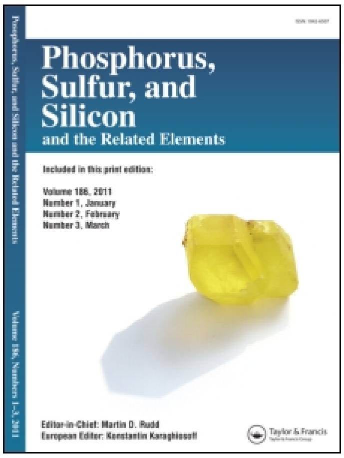

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New Synthetic Approaches to Chiral Cyclic and Macrocyclic Phosphine Ligands

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Keywords 1-Aza-3,7-diphosphacyclooctanes; 1,5-di-aza-3,7-diphosphacyclooctanes; 1-aza-3,6-diphosphacycloheptanes; 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes; chiral phosphines

RESULTS AND DISCUSSION

Designof chiral ligands has been a central subject in the development of catalytic and stoichiometric asymmetric reactions. However, studies involving diphosphine ligands and especially chiral polyfunctional diphosphines have mostly been focused on linear compounds; in contrast, heterocyclic diphosphines in which the phosphorus atoms are incorporated into the ring have not been extensively investigated, though such incorporation leads to essential differences in the structures and the properties of acyclic and cyclic compounds. Condensation in the three-component system of primary chiral/achiral phosphines and amines with formaldehyde is a powerful method of constructing various heterocyclic air-stable aminomethylphosphines.

A number of enantiopure heterocyclic di- and monophosphines had been obtained via above-mentioned condensation with chiral amines[1,2] and amino acid salts[3] (Scheme 1). Due to heterocyclic structure of the phosphines, their asymmetric center disposed at close proximity of the transition metal coordinated with phosphorus. It should be mentioned

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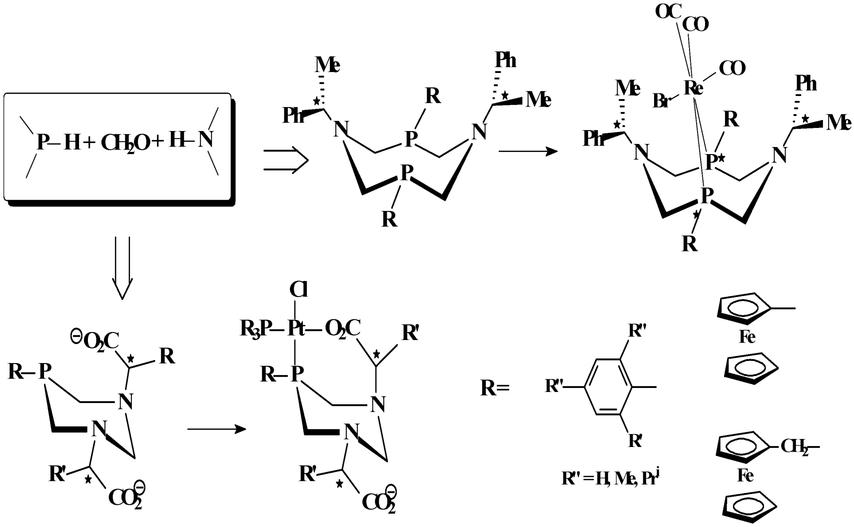
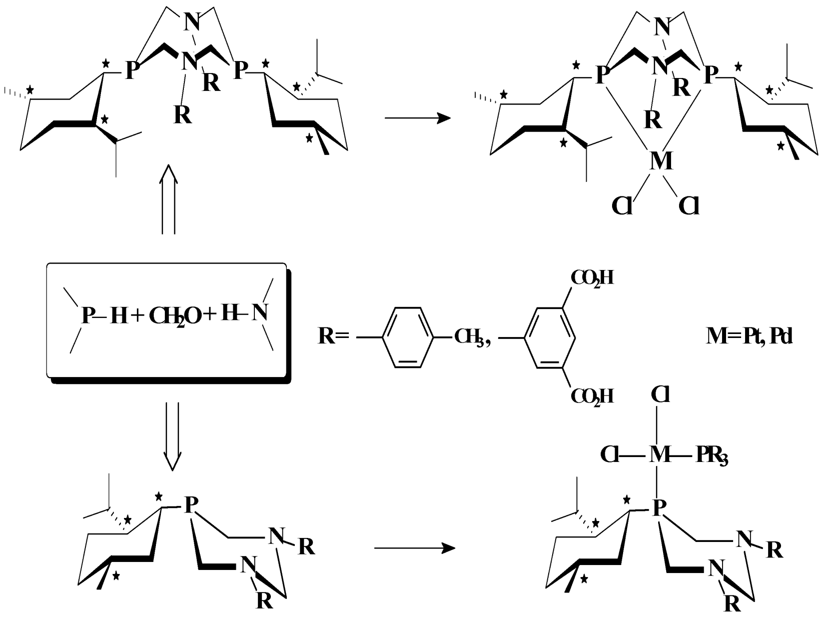


SCHEME 1

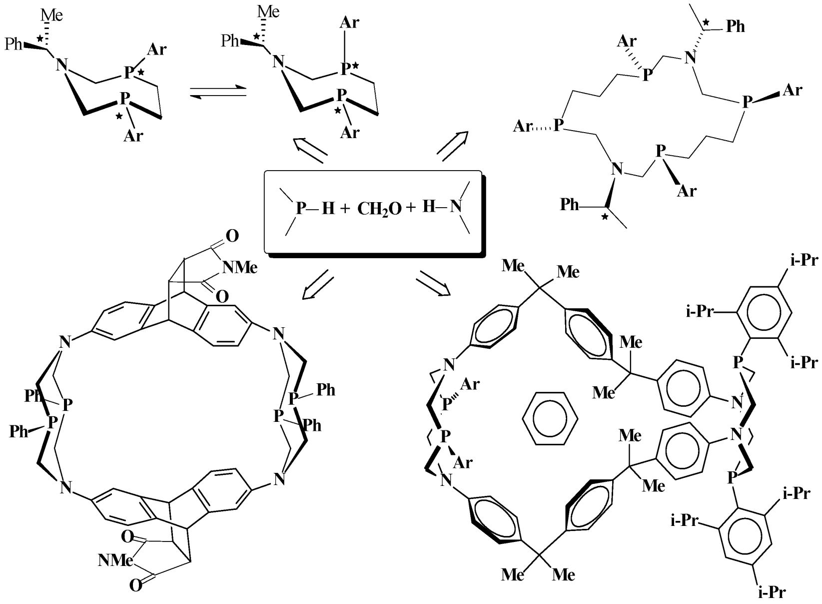
that phosphino amino acid salts and their complexes are water-soluble and could be used in the biphasic catalysis.

The condensation of *l*-menthylphosphine gives us a row of chiral heterocyclic di- and monophosphine ligands with chirality in the α-position to phosphorus atoms (Scheme 2). Lipo- and hydrophilicity of the obtained phosphines and their complexes could be tuned by varying the substituents on nitrogen atoms.

In order to obtain systems with asymmetrical phosphorus atoms we have studied the reactivity of secondary diphosphines. Condensation of di(arylphosphino)ethane and chiral methylbenzylamine with formaldehyde produces a *meso*-isomer of 1,3,6-azadiphosphacycloheptane[4] as a main product (Scheme 3). The *meso*-isomer demonstrates relatively high lability of the phosphorus configuration. Within a few days, it converted into the equilibrium mixture of *meso*- and *rac*-isomers with predominance of one of the *rac*-isomers. However, analogues with a propylene chain between two phosphorus atoms have not been described yet. We have showed that instead of the desired eight-membered 1-aza-3,7-diphosphacyclooctanes the unusual macrocyclic 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecane[5] is formed in the reaction of 1,3-bis(mesitylphosphino)propane with formaldehyde and chiral methylbenzylamine (Scheme 3). The high yield of the macrocycle was explained in terms of covalent self-assembly.



SCHEME 2



SCHEME 3

Covalent self-assembly of macrocycles appears to be a general process in aminomethylphosphine chemistry and is a useful method for a simple and effective one-pot synthesis of macroheterocyclic polyphosphines with large chiral intamolecular cavities (Scheme 3).

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