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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### Stereoselective Synthesis and Complexation of a New Chiral Hybrid Phosphine-Phosphine Oxide Ligand from (S)-(+)-Prolinol

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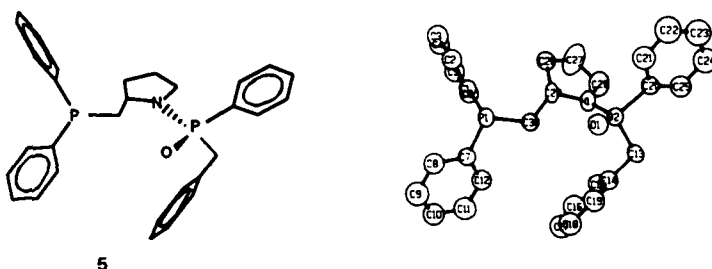
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## Stereoselective Synthesis and Complexation of a New Chiral Hybrid Phosphine-Phosphine Oxide Ligand from (*S*)-(+)-Prolinol.

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The synthesis and the complex formation of chiral heterotopic ligands with two different binding sites each capable of bonding a different type of metal are described. The action of bis(dimethylamino) aryl phosphine on (*S*)-(+)-prolinol gives rise to the kinetic stereoisomer (2*S*,4*S*)-2-phenyl-1,3,2-oxazaphospholidine **1** and the thermodynamic stereoisomer (2*R*,4*S*)-2-phenyl-1,3,2-oxazaphospholidine **2**. **1** is then totally converted into **2** at the end of the reaction. The Michaelis Arbuzov reaction of **2** with benzylbromide affords (*R<sub>p</sub>*)-benzylaryl-(2-(*S*)-bromomethyl pyrrolidine-1-yl) phosphine oxide **3** in 80% yield. Compound **3** is an ideal chiral precursor for the synthesis of chiral hybrid phosphine-phosphine oxide ligands. The bromide atom is smoothly displaced by lithium diphenylphosphide to afford in 80% yield (*R<sub>p</sub>*)-benzylaryl-(2-(*S*)-diphenylphosphinomethylpyrrolidine-1-yl) phosphine oxide **5**. These reaction are proved to be totally stereoselective : the Michaelis Arbuzov reaction does not change the configuration at C2 in the proline ring. The relative configuration (*R<sub>p</sub>*) of **5** ( aryl = phenyl ) was determined by X-ray diffraction, from the known configuration of (*S*)-(+)-prolinol.



Preliminary studies of complex formation with transition metals show that **5** can behave as mono or bidentate ligand. The transition metals, such as Pd, Pt, Rh are coordinated by the phosphine group, whilst the phosphine oxide group complexes either alkali or alkaline earth metals, or Lewis acids such as TiCl<sub>4</sub> and nBu<sub>2</sub>SnCl<sub>2</sub>. Chiral ligand **5** seems to be promising in the asymmetric synthesis catalyzed by transition metal complexes.