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Modular chiral diphosphite derived from L-tartaric acid. Applications in metal-catalyzed asymmetric reactions

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ABSTRACT

A new family of C_2-symmetric chiral diphosphites was synthesized using two different chiral backbones derived from tartaric acid, combined with chiral binaphthyls or non-chiral substituted biphenyl moieties. Diphosphites were applied to Rh-catalyzed hydroformylation of styrene producing good conversions in mild conditions, fair regioselectivities but low enantioselectivities in all cases. Ligands were also essayed in Pd-catalyzed allylic substitution reactions of linear and cyclic substrates using dimethyl malonate as nucleophile. Conversion rates up to 7200 h^{-1} were reached, while moderated ee's were attained. In this reaction, a kinetic resolution of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene was observed, leading to 99% ee of for the unreacted *S*-substrate and 60% ee of *S*-alkylated product. Coordination properties of diphosphites in rhodium and palladium complexes related to catalytic species involved in the two previous reactions were investigated. Some ligands form equatorial-equatorial chelates in pentacoordinated complexes [RhH(CO)(PPh_3)(diphosphite)], while other act as bridge between two metal atoms. In the catalytic active species [Pd(η^3-PhCHCHCHPh)(diphosphite)]PF_6 one or two diastereoisomers are formed, depending on the diphosphite structure.

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1. Introduction

The development of asymmetric transition-metal catalysis depends on the availability of enantiomerically pure ligands. Among them, chiral diphosphites are especially attractive because their structural properties can be easily modified allowing a fine-tuning of the performance of the corresponding metal catalyst [1]. Since chiral diphosphites are readily prepared from a diol backbone and an appropriate phosphorochloridite, a great variety of these ligands have been described generating libraries in which both, electronic and steric properties are systematically modified. These libraries have been very often screened in hydroformylation and allylic substitution reactions [2,3].

Asymmetric rhodium-catalyzed hydroformylation using diphosphites derived from chiral alkyl-diol backbones was initially explored by Babin and Whiteker [4] and later by van Leeuwen and coworkers [5]. High enantioselectivities were achieved in the hydroformylation of vinylarenes with Chiraphite, a ligand derived from (2*R*,4*R*)-pentanediol, but similar diphosphites based on shorter or longer alkyl backbones, render poorly enantioselective catalysts. This difference has been attributed to the ability of Chiraphite to form *bis*-equatorial chelate in [RhH($CO)_2$(diphosphite)] catalytically active species. As (*R*,*R*)-Chiraphite, sugar-based diphosphites producing good enantioselectivities form eight-membered chelate rings when they coordinate to the metal center [6,7]. In contrast, (*S*,*S*)-Kelliphite, one of the most efficient ligands for asymmetric hydroformylation forms a nine-membered metal chelate [2,8]. Moreover, it has been shown that a diphosphite forming 16-membered chelate ring is able to produce fair asymmetric induction in the hydroformylation of vinylarenes [9].

Since the beginning of this decade, reports on the application of chiral diphosphites to the allylic substitution reaction have greatly increased [10–19]. Most of the new ligands synthesized have been tested in alkylation of *rac*-1,3-diphenyl-3-acetoxy-1-ene, which often gave better enantioselectivities than unsymmetrically substituted or less-sterically demanding allylic substrates. It should be noted that (*R*,*R*)-Chiraphite and sugar-based diphosphites that perform well in asymmetric hydroformylation are among the best ligands for the alkylation of *rac*-1,3-diphenyl-3-acetoxy-1-ene [13,14]. These type of ligands produced ee's near to 95%, with high turnover frequencies (>2000 h^{-1}). Even higher rates and 98% ee, were achieved in the same reaction using a C_2 diphosphite, containing bulky silyl substituents on furanoside backbone [15] however; this ligand produces poor stereoselectivity in the rhodium-catalyzed styrene hydroformylation [20].

With the aim to get further insight into the relation between the structure of diphosphites and their catalytic performance, we report here a new family of these ligands (Scheme 1) and their

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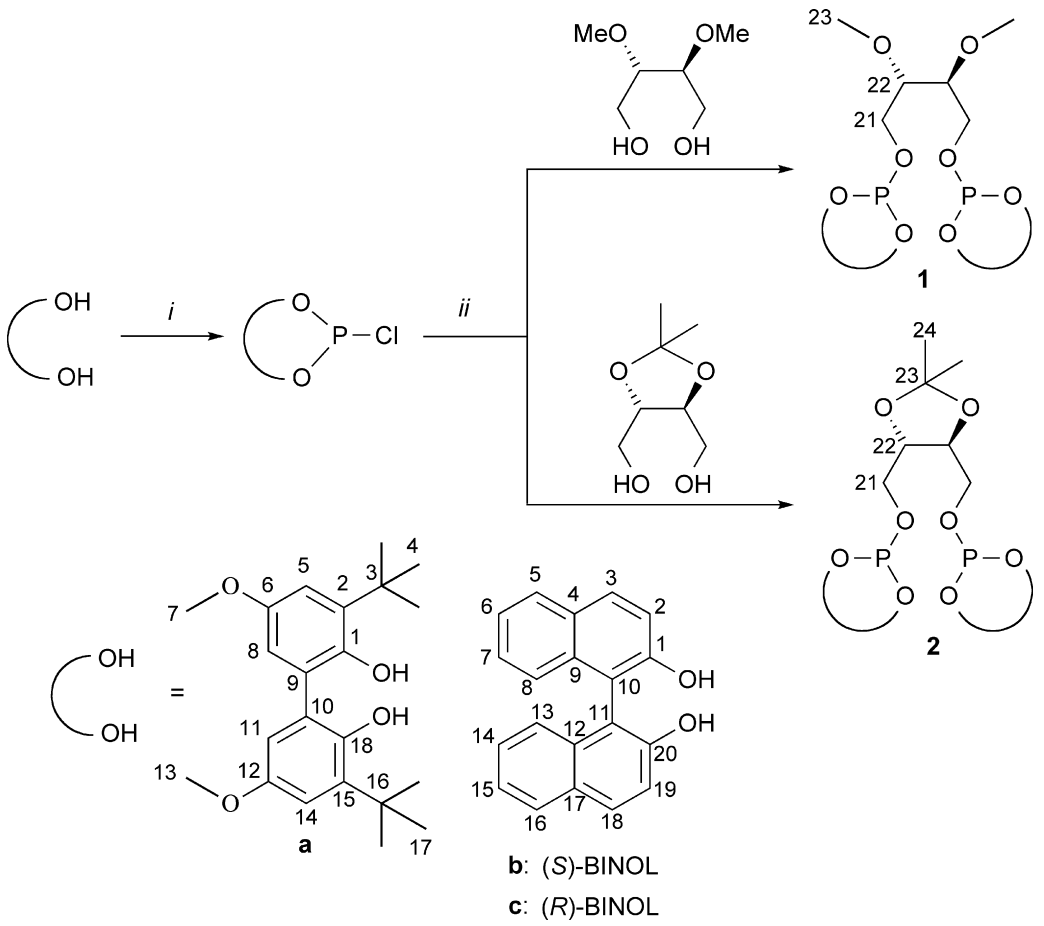

Scheme 1. Syntheses of chiral diphosphite ligands **1**-**2**. (i) PCl_3, NEt_3, THF, −40 °C to 20 °C, 4 h; (ii) NEt_3, THF, −40 °C to 20 °C, 18 h.

catalytic screening in hydroformylation and allylic alkylation reactions. The backbone of these diphosphites was built from tartaric acid, a natural and readily available chiral source. Ligands **2b** and **2c**, bearing four carbon atoms at the backbone, with some restricted flexibility imposed by the 1,3-dioxolane fragment, and atropoisomeric phosphite moieties, could mimic the conformational constrains of Kelliphite. For comparative purposes, ligand **2a**, with a non-chiral fragment as terminal phosphorous substituents, has also been synthesized. The homologous series of ligands **1a**–**c**, in which the stiffness of the four carbon atoms backbone has been released, is also studied.

2. Experimental

2.1. General methods

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures. NEt_3 over KOH and PCl_3 and were distilled prior to use. Diols (2*S*,3*S*)-2,3-dimethoxy-1,4-butanediol [21,22], (4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol [23] and 3,3′-di-*tert*-butyl-5,5′-dimethoxy-2,2′-biphenyldiol [24] were prepared according to literature procedures. Phosphorochloridite intermediates, 6-chloro-4,8-*bis*(1,1-dimethylethyl)-2,10-dimethoxy-dibenzo[d,f][1,3,2]dioxaphosphepine [25], and (*R*)- and (*S*)-(1,1′-binaphthalene-2,2′-dioxy)chlorophosphine [9] were prepared as previously described. Styrene (**S1**) was filtered through neutral activated alumina and substrates *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (**S2**), 1-phenyl-3-acetoxyprop-1-ene (**S3**) and *rac*-3-acetoxycyclohexene (**S4**) were prepared following standard procedures [26]. The rest of reagents were from commercial origin and were used as received.

NMR spectra were recorded in *Bruker Avance-250, Varian Unity Inova-300, -400* and *Bruker ARX-400* instruments using $CDCl_3$ as solvent. Coupling constants are in hertz and chemical shifts are given in ppm referenced to solvent (^1H and ^{13}C) or external reference of 85% aqueous solution of H_3PO_4 (^{31}P). FAB^+ mass spectra were acquired in a Jeol SX102A spectrometer using 3-nitrobenzylalcohol matrix. High resolution TOF mass spectra were obtained by LC/MSD TOF on an Agilent Technologies equipment. Optical rotations were measured in a Perkin-Elmer 241 polarimeter, $[\alpha]^D$ values are in units of 10^{-1} deg cm^2 g^{-1}. Catalytic reaction mixtures were analyzed by GC-Varian 3800, GC-HP 5890 or HPLC Alliance-Waters chromatographs. Absolute configurations of chiral products were assigned by comparing their retention times with those of optically pure compounds. For further experimental details see supplementary data.

2.2. Syntheses of diphosphites: general method

To a solution containing 4.18 mmol of the (1,1′-biaryl-2,2′-dioxy)chlorodiphosphine and NEt_3 (2.28 g, 22.6 mmol) in THF (20 mL), 2.1 mmol of the corresponding diol in THF (5 ml) were slowly added at −40 °C. The mixture was allowed to reach room temperature and it was stirred overnight. The ammonium salt formed was filtrated over celite and the filtrate was evaporated to dryness. The solid residue was purified over silica using CH_2Cl_2 as eluent. The analytically pure products were recovered by evaporating the solvent, yielding white to slightly yellow powders (see Scheme 1 for the labeling used for NMR data).

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