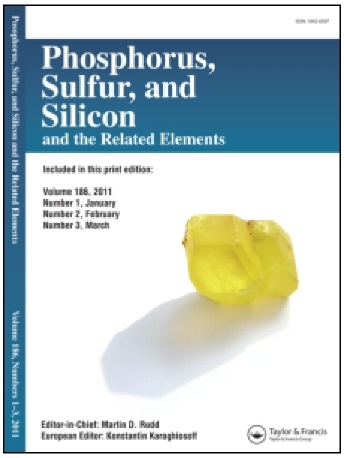

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Stereoselective Synthesis and Interconversions of 1,9-Diaza-3,7,11,15-Tetraphosphacyclohexadecanes

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We report here the novel stereoselective method of design of macrocyclic tetraphosphines, based on the principles of covalent self-assembly.

Keywords Macrocyclic polyphosphine; self-assembly, stereoselectivity

INTRODUCTION

Phosphine ligands are one of the most usable in the catalysis whereas the catalytic systems with macrocyclic polyphosphines have been investigated very poorly.[1] The reasons of such insignificant attention are explained by the difficulties of preparation of macrocyclic polyphosphines, such as the problems with decomplexation of desired macrocycle in the course of template synthesis[2] and low yields of reactions at high dilution conditions.[3] One more problem arises from the high pyramidal inversion barrier of sp^3-phosphorus in tertiary phosphines, ranging from 30

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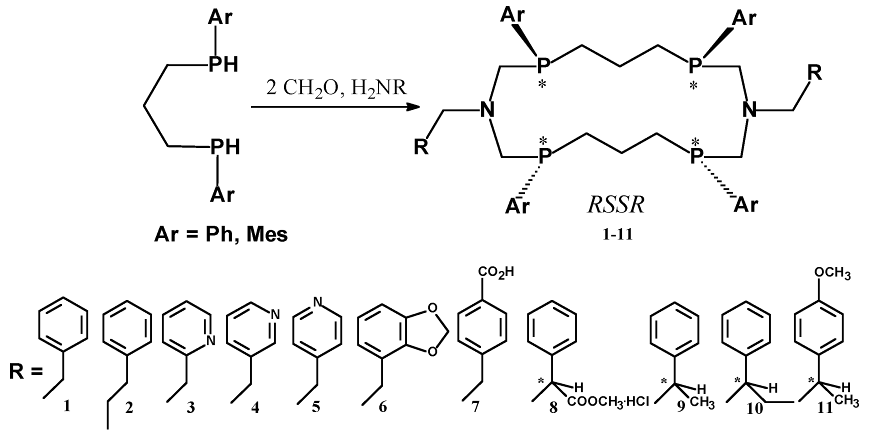
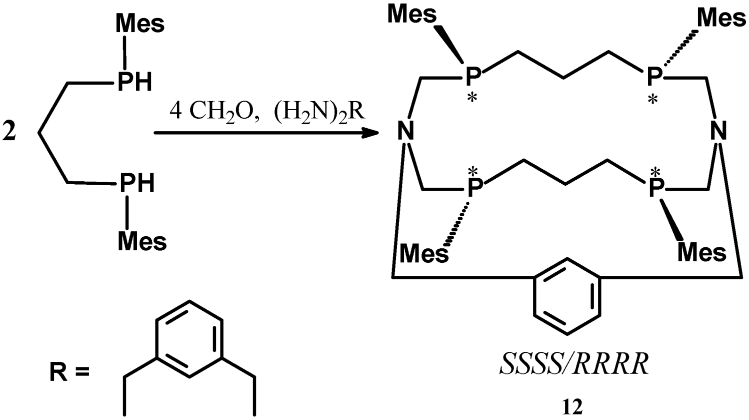
to 38 kcal/mol,[4] and corresponding existence of macrocyclic polyphosphines as a mixture of stereoisomers. Thus, the search of stereoselective and handy methods for preparation of macrocyclic polyphosphines is of great importance.[5]

The first representative of 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes (**1**) has been synthesized in the course of covalent self-assembly in three-component system: bis(mesitylphosphino)propane, formaldehyde and benzylamine.[6] Expected 8-membered 1-aza-3,7-diphosphacyclooctanes have been formed when primary arylamines were used in this reaction.[7] An introduction of various analogues of benzylamine and even phenethylamine into this reaction afforded a wide row of 1,9-diaza-3,7,11,15-tetraphosphacyclo -hexadecanes (Scheme 1). In most cases the macrocycles (**1–11**) were obtained with moderate and high yield and their structures were proved by ^{31}P, ^{1}H, ^{13}C NMR data, mass-spectroscopy and elemental analysis. Structures (**1**, **3**, **6**, **9**, **11**) were also established by X-ray analysis. A stereoselective formation of single $S_{(P)}S_{(P)}R_{(P)}R_{(P)}$-stereoisomer was detected for all of 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes. The polydentate macrocyclic phosphino amino pyridines (**3–5**) and other functionalized derivatives (**6–8**), which potentially can participate in co-ordination with transition metals via phosphorus and additional donor (N, O) atoms, were synthesized. Reactions with 4-(aminomethyl)benzoic acid and 2-phenylglycinemethylester hydrochloride leads to the formation of water-soluble macrocyclic phosphines (**7**, **8**). Corresponding optically active 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes (**8–11**), containing six asymmetrical atoms, were synthesized as single enantiomers with excellent yields.



SCHEME 1

A true racemic mixture of *rac*-isomers with *RRRR*- and *SSSS*-configuration of phosphorus atoms of novel cage-like tetraphosphine was obtained in three-component reaction of bis(mesitylphosphino)propane, formaldehyde and *meta*-xylylenediamine (Scheme 2). ^{31}P, ^{1}H, ^{13}C NMR data, FAB mass-spectra and X-ray analysis confirm the formation of cryptand (**12**).

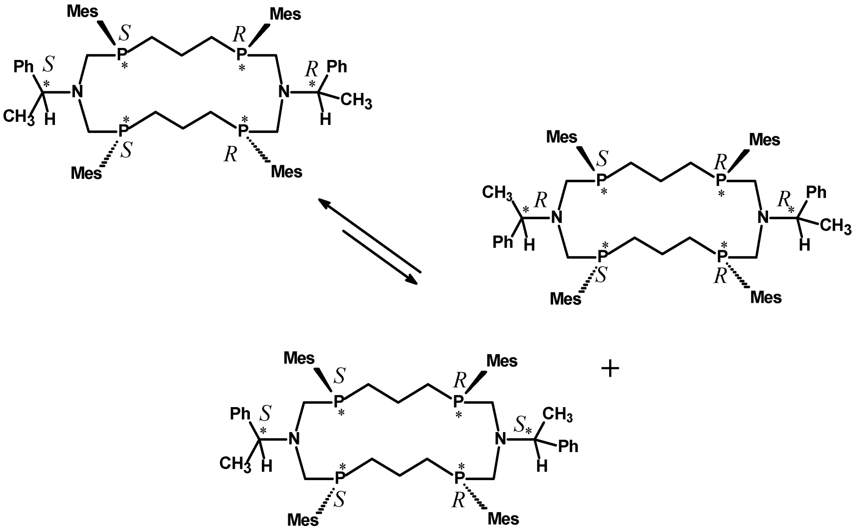


SSSS/RRRR

12

SCHEME 2

Interconversions between the stereoisomers of 1,9-diaza-3,7,11,15-tetraphospha-cyclohexadecanes were found in solution demonstrating



SCHEME 3

a relatively high lability of phosphorus atom's configuration in these macrocyclic compounds in comparison with common tertiary phosphines. It was also shown that molecules of two different enantiomers of chiral 1,9-diaza–3,7,11,15–tetraphosphacyclohexadecanes can interact with each other in solution with a formal exchange of amine units (Scheme 3).

So the stereoselective methods of synthesis of various functionalized derivatives of 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes have been developed and their unusual interconvertions in solution have been discovered.

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