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Synthesis and evaluation of P-chirogenic monodentate binaphthyl phosphines

Marie-Christine Duclos [a], Yuttapong Singjunla [a], Christelle Petit [a], Alain Favre-Réguillon [a], Erwann Jeanneau [b], Florence Popowycz [a], Estelle Métay [a], Marc Lemaire [a,*]

[a] Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, UMR-CNRS 5246, Equipe Catalyse Synthèse Environnement, Université de Lyon, Université Claude Bernard-Lyon 1, Bâtiment Curien, 43 Bd du 11 novembre 1918, F-69622 Villeurbanne Cedex, France
[b] Centre de Diffractométrie Henri Longchambon, Université Claude Bernard Lyon1, 43 Bd du 11 novembre 1918, 69622 Villeurbanne cedex, France

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ABSTRACT

P-Chirogenic monodentate binaphthyl phosphines were prepared in five steps from enantiomerically pure BINOL. This approach supposes the utilization of two methods previously developed in our group, the formation of secondary phosphine oxide, and the reduction of tertiary phosphine oxide using the association of tetramethyldisiloxane and $Ti(O^iPr)_4$. During the last reduction step, only the formation of the more stable diastereoisomer was observed. This product was employed as a ligand for the palladium catalyzed hydrosilylation of styrene to afford the corresponding alcohol with high yield and enantiomeric excess.

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Asymmetric catalysis represents an extremely powerful tool to induce high enantiomeric purity expected in molecules of high-value added from industry. To induce asymmetry with excellent enantio-/diastereoselectivities, chiral diphosphines such as (*S*,*S*)-DIOP,[1] (*R*,*R*)-DIPAMP[2], and well-known atropoisomeric (*R*)-BINAP[3] have been largely employed by academic research groups. The first industrial process using BINAP was performed by Takasago International Corporation for the production of menthol in 1984.[4] Inspired by the success of this ligand, a wide range of atropoisomeric ligands have been thus described for these last twenty years.[5]

In particular Hayashi has devised the methoxyphosphine ligand family (MOP), organized through a heterobinaphthyl scaffold with biaryl axial chirality.[6] In parallel, ligands bearing the chirality on phosphorus atom were developed.[7]

Classical methods for the synthesis of optically pure P-chirogenic phosphines referred to the separation of a pair of so-formed diastereoisomers (phosphines or boron-phosphinites)[8] or to the use of a chiral inducer such as ephedrine also called the Jugé method.[9] Evans described the asymmetric deprotonation of prochiral aryl dimethyl phosphine boranes.[10] Preliminary research performed in the laboratory reported the synthetic access to chiral phosphorus ligand derived from Binap.[10]

In this Letter we report the last results obtained on the synthesis and evaluation of monophosphine with double chirality (axial along with chiral phosphorus).

First part on the synthesis aimed to obtain a diversity of non-symmetric secondary phosphine oxides. A new one-pot methodology was recently reported in our group, by the reaction of dichlorophenylphosphine with methylimidazole as a base, generating the ionic liquid 1-methylimidazolium chloride separated by simple extraction.[11] This methodology inspired from the BASIL process (Biphasic Acid Scavenger using Ionic Liquids)[12] was applied to the synthesis of isopropyl(phenyl)phosphine oxide **1** in 73% yield.

The route to innovative MOP ligands begins with the pallado-catalyzed coupling of isopropylphenyl phosphine oxide **1** with (*R*)-2,2′-bis(trifluoromethanesulfonyloxy)-1,1′-binaphthyl (obtained from (*R*)-Binol reacting with triflic anhydride (1.05 equiv) in pyridine/dichloromethane).[13] The optimized coupling conditions require the use of $Pd(OAc)_2$ (10 mol %) as a catalyst, diphenylphosphinobutane (10 mol %) as a ligand, diisopropylethylamine (4 equiv) as a base in pre-heated anhydrous DMSO at 100 °C for 16 h affording compound **2** in 65% yield with around 1:1 ratio of both diastereoisomers (Scheme 1). At this stage of the synthesis, the diastereoisomers (**2′** and **2″**) were successfully separated by flash chromatography in respectively 30% and 35% yields.

Both compounds **2′** and **2″** were independently submitted to hydrolysis of the triflate group. Subsequent methylation conditions on crude phenol intermediates provided **3′** and **3″**, respectively in 63% and 50% yields. Final step implied the reduction of phosphine oxides into non-symmetrical mono-phosphine ligands. The reduction of phosphine oxide into the corresponding phosphine has been largely described in the literature with the use of $LiAlH_4$,[14] DIBAL-H,[15] $BH_3{\cdot}Me_2S$,[16] Ph_2SiH_2,[17] and $HSiCl_3$.[18] Specifically, Gilhe-

* Corresponding author. Tel.: +33 4 72 43 14 07; fax: +33 4 72 43 14 08.
E-mail address: marc.lemaire@univ-lyon1.fr (M. Lemaire).

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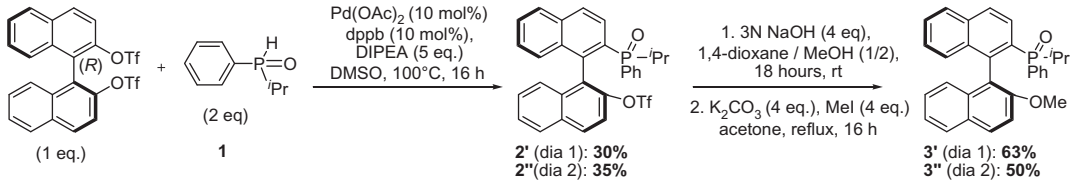
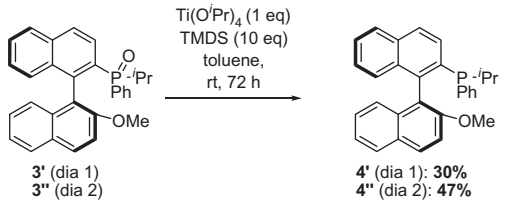


Scheme 1. Synthetic scheme of phosphine oxides.

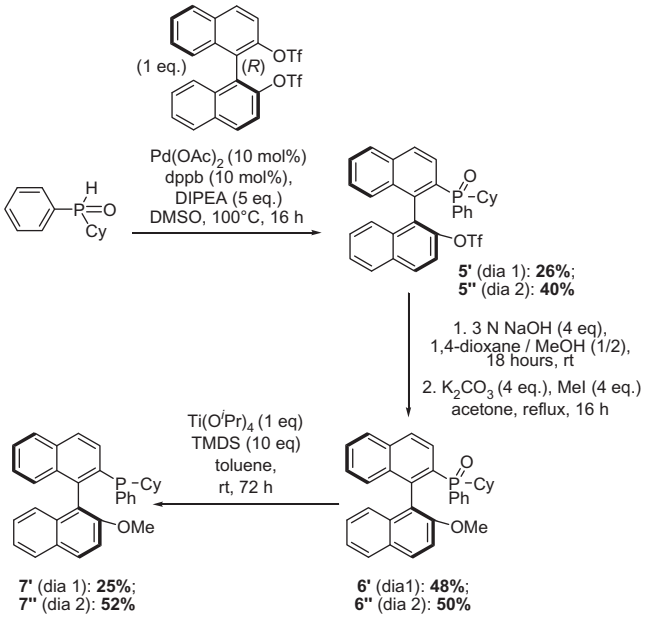
any already studied the reduction of P-chirogenic MOP-oxides to P-chirogenic MPOs with different reducing agents, and only the use of Si_2Cl_6 prevent the epimerisation.[19] In our continuing efforts to find new alternate reducing agents in a sustainable approach, regarding the criteria of toxicity and security, the already in-use methods cited above are no more compatible with future industrial development. Indeed boron and aluminum salts as well as silanes are reported to be toxic. Metal hydrides react with strong evolution of heat when exposed to either water or air. Silanes have the potential of redistributing themselves in pyrophoric SiH_4 gas. In this context, hydrosiloxanes represent an alternative hydride source in comparison with other classical methods, with a significant advantage on the security and ease of handling parameters. Hydrosiloxanes are low viscous liquids, soluble in most of the organic solvents, sluggish to water and air. Taking advantage of these attractive properties, 1,1,3,3,-tetramethyldisiloxane (TMDS) was investigated in the laboratory on miscellaneous functional groups to evaluate its potential as a reducing agent.[20] The reduction of phosphine oxide was already optimized in our laboratory and best conditions were defined as following: 10 mol % of $Ti(OiPr)_4$ 1.25 equiv of TMDS at 60 °C with 10 wt % of Na_2SO_4 as a desiccant. Experiments realized on the MOP ligand oxide pushed us to define new conditions. Phosphine oxide **3′** was treated by one equivalent of titanium tetraisopropoxide in the presence of a large excess of 1,1,3,3,-tetramethyldisiloxane in toluene at room temperature during 72 h providing compound **4′** in 30% recrystallisation yield. Reduction was also performed on the other **3″** diastereoisomer and the corresponding phosphine was collected in 47% after recrystallisation (Scheme 2).

If both diastereoisomers **3′** and **3″** display two different phosphorus NMR chemical shifts, the same one was observed for the corresponding reduced products. This was confirmed by another analytical technique. Indeed, both molecules **4′** and **4″** were crystallized and analyzed through X-ray diffraction and the configuration of phosphorus atom was clearly identified for both isopropyl diastereoisomers. The X-ray study unfortunately reveals that the reduction of **3′** and **3″** affords the same product with the same stereochemistry. A complete inversion of the phosphorus configuration took place during the reduction step to afford the formation of the most stable substrate. In order to control if this phenomenon was not due to the presence of isopropyl substituent, the cyclohexyl derivative was also prepared following the same synthetic approach (Scheme 3).

Similar results were obtained with the cyclohexyl pattern for the conversion and isolated yield of each step. Same observations



Scheme 2. Reduction of phosphine oxide by TMDS/$Ti(O^iPr)_4$ system.



Scheme 3.

were noticed in the reduction step, the chemical shifts of the phosphorus NMR of products **6′** and **6″** were different while the same was observed for both **7′** and **7″**. The X-ray analysis confirmed the formation of a unique diastereoisomer during the reduction step. (Fig. 1)

The MOP ligands were thus evaluated for their activity on the hydrosilylation reaction (Scheme 4 and Table 1). First step of hydrosilylation was performed in the presence of allyl palladium (II) chloride dimer (0.04 mol %) and a chiral phosphine ligand L* (0.08 mol %).[21] The investigation included the commercially available (*R*)-MOP ligand (also named as (*R*)-(+)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl as an internal reference. In the conditions settled up in our laboratory, the (*R*)-MOP ligand induced a moderate enantioselectivity of 36%. This modest result could be explained by the difference of temperature, Hayashi

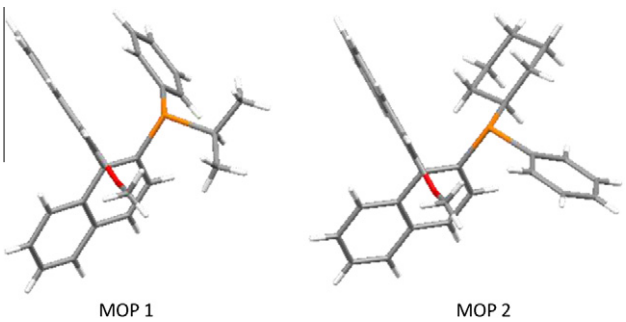
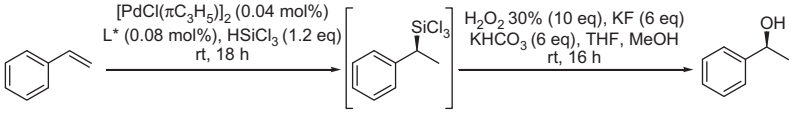


Figure 1. X-ray study of MOPs (***R,S***)-**4′** and (***R,R***)-**7′**.



Scheme 4. Conditions used for asymmetric hydrosilylation of styrene.

Table 1
Isolated yield and enantiomeric excess of the alcohol obtained after asymmetric hydrosilylation of styrene with trichlorosilane catalyzed by palladium complexes

Entry	Ligand	Yield (%)	ee[a] (%)
1	(*R*)-MOP	67	36
2	**4**	92	91
3	**7**	85	72

[a] Determined by GC analysis on a Chiralcell column (70 °C during 3 min, increase of 3 °C per min until 150 °C, 5 min at 150 °C).

describing an excellent enantioselectivity of 92% by running the reaction at 0 °C. In our case, our ligands are not sensitive to the temperature as satisfactory enantioselectivities (respectively 91% and 72%) were determined for ligands **4'** and **7'**. This transformation is regioselective as only the branched silylated derivatives were formed. The chirality of the alcohols (*S*) coming from the oxidation of silyl derivatives was determined by GC analysis and by co-injection with a reference. It was the same whatever be the chirality of the phosphorus. These results are in agreement with the literature data explaining the influence of the naphthyl ring of the ligand which is close to the palladium.[22] From previous results, Hayashi[6] assumed that the enantioselectivity during the hydrosilylation of styrene is related to the dihedral angle between the two naphthyl rings in the binaphthyl skeleton which is controlled by the steric bulkiness of the 2′-substituent.[23] In this work, the dihedral angle is not controlled by the –OMe group indeed these values are different (79.99 for compound **4**, 84.94 for the R-MOP, and 89.93 for the **7**) as a consequence these angles are not related to the enantioselectivity.[24] However, an electronic, a steric, and/or a match/mismatch effect of the cyclohexyl and isopropyl groups can explain the higher enantiomeric excess.

The MOP ligands (*R*,*S*)-**4′** and (*R*,*R*)-**7″** produce similar global effects on the scope of the hydrosilylation reaction, both on the yield and the enantioselectivity. Also the most important result from this study is that the configuration of the phosphorus atom is not decisive for the asymmetric induction. Axial chirality is definitely the most influential factor or the driving force to obtain efficiently chiral secondary alcohols. Nevertheless, both electronic and/or steric effects seem important to increase the yield and selectivity. The mechanism is currently under investigation.

Acknowledgments

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24. Crystal data for (*R*,*S*)-2-(isopropylphenylphosphino)-2′-methoxy-1,1′-binaphthyl **4′**:Molecular formula: $C_{30}H_{27}OP$, MW = 434.52, Orthorhombic, space group $P2_12_12_1$, a = 9.076 (1) Å, b = 15.049 (2) Å, c = 17.050 (2) Å, V = 2328.8 (5) Å3, Z = 4, D_x = 1.239 Mg m^{-3}, μ = 0.14 mm^{-1},T = 110 K, F(000) = 920, Flack parameter: −0.18 (12), 17567 measured reflections, 5700 independent reflections (R_{int} = 0.056), CCDC deposition number : 871758.
Crystal data for (*R*,*R*)-2-(cyclohexylphenylphosphino)-2′-methoxy-1,1′-binaphthyl **7′**: Molecular formula: $C_{33}H_{31}OP$, MW = 474.58, Orthorhombic, $P2_12_12_1$, a = 8.2439 (9) Å, b = 15.923 (2) Å, c = 19.648 (2) Å, V = 2579.1 (5) Å^3, Z = 4, D_x = 1.222 Mg m^{-3}, μ = 0.13 mm^{-1}, T = 110 K, Flack parameter: 0.07 (12), 19324 measured reflections, 6237 independent reflections(R_{int} = 0.058), CCDC deposition number 871759.