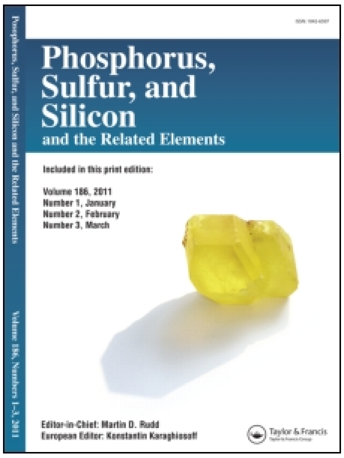

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2-Hydroxy-1, 1-Biphenyl- and -Binaphthyl-2'-Phosphines - Synthesis, Structure and Use in Rh-Catalyzed Carbonylation

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2-Hydroxy-1,1-Biphenyl- and -Binaphthyl-2'-Phosphines – Synthesis, Structure and Use in Rh-Catalyzed Carbonylation

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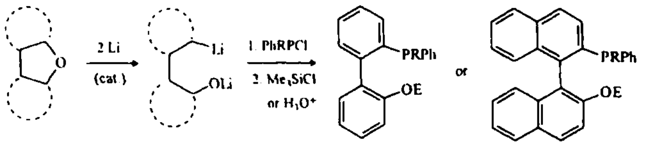
Dibenzofuran and dinaphthofuran are cleaved by lithium in presence of electron transfer catalysts to yield C,O-dilithium reagents. These are reacted with chloro- or alkoxyphosphines providing 2-hydroxy-1,1'-biphenyl-2'-phosphines and 2-hydroxy-1,1'-binaphthyl-2'-phosphines which form solvent complexes with O...H-O or P...H-O bridging bonds. The planes of the benzene rings of the biphenyl units are nearly perpendicular in the unit cell. Line form analysis of the temperature dependent solution NMR spectra of diastereoisomeric 2-HO-C_6H_4-C_6H_4-P(*t*Bu)Ph revealed a barriere of rotation of $\Delta H^{\#}$ = 12.87 kcal/mol. The respective O-trimethylsilyl ethers have a higher barrier, and 2-hydroxybinaphthyl-2'-phosphines dont racemize after separation by HPLC.



Tests of the title compounds in homogenous rhodium catalyzed hydroformylation of vinyl acetate, metal-ligand ratio of 1:1, gave high yields and selectivities of the *branched*-product, in contrast to a low activity with *o*-phosphinophenols and 1-phosphino-2-naphthols which form five-membered P,O^--chelates.