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Highly enantioselective Rh-catalyzed hydrogenations with heterocombinations of pentafluorobenzyl- and methoxybenzyl-derived binaphthyl phosphites

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Abstract

The Rh-catalyzed hydrogenations of dimethyl itaconate and methyl acetamido acrylate using selected heterocombinations of pentafluorobenzyl- and methoxybenzyl-derived binaphthyl phosphites proved to be highly enantioselective (ee 93–99%). In these selected cases the Rh-heterocomplexes, which were formed in a statistical amount (ca. 50% by ^{31}P NMR), turned out to be more active and selective than the two homocomplexes.

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In recent years, monodentate phosphorus ligands have held the stage in asymmetric catalysis.[1] In addition to their outstanding activity and selectivity, comparable or even superior to those of bidentate ligands, their convenient, fast and practical synthesis from commercially available materials underlines their potential for industrial applications.[2] Furthermore, the simple preparation of the phosphite,[3] phosphonite[4] and phosphoramidite[5] functional groups, which are the most frequently represented in monodentate ligands, allows for a facile variation of their design.

Still, the presence of a bidentate ligand is sometimes an inevitable requirement for a successful (stereo)chemical result. Supramolecular bidentate ligands, based on the self-assembly of monodentate ligands possessing complementary functionalities, thus represent a clever solution which combines the important features of bidentate ligands (preorganization and rigidity) with the economy and efficiency of monodentate ligands.[6]

The non-covalent assembly of monodentate ligands reported so far in the literature relies mostly on coordinative bonding of nitrogen to zinc[7] or hydrogen bonding.[8] More recently, ionic interactions[9] and the formation of inclusion complexes[10] were exploited to bring monodentate ligands into close proximity. We felt intrigued by these approaches and decided to investigate other non-covalent interactions, that is, the perfluroarene-arene π–π interactions.

Perfluroarene-arene π–π interactions were observed for the first time in 1960.[11] Their relevance in the solid state has been confirmed several times since then,[12] and they have found widespread application in supramolecular design and crystal engineering.[13] The contribution of perfluoroarene-arene π–π interactions to the efficient photodimerization of olefins in the solid state was also investigated.[14] On the contrary, only a few papers report a quantitative description of the perfluoroarene-arene π–π interactions in solution,[15] and a few applications supposedly exploited them in solution-phase synthetic processes.[16]

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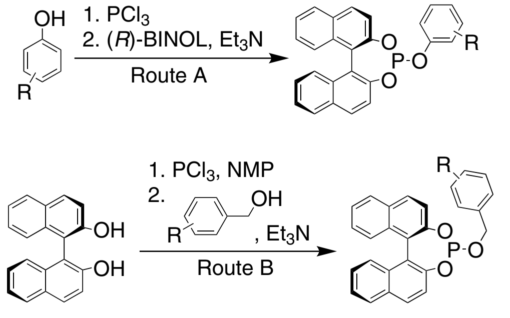
In this Letter we report the synthesis of a series of novel perfluroarene- and methoxyarene-derived phosphites, which were used to investigate (by ^{31}P NMR) the possible formation of supramolecular bidentate ligands in the Rh-complexes via a non-covalent assembly induced by the perfluroarene–methoxyarene π–π interactions. Homo- and hetero-combinations of these ligands were used in enantioselective Rh-catalyzed hydrogenations of dimethyl itaconate and methyl acetamido acrylate.

Two strategies were applied to the synthesis of the designed binaphthyl phosphites (Scheme 1). The commercially available methoxy substituted phenols were refluxed with PCl_3 to give the corresponding methoxy substituted-phenyl dichlorophosphites (Route A). Subsequent reaction with BINOL in the presence of Et_3N furnished the electron-rich phosphites (*R*)-**1**–(*R*)-**3** (Fig. 1), which were obtained in moderate yields as pure compounds after chromatographic purification.

In the case of methoxy substituted benzylalcohols, an alternative approach (Route B) was followed. BINOL was thus treated with PCl_3 in the presence of a catalytic amount of NMP[17] to give the corresponding binaphthyl chlorophosphite, which was then reacted with benzylalcohols in the presence of Et_3N to afford phosphites (*R*)-**4**–(*R*)-**8** (Fig. 1). The same protocol was used also for the synthesis of the electron-poor phosphites (*R*)-**9** and (*S*)-**10**, containing the pentafluorobenzyl moiety.



Scheme 1. Synthesis of benzylalcohol- and phenol-derived binaphthyl phosphites.

We thus synthesized a small library of eight electron-rich phosphites (including six BINOL and two octahydro-BINOL derivatives) and two electron-poor pentafluorobenzyl binaphthyl phosphites (Fig. 1).

With the ligand library in our hands, we proceeded with the ^{31}P NMR investigations of perfluoroarene–methoxyarene π–π interactions in the rhodium complexes. At first, the ^{31}P NMR spectra of a single ligand in the presence of $Rh(acac)(eth)_2$ (L:Rh ratio = 2:1) were recorded revealing the fast formation of the corresponding homocomplexes $L_2Rh(acac)$ (Fig. 2). Then two different ligands (one electron-rich and the other electron-poor) were mixed in the presence of the Rh source (ratio 1:1:1) and the formation of two homocomplexes and one heterocomplex was observed. The NMR spectra were recorded in a broad range of solvents ($CDCl_3$, THF-d_8, CD_3OD, *i*-PrOH/CD_3OD, CD_2Cl_2, toluene-d_8, CCl_4). In all these solvents, the observed ratio was essentially statistical within the experimental error (RhL_AL_A:RhL_BL_B:RhL_AL_B = 1:1:2), which means that there is no detectable preference for the formation of the heterocomplex due to the methoxyarene–perfluoroarene interactions. In crystals featuring arene–perfluoroarene interactions, the packing energy is dispersion-dominated and coulombic terms are selective rather than quantitatively predominant.[12f] This means that these interactions are likely to be very weak in solution.[15b,c]

Although we did not observe any relevant π–π-interaction between electron-rich and electron-poor ligands, we screened the library, using both homo- and heterocombinations of the ligands, in the Rh-catalyzed asymmetric hydrogenation of prochiral alkenes. Typically, the substrate was added to a stirred mixture of $Rh(cod)BF_4$ (1 mol %) and ligand [2 mol % (1:1 ratio in the case of heterocombinations)] in dichloromethane and the mixture was hydrogenated for 24 h at room temperature and pressure.

In the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate, the use of homocombinations of

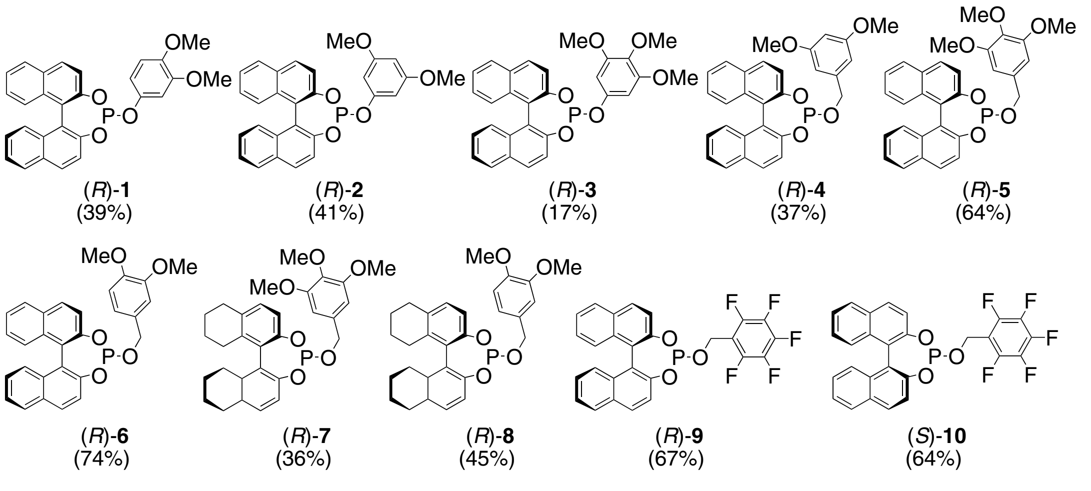


Fig. 1. Library of phosphite ligands (isolated yields are reported in the brackets).

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