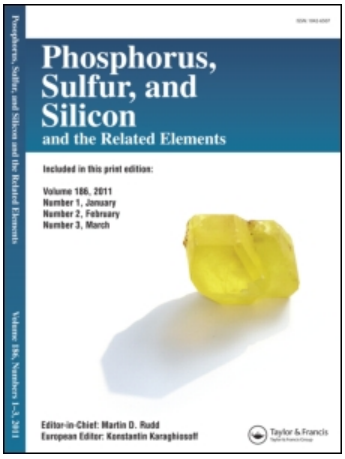

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Phosphino Amino Acids: Novel Water-Soluble Ligands for Coordination Chemistry of Transition Metals

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PHOSPHINO AMINO ACIDS: NOVEL WATER-SOLUBLE LIGANDS FOR COORDINATION CHEMISTRY OF TRANSITION METALS

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An easy and effective access to water-soluble phospino amino acids by condensation of PH-containing phosphines with formaldehyde and amino acids is presented here.

Keywords: Amino acids; phosphino amino acids; primary phosphines

The advantage of homogenous over heterogeneous catalysis with respect to activity (relative to metal content), selectivity (particularly enantioselectivity), mildness of reaction conditions, lack of diffusion problems, sensitivity toward catalyst poisons, variability of steric and electronic properties of catalysts, and mechanistic understanding of processes are well established; however, problems in separating the very expensive catalysts from the products often represent major obstacles to industrial applications. The main way of overcoming this problem is the "heterogenization" of a homogeneous catalyst by utilizing liquid-liquid (usually water-organic solvent) biphasic systems in which solutions of the catalyst and of the substrate are separated by a phase barrier. This approach aroused great interest in water-soluble ligands, especially phosphines.

An easy and effective access to water-soluble tertiary phosphines consists of the condensation of PH-functional phosphines with formaldehyde and amino acids.

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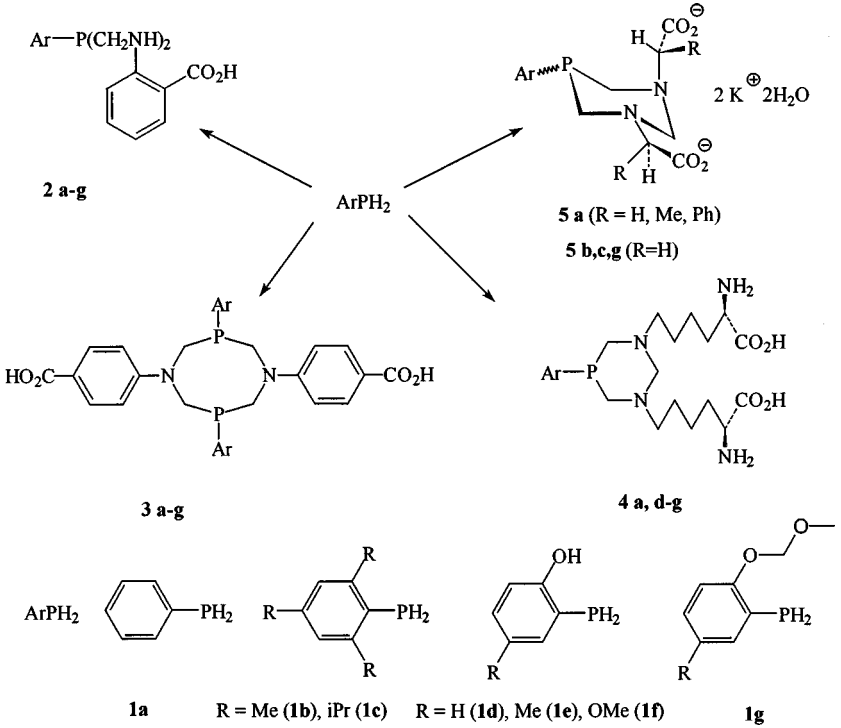
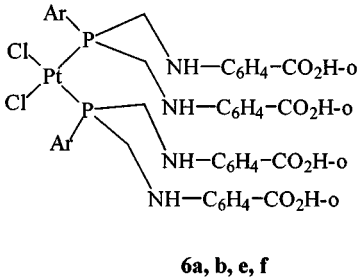


Amino acid derivatives of a wide range of primary aryl phosphines have been synthesized by reaction of the corresponding phosphines **1a–g** with formaldehyde and amino acids (*o*- and *p*-aminobenzoic acid, glycine, d- or l-phenylglycine, l-alanine, l-lysine). It was found that the type of amino acid used determines the type of phosphine that results. *o*-Aminobenzoic acid gives rise to linear bis(*o*-carboxyphenylaminomethyl)phosphines (**2a–g**).[1,4] Depending on the reaction conditions, *p*-aminobenzoic acid affords bis(*p*-carboxyphenylaminomethyl)phosphines, as well as eight-membered heterocyclic 1,5,3,7-diazadiphosphacyclooctanes (**3a–g**).[4] The aliphatic amino acids glycine, d- or l-phenylglycine, l-alanine, and l-lysine form six-membered heterocyclic 1,3-carboxylatomethyl-1,3,5-diazaphosphorinanes (**4a, d–g**; **5a, b, c, g**).[2,3,4] The structures of the compounds were determined by multinuclear (^{1}H, ^{31}P, ^{13}C) NMR and IR spectroscopy.

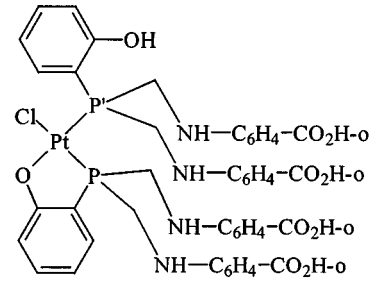
Salts of the phosphino amino acids, like the free acids in the presence of a base, are soluble in water. Water solubility increases with increasing number of hydrophilic groups (i.e., bis(*p*-carboxyphenylaminomethyl)phosphines are more soluble than

1,5,3,7-diazadiphosphacyclooctanes), and the phenol derivatives are more soluble than their ethers. Ligand concentrations in water of 0.1 to 1 m were observed.

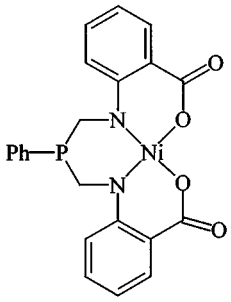
Phosphino amino acids **2–5** are novel types of hybrid water-soluble phosphine ligands that contain several donor atoms (P,N,O) with the possibility of polydentate coordination.



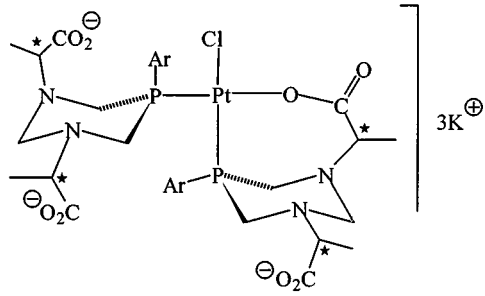
6a, b, e, f



7d



8a



9a (R= H, Me, Ph), g

A number of water-soluble phosphino amino acid P-donor complexes (**6**), as well as chelate P,O (**7**,**9**) and O,N complexes (**8**) of transition metals, have been obtained in the course of preliminary investigations.

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