS_PS_PS_P/R_PR_PR_PR_P$ or $R_PS_PS_PR_P$ stereoisomers of 18- and 20-membered macrocyclic tetrakisphosphines. It is established that the even or odd number of methylene groups between two chiral phosphorus atoms favors the selection of relative configuration of phosphorus atoms (*SSSS*/*RRRR* or *RSSR* respectively) in the row of 14-, 16-, 18-, and 20-membered aminomethylphosphine corands.

## Experimental

### General procedures

All manipulations were carried out with standard high-vacuum and dry-nitrogen techniques. Solvents were dried and degassed prior to use and stored under a nitrogen atmosphere. The NMR experiments were performed on an Avance 600 (Bruker) spectrometer, standards: $^{31}$P NMR (242.97 MHz): external 85% $H_3PO_4$; $^1$H NMR (600.13 MHz): internal solvent; $^{13}$C NMR (150.90 MHz): internal solvent; Avance DRX 400 (Bruker) spectrometer, standards: $^1$H NMR (400 MHz): internal solvent; $^{13}$C NMR (100.6 MHz): internal solvent; $^{31}$P NMR (162 MHz): external 85% $H_3PO_4$. The ESI mass spectra were obtained on a Bruker Esquire 3000 Plus. The melting points were determined on Boetius apparatus and are uncorrected.

**Synthesis of 1,4-bis(mesitylphosphino)butane (3) and 1,5-bis(mesitylphosphino)pentane (4).** 1,4-Bis(mesitylphosphino)-butane and 1,5-bis(mesitylphosphino)pentane were synthesized similarly to the method applied earlier for the preparation of 1,3-bis(mesitylphosphino)propane.[11a]

0.23 mmol of freshly prepared KOH powder was suspended in 50 mL DMSO and added to a solution of 0.12 mmol of mesitylphosphine in 50 mL DMSO. The yellow reaction mixture was stirred for 1 h. Then 0.06 mmol of the corresponding 1,4-dibromobutane or 1,5-dibromopentane in 50 mL of DMSO was added dropwise. The resulting white suspension was stirred for 5 h, and then 100 mL of degassed water was added giving an exothermic reaction. The product was extracted with three 100 mL portion of *n*-hexane. The *n*-hexane solution was dried for 12 h over $CaCl_2$.1,4-Bis(mesitylphosphino)butane (**3**) and 1,5-bis(mesitylphosphino)pentane (**4**) were isolated as a white solid after evaporation of the solvent.

**1,4-Bis(mesitylphosphino)butane (3).** Yield: 16.3 g, 76%, mp 56–58 °C. $^{31}$P NMR ($CDCl_3$, ppm): −87.3 (d, $^1J_{PH}$ 217.1 Hz). $^1$H NMR ($CDCl_3$, ppm): 1.47 (4H, br. m, $PCH_2CH_2$), 1.55 (2H, br. m, $PCH_2$), 1.72 (2H, br. m, $PCH_2$), 2.25 (6H, s, *p*-$CH_3$ in Mes), 2.43 (12H, s, *o*-$CH_3$ in Mes), 4.21 (2H, br. d, $^1J_{HP}$ 217.1 Hz, P-H), 6.87 (4H, s, *m*-H in Mes). $^{13}$C{$^1$H} NMR ($CDCl_3$, ppm): 21.09 (s, *p*-$CH_3$ in Mes), 21.25 (d, $^1J_{CP}$ 12.0 Hz, $PCH_2$), 23.15 (d, $^3J_{CP}$ 11.1 Hz, *o*-$CH_3$ in Mes), 30.17 (t, $^2J_{CP} \approx {}^3J_{CP}$ 8.5 Hz, $PCH_2CH_2$), 128.99 (d, $^3J_{CP}$ 2.9 Hz, *m*-C in Mes), 130.26 (d, $^1J_{CP}$ 14.0 Hz, *ipso*-C in Mes), 137.98 (s, *p*-C in Mes), 141.82 (d, $^2J_{CP}$ 11.6 Hz, *o*-C in Mes).

**1,5-Bis(mesitylphosphino)pentane (4).** Yield: 18.3 g, 82%, mp 59–61 °C. $^{31}$P{$^1$H} NMR ($CDCl_3$, ppm): −86.9, −86.8. $^{31}$P NMR ($CDCl_3$, ppm): −86.8 (d, $^1J_{PH}$ 217.6 Hz). $^1$H NMR ($CDCl_3$, ppm): 1.40 (6H, br. m, $PCH_2(CH_2)_3CH_2P$), 1.55 (2H br. m, $PCH_2$), 1.74 (2H, br. m, $PCH_2$), 2.26 (6H, s, *p*-$CH_3$ in Mes), 2.45 (12H, s, *o*-$CH_3$ in Mes), 4.22 (2H, dt, $^1J_{HP}$ 217.6 Hz, $^3J_{HP}$ 6.7 Hz, P-H), 6.89 (4H, s, *m*-H in Mes). $^{13}$C{$^1$H} NMR ($CDCl_3$, ppm): 21.11 (s, *p*-$CH_3$ in Mes), 21.51 (d, $^1J_{CP}$ 11.6 Hz, $PCH_2$), 23.17 (d, $^3J_{PC}$ 11.2 Hz, *o*-$CH_3$ in Mes), 28.48 (d, $^2J_{CP}$ 8.3 Hz, $PCH_2CH_2$), 32.36 (t, $^3J_{CP}$ 8.5 Hz, $PCH_2CH_2CH_2CH_2CH_2P$), 129.03 (d, $^3J_{CP}$ 2.9 Hz, *m*-C in Mes), 130.45 (d, $^1J_{CP}$ 14.9 Hz, *ipso*-C in Mes), 137.97 (s, *p*-C in Mes), 141.86 (d, $^2J_{CP}$ 11.5 Hz, *o*-C in Mes).

**(*RRRR*/*SSSS*)-1,10-Dibenzyl-3,8,12,17-tetramesityl-1,10-diaza-3,8,12,17-tetraphosphacyclooctadecane (5).** A solution of 1,4-bis(mesitylphosphino)butane (**3**) (0.33 g, 0.9 mmol) and paraformaldehyde (0.06 g, 2.0 mmol) in DMF (5 mL) was stirred for 2 hours at 80 °C. Then a solution of benzylamine (0.11 g, 1.0 mmol) in DMF (5 mL) was added dropwise for 3 hours at 80 °C. After the reaction mixture was cooled to room temperature, the formation of a crystalline product was observed after 24 hours. The white crystals were filtered off, the crystals suitable for X-ray diffraction were hand picked and then the precipitate was washed with DMF and dried under reduced pressure. Yield: 0.21 g, 47%, mp 183–185 °C. $^{31}$P{$^1$H} NMR, ($CDCl_3$, ppm): −41.6. $^1$H NMR ($CDCl_3$, ppm): 1.49–1.67 (8H, br. m, $PCH_2CH_2$), 1.93–2.03 (8H, m, $PCH_2$), 2.22 (12H, s, *p*-$CH_3$ in Mes), 2.45 (24H, s, *o*-$CH_3$ in Mes), 2.63 (4H, dd, $^2J_{HH}$ 12.7 Hz, $^2J_{HP}$ 9.3 Hz, $PCH_2N$), 3.16 (2H, d, $^2J_{HH}$ 12.7 Hz, $CH_2Ph$),

3.96 (4H, d, $^2J_{HH}$ 12.7 Hz, $PCH_2N$), 4.42 (2H, d, $^2J_{HH}$ 12.7 Hz, $CH_2Ph$), 6.80 (8H, s, *m*-H in Mes), 7.21 (10H, m, Ph). $^{13}C\{^1H\}$ NMR ($C_6D_6$, ppm): 20.95 (s, *p*-$CH_3$), 23.87 (d, $^3J_{CP}$ 19.0 Hz, *o*-$CH_3$), 26.33–27.02 (br. m, $PCH_2$ overlapped with $PCH_2CH_2$), 55.93 (d, $^1J_{CP}$ 8.7 Hz, $PCH_2N$), 62.86 (br. m, $CH_2Ph$), 127.14 (s, *p*-C in Ph), 127.82–128.31 (*o*-C and *m*-C in Ph overlapped with $C_6D_6$), 129.84 (br. d, $^1J_{CP}$ 28.0 Hz, *ipso*-C in Mes overlapped with *m*-C in Mes), 130.02 (br. s, *m*-C in Mes overlapped with *ipso*-C in Mes), 138.80 (d, $^4J_{CP}$ 2.9 Hz, *p*-C in Mes), 140.33 (s, *ipso*-C in Ph), 144.87 (d, $^2J_{CP}$ 14.9 Hz, *o*-C in Mes). MS (ESI+) *m*/*z* (%): 995 (20, $[M + H + O]^+$), 1011 (60, $[M + H + 2O]^+$), 1015 (100,$[M + 2H_2O]^+$), 1027 (33, $[M + H + 3O]^+$), 1043 (19, $[M + H + 4O]^+$). Anal. calc. for $C_{62}H_{82}N_2P_4$ [979]: C, 76.1; H, 8.4; N, 2.9; P, 12.7. Found: C, 75.9; H, 8.4; N, 2.8; P, 12.6%.

**(*RSSR*)-1,11-Dibenzyl-3,9,13,19-tetramesityl-1,11-diaza-3,9,13,19-tetraphosphacycloeicosane (6).** Compound **6** was synthesized similar to **5** from 1,5-bis(mesitylphosphino)pentane (**4**) (0.35 g, 0.9 mmol). Yield: 0.27 g, 57%, mp 189–191 °C. $^{31}P\{^1H\}$ NMR, ($CDCl_3$, ppm): −42.0. $^1H$ NMR ($CDCl_3$, ppm): 1.48–1.58 (12H, br. m, $PCH_2(CH_2)_3CH_2P$), 1.83 (4H, m, $PCH_2$), 2.02 (4H, m, $PCH_2$), 2.24 (12H, s, *p*-$CH_3$ in Mes), 2.46 (24H, s, *o*-$CH_3$ in Mes), 2.71 (4H, dd, $^2J_{HH}$ 12.7 Hz, $^2J_{HP}$ 7.2 Hz, $PCH_2N$), 3.14 (2H, d, $^2J_{HH}$ 12.7 Hz, $CH_2Ph$), 3.90 (4H, d, $^2J_{HH}$ 12.7 Hz, $PCH_2N$), 4.32 (2H, d, $^2J_{HH}$ 12.7 Hz, $CH_2Ph$), 6.82 (8H, s, *m*-H in Mes), 7.17–7.20 (10H, br. m, Ph). $^{13}C\{^1H\}$ NMR ($C_6D_6$, ppm): 20.95 (s, *p*-$CH_3$), 23.87 (d, $^3J_{CP}$ 19.0 Hz, *o*-$CH_3$), 27.32 (d, $^1J_{CP}$ 14.2 Hz, $PCH_2$), 29.34 (d, $^2J_{CP}$ 24.0 Hz, $PCH_2CH_2$), 33.91 (t, $^3J_{CP}$ 14.3 Hz, $PCH_2CH_2CH_2CH_2CH_2P$), 56.44 (d, $^1J_{CP}$ 10.0 Hz, $PCH_2N$), 61.44 (t, $^3J_{CP}$ 9.2 Hz, $CH_2Ph$), 127.16 (s, *p*-C in Ph), 127.82–128.30 (*m*-C in Ph overlapped with $C_6D_6$), 129.74 (br. s, *o*-C in Ph overlapped with $C_6D_6$), 130.02 (d, $^3J_{CP}$ 3.8 Hz, *m*-C in Mes), 131.48 (br. d, $^1J_{CP}$ 20.5 Hz, *ipso*-C in Mes), 138.77 (s, *p*-C in Mes), 140.25 (s, *ipso*-C in Ph), 144.73 (d, $^2J_{CP}$ 14.7 Hz, *o*-C in Mes). MS (ESI+) *m*/*z*: 1024 (24, $[M + H + O]^+$), 1040 (24, $[M + H + 2O]^+$), 1043 (44, $[M + 2H_2O]^+$), 1056 (20, $[M + H + 3O]^+$), 1072 (100, $[M + H + 4O]^+$), 1094 (68, $[M + Na + 4O]^+$). Anal. calc. for $C_{64}H_{86}N_2P_4$ [1007]: C, 76.3; H, 8.6; N, 2.8; P, 12.3. Found: C, 76.2; H, 8.5; N, 2.7; P, 12.2%.

### X-ray crystallography data

The crystals of **5** and **6** suitable for X-ray diffraction were hand picked from precipitates that separated from the reaction mixtures. The data of **5** were collected on a Gemini diffractometer (Agilent Technologies) using MoKα radiation ($\lambda$ = 0.71073 Å) and $\omega$-scan rotation. Data reduction was performed with CrysAlis-Pro[15] including the program SCALE3 ABSPACK for empirical absorption correction. The structure was solved by direct methods and the refinement of all non-hydrogen atoms was performed with SHELX97.[16] The molecule is located on a special position ($C_2$-axis) and mesityl substituents and solvent molecules (DMF) were found to be disordered. All non-hydrogen atoms were refined anisotropically, H atoms were calculated on idealized positions and refined isotropically. Data of **6** were collected on a Bruker Smart Apex II CCD diffractometer using graphite monochromated MoKα ($\lambda$ = 0.71073 Å) radiation and $\omega$-scan rotation. Data collection images were indexed, integrated, and scaled using the APEX2 data reduction package[17] and corrected for absorption using SADABS.[18] The structure was solved by direct methods using SHELX97. All non-hydrogen atoms were refined anisotropically. H atoms were calculated on idealized positions and refined as riding atoms. Pictures were generated with ORTEP3 for Windows.[19] CCDC 973340 (**5**), 974210 (**6**) contain the supplementary crystallographic data for this paper.

### Crystal data, structure refinement for compound 5

$C_{62}H_{82}P_4N_2$ 2 DMF (**5**); $M$ = 1125.37, monoclinic, space group $C2/c$, $a$ = 32.657(1), $b$ = 12.9533(4), $c$ = 16.2958(5) Å, $\beta$ = 105.974(3)°, $V$ = 6627.1(4) Å$^3$, $Z$ = 4, $D_{calc}$ = 1.128 g cm$^{-3}$; $\mu$(Mo-Kα) = 0.158 mm$^{-1}$; 30 265 reflections measured, 4752 independent reflections. Final $R_1$ = 0.0532, $R$w = 0.1195 for reflections with $I \geq 2\sigma(I)$, and $R_1$ = 0.1134, $R$w = 0.1394 for all reflections.

### Crystal data, structure refinement for compound 6

$C_{64}H_{86}P_4N_2$ (**6**); $M$ = 1007.22, triclinic, space group $P\bar{1}$, $a$ = 8.978(7), $b$ = 11.999(9), $c$ = 15.378(11) Å, $\alpha$ = 77.012(8), $\beta$ = 86.156(9), $\gamma$ = 70.547(8)°, $V$ = 1522.2(19) Å$^3$, $Z$ = 1 (molecule is located on a special position), $D_{calc}$ = 1.099 g cm$^{-3}$; $\mu$(Mo-Kα) = 0.162 mm$^{-1}$; 11 374 reflections measured, 5840 independent reflections. Final $R_1$ = 0.0778, $R$w = 0.2112 for reflections with $I \geq 2\sigma(I)$, and $R_1$ = 0.1370, $R$w = 0.2573 for all reflections.

## Acknowledgements

This work was supported by RFBR (no.12-03-97083-r_povolzhye_a, 13-03-00563).

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