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TETRAHEDRON: *ASYMMETRY*

# Enantioselective copper-catalysed 1,4-addition of diethylzinc to cyclohexenone using chiral diphosphite ligands

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**Abstract**

Bulky diphosphite ligands derived from ribo- and xylofuranose were tested in the copper asymmetric catalytic addition of diethylzinc to 2-cyclohexenone. The xylose derivatives provide enantiomeric excesses in the range of 22–53%. We also describe the preparation of the ribofuranose diphosphite ligands. 

## 1. Introduction

Conjugate addition reactions of organometallic reagents to α,β-unsaturated compounds,[1] in particular the addition of organocuprates to enones, is an attractive method for the synthesis of enantiomerically pure products.[2–4] Although stoichiometric enantioselective additions have been widely studied,[5–9] the catalytic version requires further investigation.

The use of dialkylzinc seems to provide a better approach for the catalytic enantioselective 1,4-additions,[10–23] than Grignard reagents which usually need the presence of additives, such as HMPA, DBU or trialkylchlorosilanes, to achieve good selectivities[24–30] (Fig. 1).

Phosphorus ligands are particularly well suited for enantioselective 1,4-addition. Excellent selectivities (>95% ee) have been obtained using phosphorus amidites[10–17] and oxazoline–phosphite ligands.[18]

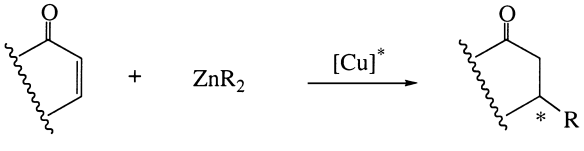


Figure 1.

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Alexakis et al. reported the use of chiral monophosphites and diphosphine ligands in this reaction.[19–21] The diphosphines and phosphites derived from tartrate gave a moderate asymmetric induction (up to 44% for diphosphines and up to 65% ee for phosphites).[19,20] Recently, a taddol monophosphite derivative gave 96% ee for the conjugate adduct of cyclohexenone.[21] As far as we know, diphosphites have only been applied more recently by Chan and co-workers with excellent results,[23] but further efforts are required in order to understand how to obtain an efficient enantiocontrol in this reaction.

In this paper, we report the synthesis of a new family of bulky diphosphites derived from ribose **1** and the results obtained using these diphosphites and an analogous family of diphosphites with the backbone derived from xylose **2** (Fig. 2) as ligands in the asymmetric copper catalytic addition of diethylzinc to 2-cyclohexenone.

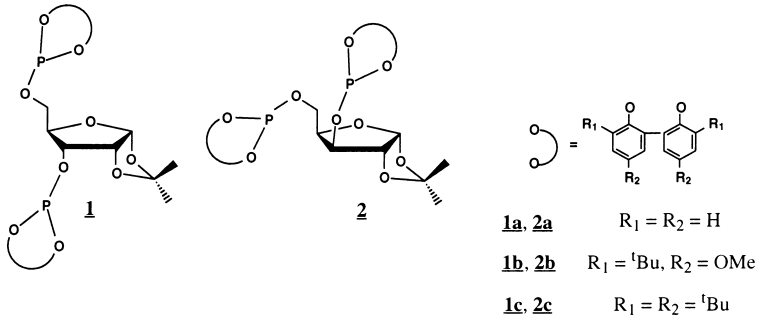



Figure 2.

## 2. Results and discussion

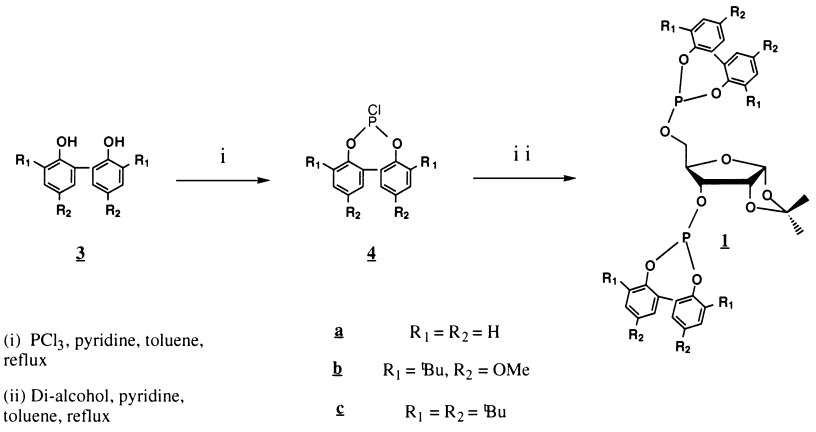
### 2.1. Synthesis of ribose diphosphites

Chiral sugar derivatives are of interest for asymmetric catalysis, due to the high chiral induction observed in different types of catalytic reactions,[31–33] the versatility and the availability of the starting materials. In spite of this, only Spescha has, to our knowledge, reported the use of ligands derived from monosacharides (sulphur monodentate glucose derivatives) in the addition of Grignard reagents to enones.[27]

Diphosphites **1a–c** were synthesised from 1,2-*O*-isopropylidene-ribofuranose and bisphenol phosphorochloridites with or without *tert*-butyl and methoxy groups at the *ortho*- or *para*-positions, in the presence of base. Phosphorochloridites **4a–c** were prepared by reaction of 1 equivalent of $PCl_3$ with the corresponding bisphenol **3a–c** in the presence of a base, according to the method of van Leeuwen et al.[34,35] The two-step sequence is shown in Scheme 1.

Compounds **1a–c** were stable during purification on neutral silica gel under an atmosphere of argon and were isolated in moderate yields (50%) as white solids stable to air at −30°C.

Two singlets (one for each non-equivalent phosphorus) could be observed in the $^{31}P$ NMR spectra. Rapid ring inversions (atropoisomerisation) in bisphenol–phosphorus moieties occurs on the NMR time-scale since the expected diastereoisomers could not be detected by low temperature phosphorus NMR (Fig. 3).[36]




Scheme 1.

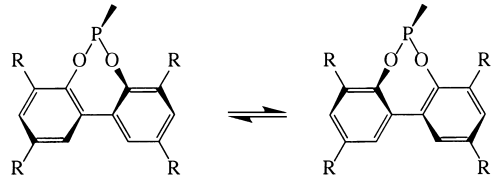


Figure 3.

## 2.2. Conjugate addition of 2-cyclohexenone

Ligands **1a–c** and **2a–c** were used in the copper catalysed conjugate addition of diethylzinc to 2-cyclohexenone. The catalytic system was generated in situ from the corresponding ligand and $Cu(OTf)_2$ in dichloromethane followed by addition of diethylzinc. The conversion and enantioselectivity results are shown in Table 1. Good conversions and almost complete regioselectivities (>95%) in the 1,4-product were found for all ligands.

The effect of the reaction temperature on the enantioselectivity was studied for ligands **2a–c** (Table 1). Isolation, purification and derivatisation of the 1,4-product obtained showed the best ees were obtained at 273 K (e.g., 53% ee using **2a**), decreasing at both higher and lower reaction temperatures (entries 1 to 9).

Dynamic behaviour with equilibria between several species is often observed for organocopper compounds in solution.[4] This would explain the observed dependence of enantioselectivity with temperature.

The obtained enantioselectivities with sugar diphosphites **2a–c** are comparable to those previously reported for monophosphites, except for one taddol-phosphite with which 96% ee was achieved.[20,21] The chelating nature and greater rigidity of the diphosphites does not seem to affect the selectivity of the reaction.

Formation of different, more active species has been observed for ligand **2a** at 298 K during the reaction (Fig. 4). The effect of these new species on the selectivity was investigated (entry 10 compared to 1). The drop in selectivity with time and the pattern of the curve in Fig. 4 suggests that the new species formed at a reaction time of 50 min, are more active aggregates with lower asymmetric induction. Addition of cyclohexenone after an incubation time of 90 min considerably lowered the conversion and enantioselectivity of the reaction (entry 11), probably due to the partial decomposition of the ligand.

Comparing the results obtained with the different substituted ligands **2a–c** it can be deduced that introduction of sterically demanding groups on both diphenyl groups of the ligand have an influence on

Table 1
Catalytic conjugate addition reactions of $ZnEt_2$ to 2-cyclohexenone

| Entry | Ligand | T (K) | t (min) | %Conv.[a] | %ee[b] |
|---|---|---|---|---|---|
| 1 | **2a** | 298 | 120 | 90 | 32[d] |
| 2 | **2a** | 273 | 120 | 60 | 53 |
| 3 | **2a** | 253 | 120 | 40 | 15 |
| 4 | **2b** | 298 | 5 | 100 | 3[d] |
| 5 | **2b** | 273 | 5 | 100 | 22 |
| 6 | **2b** | 253 | 40 | 100 | 15[d] |
| 7 | **2c** | 298 | 15 | 100 | 9 |
| 8 | **2c** | 273 | 120 | 75 | 24[d] |
| 9 | **2c** | 253 | 120 | 75 | 6 |
| 10 | **2a** | 298 | 60 | 44 | 41 |
| 11[c] | **2a** | 298 | 720 | 100 | 11 |
| 12 | **1a** | 273 | 120 | 90 | 8 |
| 13 | **1b** | 273 | 5 | 100 | 2[d] |
| 14 | **1c** | 273 | 120 | 96 | 3 |

[a] Determined by GC of crude reaction mixture. [b] Determined by $^{13}C$ NMR.[37c] Cyclohexenone was added 90 minutes after the addition of $ZnEt_2$ to the catalyst. [d] Determined also by GC using an *octakis*-(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin column.

both conversion and selectivity. The presence of *tert*-butyl groups on the *ortho*-positions has a negative influence on the enantioselectivity, thus with ligands **2b** and **2c** only 22% ee and 27% ee (273 K) were achieved respectively (entries 5 and 8). A possible explanation could be that the bulkier the ligands, the greater is the amount of ligand-free copper in the reaction system and the more readily the reaction proceeds via achiral ligand-free copper compounds. From Table 1 it can also be observed that the presence of a methoxy group on the *para*-position accelerates the reaction, since complete conversion was obtained in 5 min at 273 K for ligand **2b** (entry 5).

The effect of changing the configuration of one carbon on the sugar backbone was also studied. Unexpectedly, ligands **1a–c** showed lower asymmetric induction and higher activity than the less rigid ligands **2a–c** (entries 12–14, Fig. 5). The complexity of the reaction and the possibility of equilibria between different aggregated species do not allow deeper interpretation of these results.

In summary, chiral diphosphites are active in the enantioselective copper-catalysed 1,4-addition of

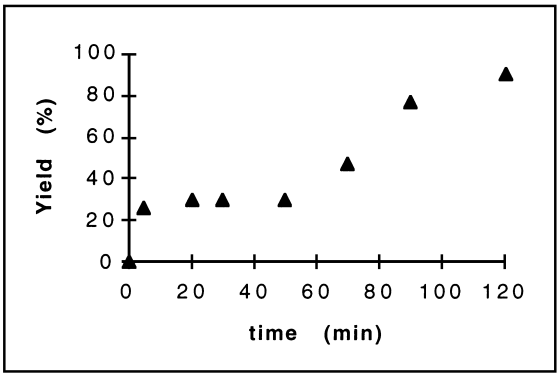



Figure 4. Variation of the conversion vs time using ligand **2a**

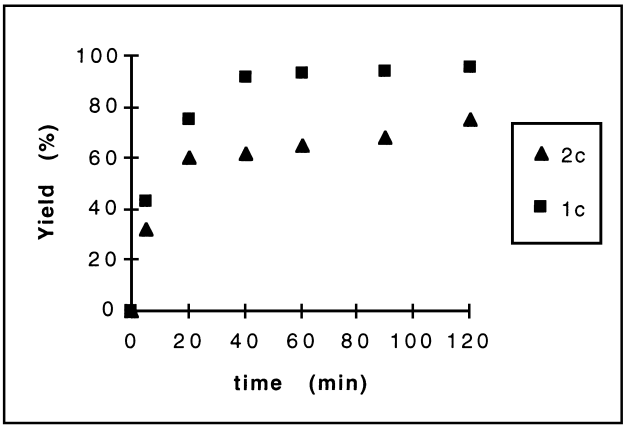



Figure 5. Variation of the conversion vs time using ligands **1c** and **2c**

diethylzinc to cyclohexenone giving ees up to 53%; nevertheless the reaction is complex, with the presence of different species depending on time and temperature. Further investigation is in progress.

## 3. Experimental

All experiments were carried out under an argon atmosphere. All solvents used were dried using standard published methods and distilled prior to use. 1,2-*O*-Isopropylidene-ribofuranose,[38] phosphorochloridites[34,35] and xylofuranose diphosphite derivatives[33] were prepared by previously described methods.

Elemental analyses were performed on a Carlo Erba EA-1108 instrument. $^{1}H$, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ ($^{1}H$ and $^{13}C$) as internal standard or $H_3PO_4$ ($^{31}P$) as external standard. All assignments in NMR spectra were determined by means of COSY and HETCOR spectra. Gas chromatographic analyses were run on a Hewlett–Packard HP 5890A instrument (split/splitless injector, J&W Scientific, Ultra-2 25 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 150 kPa He, FID detector) equipped with a Hewlett–Packard HP 3396 series II integrator. Optical rotations were measured at 20°C on a Perkin–Elmer 241 MC polarimeter. The specific rotations are given in deg $cm^3$ $g^{-1}$ $dm^{-1}$ units.

### 3.1. 3,5-Bis[(1,1′-biphenyl-2,2′-diyl)phosphite]-1,2-O-isopropylidene-D-(+)-ribofuranose **1a**

In situ formed **4a** (5 mmol) was dissolved in toluene (5 ml) to which pyridine (12.5 mmol, 1 ml) was added. 1,2-*O*-Isopropylidene-D-ribofuranose (2.2 mmol, 0.42 g) was azeotropically dried with toluene (3×1 ml) and dissolved in toluene (15 mmol) to which pyridine (12.5 mmol, 1 ml) was added. The 1,2-*O*-isopropylidene-D-ribofuranose solution in toluene was added in 30 min to the solution of **4a** at room temperature. The reaction mixture was stirred overnight at reflux and the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: toluene, $R_f$ 0.20). Yield: 0.52 g (41%) of a white powder. Elemental analysis: found (%): C, 61.98; H, 4.59; calculated (%) for $C_{32}H_{28}O_9P_2$: C, 62.14; H, 4.56; $^{31}$P NMR ($CDCl_3$), δ (ppm): 137.7 (s), 139.2 (s); $^1$H NMR ($CDCl_3$), δ (ppm): 1.19 (s, 3H, $CH_3$), 1.41 (s, 3H, $CH_3$), 4.01 (ddd, 1H, H-5′, $J_{5'-5}$=12 Hz, $J_{5'-4}$=3.6 Hz, $J_{5'-P}$=7.8 Hz), 4.18 (m, 1H, H-4), 4.29 (ddd, 1H, H-5, $J_{5-5'}$=12 Hz, $J_{5-4}$=1.8 Hz, $J_{5-P}$=6.9 Hz), 4.50 (m, 2H, H-3, H-2), 5.72 (d, 1H, H-1, $J_{1-2}$=3.2 Hz), 7.0–7.6 (m, 16H, arom); $^{13}$C NMR ($CDCl_3$), δ (ppm): 26.5 ($CH_3$), 26.7 ($CH_3$), 61.8 (d, C-5, $J_{P-C}$=4.0 Hz), 71.8 (d, C-3, $J_{P-C}$=2.3 Hz), 77.6 (t, C-4, $J_{P-C}$=4.0 Hz), 78.8 (C-2), 103.9 (C-1), 113.4 ($CMe_2$), 121.9, 122.0, 122.1, 122.3, 125.2, 125.3, 125.4, 125.5, 129.3, 129.4, 129.5, 129.6, 129.9, 130.0, 130.1, 130.2 (CH=). $[\alpha]_D^{20}$=+27.0 (*c* 1, $CHCl_3$).

### 3.2. 3,5-Bis[(3,3′-bis-tert-butyl-5,5′-bis-methoxy-1,1′-biphenyl-2,2′-diyl)phosphite]-1,2-O-isopropylidene-D-(−)-ribofuranose **1b**

In situ formed **4b** (5 mmol) was dissolved in toluene (10 ml) to which pyridine (12.5 mmol, 1 ml) was added. 1,2-*O*-Isopropylidene-D-ribofuranose (2 mmol, 0.38 g) was azeotropically dried with toluene (3×1 ml) and dissolved in toluene (20 mmol) to which pyridine (12.5 mmol, 1 ml) was added. The 1,2-*O*-isopropylidene-D-ribofuranose solution in toluene was added in 30 min to the solution of **4b** at room temperature. The reaction mixture was stirred overnight at reflux and the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: toluene, $R_f$ 0.25). Yield: 0.98 g (54%) of a white powder. Elemental analysis: found (%): C, 68.95; H, 8.64; calculated (%) for $C_{52}H_{76}O_9P_2$: C, 68.85; H, 8.44; $^{31}$P NMR ($CDCl_3$), δ (ppm): 142.9 (s), 144.1 (s); $^1$H NMR ($CDCl_3$), δ (ppm): 1.21 (s, 3H, $CH_3$), 1.28 (s, 9H, $^t$Bu), 1.32 (s, 9H, $^t$Bu), 1.35 (s, 18H, $^t$Bu), 1.44 (s, 3H, $CH_3$), 3.72 (s, 12H, $OCH_3$), 3.78 (m, 1H, H-5′), 4.07 (m, 1H, H-4), 4.15 (m, 1H, H-5), 4.28 (m, 1H, H-3), 4.35 (dd, 1H, H-2, $J_{2-3}$=4.0 Hz, $J_{2-1}$=3.3 Hz), 5.62 (d, 1H, H-1, $J_{1-2}$=3.3 Hz), 6.61 (m, 4H, arom), 6.83 (m, 4H, arom); $^{13}$C NMR ($CDCl_3$), δ (ppm): 26.4 ($CH_3$), 26.7 ($CH_3$), 30.7 ($CH_3$, $^t$Bu), 30.8 ($CH_3$, $^t$Bu), 35.2 (C, $^t$Bu), 55.4 ($OCH_3$), 62.0 (d, C-5, $J_{P-C}$=9.1 Hz), 72.7 (d, C-3, $J_{P-C}$=6.2 Hz), 77.8 (dd, C-4, $J_{P-C}$=3.4 Hz, $J_{P-C}$=5.1 Hz), 78.4 (d, C-2, $J_{P-C}$=3.4 Hz), 103.6 (C-1), 112.6, 112.8, 112.9 (CH=), 113.2 ($CMe_2$), 114.2, 114.3 (CH=), 133.5, 133.8, 142.4, 142.8, 155.5, 155.6, 155.8 (C). $[\alpha]_D^{20}$=−17.5 (*c* 1, $CHCl_3$).

### 3.3. 3,5-Bis[(3,3′,5,5′-tetra-tert-butyl-1,1′-biphenyl-2,2′-diyl)phosphite]-1,2-O-isopropylidene-D-(−)-ribofuranose **1c**

In situ formed **4c** (10 mmol) was dissolved in toluene (40 ml) to which pyridine (12.5 mmol, 1 ml) was added. 1,2-*O*-Isopropylidene-D-ribofuranose (4 mmol, 0.76 g) was azeotropically dried with toluene (3×1 ml) and dissolved in toluene (15 mmol) to which pyridine (12.5 mmol, 1 ml) was added. The 1,2-*O*-isopropylidene-D-ribofuranose solution in toluene was added in 30 min to the solution of **4c** at room temperature. The reaction mixture was stirred overnight at reflux and the pyridine salts were

removed by filtration. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: toluene, $R_f$ 0.75). Yield: 1.8 g (45%) of a white powder. Elemental analysis: found (%): C, 71.89 ; H, 8.47; calculated (%) for $C_{64}H_{92}O_9P_2$: C, 72.02; H, 8.69; $^{31}$P NMR ($CDCl_3$), δ (ppm): 142.3 (s), 143.4 (s); $^1$H NMR ($CDCl_3$), δ (ppm): 1.27 (s, 3H, $CH_3$), 1.32 (s, 18H, $^t$Bu), 1.33 (s, 18H, $^t$Bu), 1.37 (s, 3H, $CH_3$), 1.38 (s, 9H, $^t$Bu), 1.41 (s, 18H, $^t$Bu), 1.44 (s, 9H, $^t$Bu), 3.82 (m, 1H, H-5′), 4.14 (m, 1H, H-4), 4.21 (m, 1H, H-5), 4.25 (dd, 1H, H-2, $J_{2-3}$=3.5 Hz, $J_{2-1}$=3.3 Hz), 4.37 (m, 1H, H-3), 5.64 (d, 1H, H-1, $J_{1-2}$=3.3 Hz), 7.14 (m, 4H, arom), 7.39 (m, 4H, arom); $^{13}$C NMR ($CDCl_3$), δ (ppm): 26.5 ($CH_3$), 26.7 ($CH_3$), 30.9 ($CH_3$, $^t$Bu), 31.1 ($CH_3$, $^t$Bu), 31.4 ($CH_3$, $^t$Bu), 34.5 (C, $^t$Bu), 35.2 (C, $^t$Bu), 63.4 (d, C-5, $J_{P-C}$=10.9 Hz), 72.8 (d, C-3, $J_{P-C}$=5.7 Hz), 78.0 (m, C-4), 78.5 (d, C-2, $J_{P-C}$=1.9 Hz), 103.7 (C-1), 113.2 ($CMe_2$), 124.2, 126.5, 126.6, 126.7 (CH═, arom), 127.7, 128.3, 128.4, 132.9, 140.0, 140.1, 140.4, 146.3, 146.4, 146.5, 146.7 (C, arom). $[\alpha]_D^{20}$=−34.5 (*c* 1, $CHCl_3$).

### *3.4. Typical procedure for the catalytic conjugate addition of diethylzinc to 2-cyclohexenone*

A solution of $Cu(OTf)_2$ (9 mg, 0.025 mmol) and **1a** (15.4 mg, 0.025 mmol) in dichloromethane (3 ml) was stirred for 30 min at room temperature. After cooling to 253 K, diethylzinc (1 M soln in hexanes, 7 ml, 7 mmol) was added followed by a solution of 2-cyclohexenone (0.5 ml, 5 mmol) in dichloromethane (3 ml). The reaction was monitored by GC using pentadecane as internal standard. After 2 h the reaction was quenched by addition of HCl (2 M). The mixture was extracted with diethyl ether (3×20 ml). The combined organic layers were washed with brine (25 ml), dried with $MgSO_4$ filtered and evaporated to give the crude 1,4-product. After purification by column chromatography (hexane:diethyl ether, 5:1) the ees were determined after derivatisation with homochiral 1,2-diphenylethylenediamine by $^{13}$C NMR spectroscopy.[37]

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