

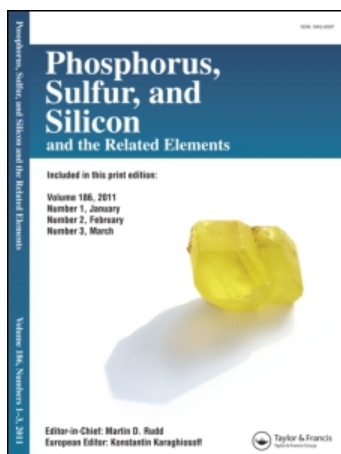
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An Effective Methodology of P,N-Macrocycles Design

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An Effective Methodology of P,N-Macrocycles Design

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The Mannich-type condensation in the systems: phosphine-formaldehyde-amine is an effective method of P,N-macrocycles design if bifunctional reagents are used.

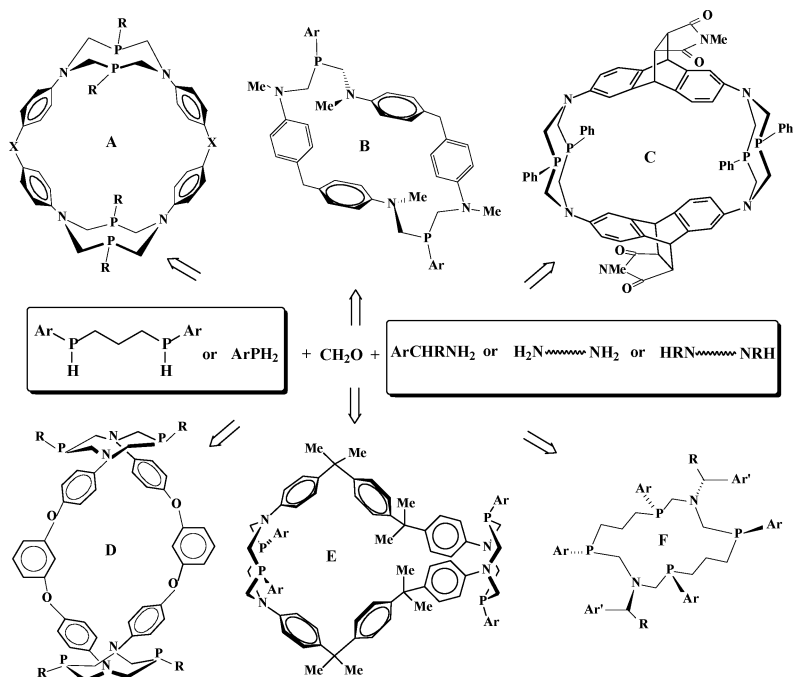
Keywords Co-valent self-assembly; diphosphines; macrocycles; tetraphosphines

RESULTS AND DISCUSSION

High effective covalent self-assembly of the macrocyclic polyphosphines has been found in the course of investigation of Mannich type condensation in the system: phosphine, formaldehyde and amine if bifunctional reagents (spatially divided diamines^{1–4} or di(arylphosphino)alkanes^{5–7}) had been used. A wide variety of 28-membered cage macrocyclic tetra- (Type A) and diphosphines (Type B) with large hydrophobic intramolecular cavities (up to 120 Å³) have been obtained on the base of condensation of (1,4-dianilino)methane and its heteroatomic analogues with different bis(hydroxymethyl)phosphines.^{1–3} The self-assembly of chiral 2,6-diamino-9,10-ethanoanthracene lead to the macrocycle (Type C) with twisted cylindrical chiral hydrophobic cavity. 36- (Type D) and 38-membered (Type E) cage macrocyclic aminomethylphosphines have been prepared on the base of corresponding spatially divided diamines.⁴ It should be mentioned that macrocycles of type E are large enough to

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SCHEME 1

encapsulate benzene molecule into the helically twisted intramolecular cavity in such manner that “guest” could not leave the “host” cavity without visible conformational changes.

Another example of the macrocycles covalent self-assembly had been found in the condensation of 1,3-diphosphinopropane and α -aminoalkylarenes with formaldehyde. Instead of expected 8-membered heterocycles^{5,6} a novel type of tetraphosphines (**F**) was formed.⁷ Reactions proceed with high selectivity giving only one (RSSR)-stereoisomer with a very good yield.

So, the formation of covalent macrocycles appears to be a general process and may be considered as a useful method for a simple one-pot synthesis of macroheterocyclic polyphosphines.

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