Catalysis Communications 53 (2014) 87–90

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

New phosphorus self-assembling ligands for the tandem hydroformylation–Wittig olefination reaction of homoallylic alcohols — A key step for stereoselective pyran synthesis

Qiao Ruan [a,b], Le Zhou [a,*], Bernhard Breit [b,**]

[a] College of Science, Northwest A&F University, Yangling, Shaanxi 712100, China
[b] Institute for Organic Chemistry, Albert-Ludwigs-Universität Freiburg, Albertstrasse 21, Freiburg 79104, Germany

ARTICLE INFO

Article history:
Received 7 March 2014
Received in revised form 23 April 2014
Accepted 28 April 2014
Available online 5 May 2014

Keywords:
Phosphorus self-assembling ligand
Homoallylic olefin
Wittig reagent
Hydroformylation–Wittig reaction
Oxa-Michael reaction
β-Pyran

ABSTRACT

New self-assembled phosphorus ligands are synthesized and used in the rhodium complex catalyzed hydroformylation–Wittig reaction of homoallylic olefins under optimized condition. A subsequent oxa-Michael intramolecular reaction yields β-pyran derivatives (conversion and diastereoselectivity up to 99%).

1. Introduction

Tandem reactions are suited to generate molecular complexity in a single step starting from simple starting materials without isolating intermediates, changing reaction conditions, or adding reagents [1–7]. In this regard the tandem hydroformylation–Wittig olefination reaction developed in our group is a useful tool to extended carbon skeletons starting from simple alkenes [8]. In our previous work, 1,1-substituted allylic alcohol derivatives were applied using a directed regio and stereoselective hydroformylation based upon the use of ortho-diphenylphosphanylbenzoate (o-DPPB) as a catalyst-directing group [9]. Helmchen and Farwick investigated the tandem hydroformylation–Wittig olefination of chiral allylamines and the subsequent intramolecular aza-Michael reaction to furnish proline derivatives [10]. Wong and Landis described a one-pot sequence with stabilized Wittig ylides to produce γ-chiral α,β-unsaturated carbonyl products [11]. To our best knowledge, the tandem hydroformylation–Wittig olefination of homoallylic alcohol furnishing 7-hydroxy functionalized enoates is well-suited for a subsequent oxa-Michael addition. This could provide a rapid and interesting entry to the preparation of pyrans, a structural motif found in numerous natural products [12–16].

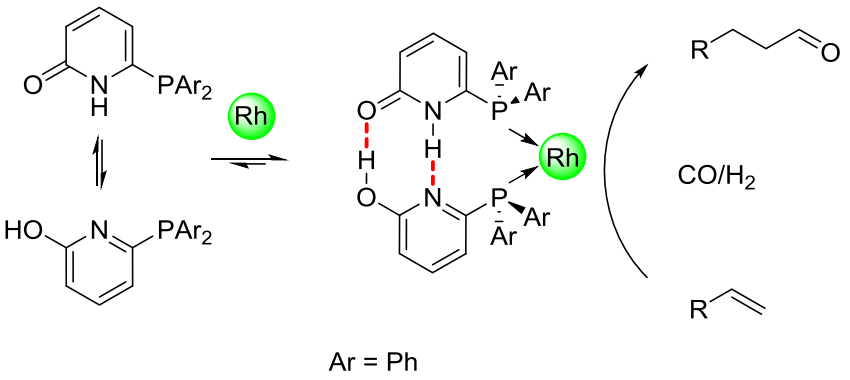
The realization of this tandem reaction would request the use of ester-substituted phosphorus ylides. However, in the previous studies of our directed tandem hydroformylation–Wittig olefination reactions, we observed hydrogenation of the enoates to form the saturated esters as a side reaction limiting its utility. In order to solve this problem we thought that the development of new ligands based on our concept of self-assembling (see Scheme 1) through complementary hydrogen-bonding might solve this chemoselectivity issue. Based on our previous work of self-assembling phosphine ligand rhodium (I) catalyst systems, we designed and synthesized four new ligands depicted in Scheme 2 [17–21].

2. Experimental

Reactions were performed in flame-dried glassware under argon (purity > 99.998%). The solvents were dried by standard procedures, distilled, and stored under argon. All temperatures quoted are not corrected. Chromatographic purification of products was accomplished using Macherey-Nagel silica gel 60® (230–400 mesh). Thin layer chromatography was performed on aluminum plates precoated with silica gel (Merck, 60 F_{254}), which were visualized by the quenching of UV fluorescence (λ_{max} = 254 nm), and/or by staining 1% w/v $KMnO_4$ in 0.5 M aqueous K_2CO_3, followed by heating. Nuclear magnetic resonance spectra were acquired on Bruker Avance 500 (500 MHz and 126 MHz for ^1H and ^{13}C respectively), Bruker Avance 400 (400 MHz and 100.6 MHz for ^1H and ^{13}C respectively), and Varian Mercury spectrometers (300 MHz and 75.5 MHz for ^1H and ^{13}C respectively). All ^1H NMR

* Corresponding author. Fax: +86 29 87092226.
** Corresponding author. Fax: +49 761 2038715.
E-mail addresses: zhoulechem@nwsuaf.edu.cn (L. Zhou), bernhard.breit@organik.chemie.uni-freiburg.de (B. Breit).

http://dx.doi.org/10.1016/j.catcom.2014.04.022
1566-7367/



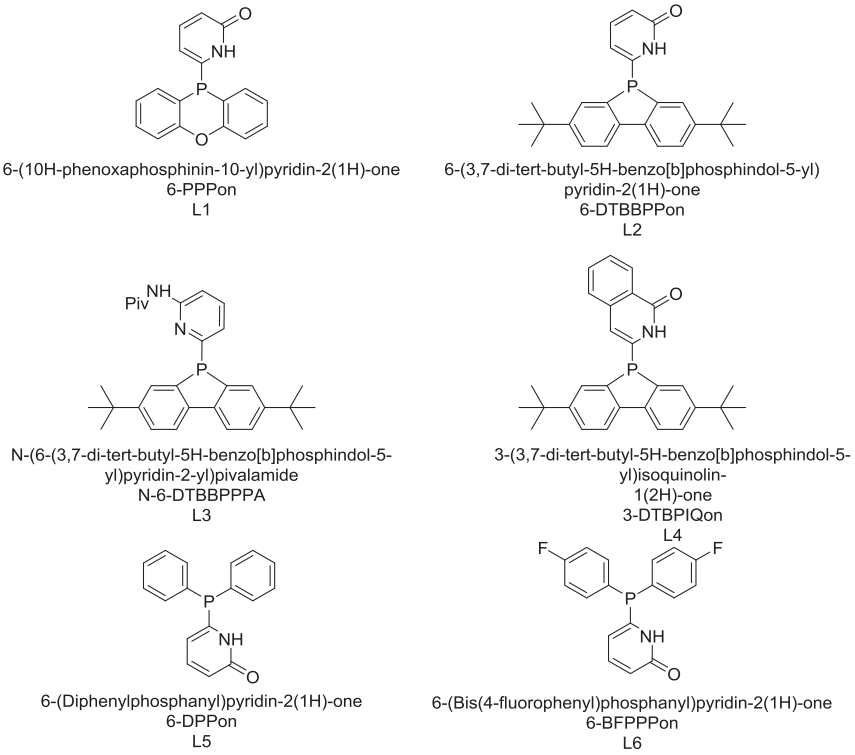
Scheme 1. Self-assembling ligands 6-DPPon [17,18].

spectra were reported in parts per million (ppm) downfield of TMS and were measured relative to the residual solvent signal. All ^{13}C NMR spectra were reported in ppm relative to the respective residual solvent signal and were obtained with H decoupling. Data for ^{1}H NMR are described as follows: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *br*, broad signal), coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are described in terms of chemical shift (δ in ppm). High resolution mass spectra were obtained on a Finnigan MAT 8200 instrument (CI/NH_3: 110 eV; EI: 70 eV) and on a Bruker maXis-ESI-Q-TOF (ESI-TOF-HRMS).

2.1. General procedure for ligand synthesis

To a solution of diphenyl ether (29.3 mmol) and 1.86 mL TMEDA (58.7 mmol) in 120 mL dry diethyl ether/hexane (1:2) under argon, *n*-BuLi (28.5 mmol, 2.5 mL in hexane) was added slowly at 0 °C. The mixture was stirred for 30 min, then warmed to room temperature and stirred at this temperature for another 1.5 h. Subsequently, Cl_2PNEt_2 (43.9 mmol, 1.27 mL) was slowly added to the above mixture at −78 °C, followed by stirring at room temperature for 1 h. After cooling to 0 °C, HCl gas was bubbled through the solution for 1.5 h then warmed up to room temperature. The reaction mixture was filtered under argon and washed with CH_2Cl_2. The combined organic phases were evaporated to furnish the crude 10-chlorophenoxaphosphine as yellow oil (5.8 g, 84%).

n-BuLi (2.21 mmol, 2.5 mL in hexane) was added dropwise to a solution of 2-bromo-6-*tert*-butoxy-pyridine (2.21 mmol) in diethyl ether (10 mL) at 0 °C and then stirred at room temperature for 30 min. Subsequently, the solution of 10-chlorophenoxaphosphine (3.02 mmol) in diethyl ether (10 mL) was added to the reaction mixture at −78 °C and stirred for 1 h, and warmed to room temperature and stirred overnight. Subsequently the reaction was quenched with water and extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The crude product was further purified by chromatography (silica, petroleum ether/CH_2Cl_2 = 4:1) and 1.33 g (36%) of protected compound was obtained as a solid. The solid was dissolved in formic acid and stirred at room temperature for 2 h.



Scheme 2. Structure of screened ligands.