Mixed thioether-phosphite and phosphine-phosphite ligands for copper-catalyzed asymmetric 1,4-addition of organometallic reagents to cyclohexenone

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Abstract

A series of thioether-phosphite and phosphine-phosphite ligands have been tested in the copper-catalyzed asymmetric addition of organometallic reagents to 2-cyclohexenone. In all the cases, excellent reaction rates (TOF $> 1200\,h^{-1}$) and chemoselectivities for the 1,4-product have been obtained, while enantioselectivities have been moderate. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The 1,4-addition of organometallic reagents to α,β-unsaturated carbonyl compounds is an important process for C–C bond formation in organic synthesis [1,2]. Although organocuprates and copper-catalyzed 1,4-additions of Grignard reagents are most frequently employed, a number of alternative reagents, based on other metal catalysts (i.e. Ni and Mn) and other organometallic reagents (i.e. ZnR_2 and AlR_3), have recently been developed [3–6].

Several successful methods have been described for enantioselective 1,4-addition. These have mainly been based on chiral auxiliaries or stoichiometric organometallic reagents. Only a few have been based on highly enantioselective catalytic processes [3,4,6]. A prominent position in the rapid development of the latter field is occupied by the copper-catalyzed, ligand-accelerated, 1,4-addition of organozinc reagents. Thus, excellent enantioselectivities have been obtained using chiral phosphoroamidites [7–11], phosphites [12–17], bidentate P–N [18,19] ligands and Schiff base [20,21] ligands. However, further research is needed to understand how to obtain an efficient enantiocontrol. In this context, the design of new ligands is still an important area of research.

Carbohydrates are particularly advantageous in this respect. They are readily available and highly functionalized compounds with several stereogenic centers. This allows a systematic regio- and stereoselective introduction of different functionalities in the synthesis of series of chiral ligands that can be screened in the search for high activities and enantioselectivities. At the same time, they can provide valuable information about the origin of the stereoselectivity of the reaction [22]. In previous studies, several types of sugar-derived ligands with a furanoside backbone have been applied to asymmetric copper-catalyzed 1,4-additions [17,23,24].

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1a R = Me; R' = *t*-Bu
1b R = *i*-Pr; R' = *t*-Bu
1c R = Ph; R' = *t*-Bu
1d R = *i*-Pr; R' = H
1e R = Ph, R' = H

2a R' = *t*-Bu
2b R' = H
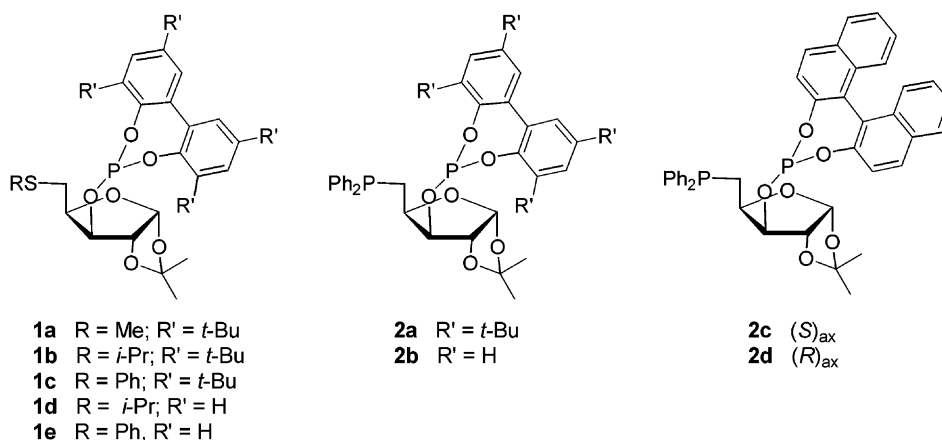
2c $(S)_{ax}$
2d $(R)_{ax}$

Fig. 1.

Following our interest in using carbohydrates as an available chiral source for ligands [22,25–28], and bearing in mind that two different donor sites can a priori match the intermediates better and therefore influence their reactivity and enantioselectivity [27,29], in this paper we report the use of thioether-phosphite **1** and phosphine-phosphite **2** ligands (Fig. 1) in the enantioselective copper-catalyzed 1,4-addition of organometallic reagents to 2-cyclohexenone.

2. Experimental

2.1. General methods

All syntheses were performed using standard Schlenk techniques under argon atmosphere. Solvents were purified by standard procedures. Ligands **1a**–**c** [25] and **2** [27] and (1,1′-biphenyl-2,2′-diyl)-phosphorochloridite [30] were prepared by previously described methods. All other reagents were used as commercially available. 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$_3$PO$_4$ (^{31}P) as external standard. All assignments in NMR spectra were determined by COSY and HETCOR spectra. Gas chromatographic analyses were run on a Hewlett-Packard HP 5890A

instrument equipped with a Hewlett-Packard HP 3396 series II integrator.

2.2. Synthesis of 5-deoxy-1,2-O-isopropylidene-3-[(1,1′-biphenyl-2,2′-diyl)phosphite]-5-isopropylsulfanyl-α-ᴅ-xylofuranose (**1d**)

In situ formed (1,1′-biphenyl-2,2′-diyl)-phosphorochloridite (1.2 mmol) was dissolved in toluene (5 ml) to which pyridine (0.36 ml, 4.6 mmol) was added. 5-Deoxy-1,2-O-isopropylidene-5-isopropylsulfanyl-α-ᴅ-(−)-xylofuranoside [25] (248.3 mg, 1 mmol) was azeotropically dried with toluene (3 × 1 ml) and dissolved in toluene (10 ml) to which pyridine (0.18 ml, 2.3 mmol) was added. The diol solution was transferred slowly over 30 min to the solution of phosphorochloridite 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 chromatography over silica (eluent: toluene) to produce 0.41 g (88%) of a white powder. Anal. Calcd. for C$_{23}$H$_{27}$O$_6$PS: C, 59.73; H, 5.88; S, 6.93. Found: C, 59.61; H, 5.92; S, 6.76. ^{31}P NMR, δ 144.9 (s, 1P). ^{1}H NMR, δ 1.302 (d, 6H, CH$_3$ *i*-Pr, $^3J_{H-H} = 12.9$ Hz), 1.31 (s, 3H, CH$_3$), 1.48 (s, 3H, CH$_3$), 2.82 (dd, 1H, H-5, $^2J_{5-5'} = 12.9$ Hz, $^3J_{5-4} = 7.8$ Hz), 2.90 (dd, 1H, H-5′, $^2J_{5'-5} = 12.9$ Hz, $^3J_{5'-4} = 6.6$ Hz), 3.03 (sp, 1H, CH, $^3J_{H-H} = 12.9$ Hz), 4.32 (m, 1H, H-4), 4.64 (d, 1H, H-2, $^3J_{2-1} = 3.9$ Hz), 4.80 (dd, 1H, H-3,

$^3J_{3-4} = 2.7\,\text{Hz}$, $^3J_{3\text{-}P} = 9.9\,\text{Hz}$), 5.88 (d, 1H, H-1, $^3J_{1-2} = 3.9\,\text{Hz}$), 7.2–7.5 (m, 8H, CH=). ^{13}C NMR, δ 23.4 (CH$_3$ i-Pr), 23.5 (CH$_3$ i-Pr), 26.3 (CH$_3$), 26.7 (CH$_3$), 28.2 (C-5), 35.7 (CH), 77.4 (d, C-3, $J_{C-P} = 11.6\,\text{Hz}$), 79.8 (d, C-4, $J_{C-P} = 5.0\,\text{Hz}$), 84.3 (d, C-2, $J_{C-P} = 2.5\,\text{Hz}$), 104.7 (C-1), 111.9 (CMe$_2$), 121.7 (CH=), 121.9 (CH=), 125.2 (CH=), 129.2 (CH=), 129.9 (CH=), 130.7 (C), 149.0 (C), 149.1 (C).

2.3. Synthesis of 5-deoxy-1,2-O-isopropylidene-3-[(1,1′-biphenyl-2,2′-diyl)phosphite]-5-phenylsulfanyl-α-D-xylofuranose (1e)

Treatment of in situ formed (1,1′-biphenyl-2,2′-diyl)phosphorochloridite (1.2 mmol) and 5-deoxy-1,2-O-isopropylidene-5-phenylsulfanyl-α-D-(−)-xylofuranoside [25] (282.4 mg, 1 mmol) as described for compound **1d** afforded thioether-phosphite **1e**, which was purified by flash chromatography over silica (eluent: toluene) to produce 0.45 g (91%) of a white powder. Anal. Calcd. for C$_{26}$H$_{25}$O$_6$PS: C, 62.89; H, 5.08; S, 6.46. Found: C, 63.11; H, 5.11; S, 6.29. ^{31}P NMR, δ 144.8 (s, 1P). ^{1}H NMR, δ 1.22 (s, 3H, CH$_3$), 1.38 (s, 3H, CH$_3$), 3.17 (dd, 1H, H-5, $^2J_{5-5'} = 13.2\,\text{Hz}$, $^3J_{5-4} = 8.4\,\text{Hz}$), 2.27 (dd, 1H, H-5′, $^2J_{5'-5} = 13.2\,\text{Hz}$, $^3J_{5'-4} = 6.0\,\text{Hz}$), 4.31 (m, 1H, H-4), 4.64 (d, 1H, H-2, $^3J_{2-1} = 3.6\,\text{Hz}$), 4.83 (dd, 1H, H-3, $^3J_{3-4} = 2.7\,\text{Hz}$, $^3J_{3\text{-}P} = 9.6\,\text{Hz}$), 5.89 (d, 1H, H-1, $^3J_{1-2} = 3.6\,\text{Hz}$), 7.1–7.6 (m, 13H, CH=). ^{13}C NMR, δ 26.3 (CH$_3$), 26.7 (CH$_3$), 31.4 (C-5), 77.3 (d, C-3, $J_{C-P} = 12.1\,\text{Hz}$), 78.4 (d, C-4, $J_{C-P} = 5.1\,\text{Hz}$), 84.4 (d, C-2, $J_{C-P} = 2.4\,\text{Hz}$), 104.7 (C-1), 112.0 (CMe$_2$), 121.8 (CH=), 121.9 (CH=), 125.4 (CH=), 126.5 (CH=), 129.0 (CH=), 129.3 (CH=), 129.4 (CH=), 129.9 (CH=), 130.0 (CH=), 130.1 (CH=), 130.8 (C), 130.9 (C), 135.2 (C), 149.2 (C), 149.4 (C).

2.4. General procedure for the catalytic conjugate addition of diethylzinc to 2-cyclohexenone

In a typical procedure a solution of Cu(OTf)$_2$ (9 mg, 0.025 mmol) and diphosphite ligand (0.025 mmol) in dichloromethane (3 ml) was stirred for 30 min at room temperature. After cooling to 0 °C, diethylzinc (1 M sol. in hexanes, 3.5 ml, 3.5 mmol) was added. A solution of 2-cyclohexenone (0.24 ml, 2.5 mmol) and undecane as GC internal standard (0.25 ml) in dichloromethane (3 ml) was then added. The reaction

was monitored by GC. The reaction was quenched with HCl (2 M) and filtered twice through silica flash. The conversion and enantiomeric excesses were obtained by GC using a Lipodex-A column.

2.5. Typical procedure for the catalytic conjugate addition of triethylaluminium to 2-cyclohexenone

In a typical procedure, triethylaluminium (1 M sol., 3.5 ml, 3.5 mmol) and enone (0.6 M sol. in CH$_2$Cl$_2$, 3.5 ml, 2.5 mmol) were introduced sequentially and in a dropwise manner over 10 min to a CH$_2$Cl$_2$ solution (3 ml) containing phosphine-phosphite (0.025 mmol) and [Cu(MeCN)$_4$]BF$_4$ (7.8 mg, 0.025 mmol) at −20 °C. After 5 min the reaction was quenched with HCl (2 M), and undecane as GC internal standard (50 ml) was added. The organic layer was filtered twice through flash silica gel. The conversion and ee's were measured by GC using a Lipodex-A column.

3. Results and discussion

3.1. Ligand design

Ligands **1** and **2** consist of chiral 1,2-O-protected xylofuranoside backbones, which determines their underlying structure and either different thioether (ligands **1**) or phosphine (ligands **2**) groups at C-5 position. To this basic framework several phosphoric acid biphenol esters are attached (Fig. 1).

The influence of the different substituents at the thioether groups was investigated using ligands **1a–c**, which have the same phosphite moiety. The effect of the different substituents in *ortho* and *para* positions of the biphenyl moiety was investigated using ligands **1b–e**.

We then used ligands **2a** and **2b** to study how a phosphine moiety rather than the thioether functionality affected catalytic performance. We also studied how the configuration of the biaryl moieties affected enantioselectivity using a series of enantiomerically pure binaphthol-based ligands **2c** and **2d**.

3.2. Synthesis of thioether-phosphite ligands 1d and 1e

The new ligands **1d** and **1e** were easily synthesized in one step from the corresponding thioether-alcohol,
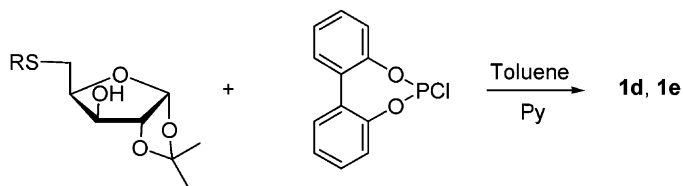
Scheme 1.

which was easily prepared on a large-scale from D-(+)-xylose using a standard procedure (Scheme 1) [25]. The reaction of the corresponding thioether-alcohol with one equivalent of in situ formed (1,1′-biphenyl-2,2′-diyl)-phosphorochloridite in the presence of pyridine afforded ligands **1d** and **e** in good overall yield. The ^{1}H, ^{13}C and ^{31}P NMR spectra agree with those expected for these C_1 ligands (see Section 2). Rapid ring inversions (atropoisomerization) of the seven-membered dioxaphosphepin rings occurred on the NMR time-scale, since the expected diastereoisomers were not detected by low temperature ^{31}P NMR [31].

3.3. Asymmetric 1,4-addition of organometallic reagents to 2-cyclohexenone

In a first set of experiments, we tested ligands **1** and **2** in the copper-catalyzed conjugate addition of diethylzinc to 2-cyclohexenone. The latter was chosen as a substrate because this reaction has been carried out with a wide variety of ligands with different donor groups enabling direct comparison of the efficacy of different ligand systems [4–6]. The catalytic system was generated in situ by adding the corresponding ligand to a dichloromethane suspension of Cu(OTf)$_2$. The results are shown in Table 1. In general, reaction rates were good for all ligands. In all cases the chemoselectivity in 1,4-product were higher than 97% and no 1,2-product was observed by gas chromatography.

The effect of different reaction parameters such as reaction temperature, ligand-to-copper ratio and the solvent were studied using ligand **1a**. The results showed that the efficiency of the process depended on the nature of the solvent (entries 1–3). The best catalyst performance (activity and selectivity) was obtained with dichloromethane as a solvent (entry 2).

As with related Cu-diphosphite [17,23] and Cu-thioether-hydroxyl [24] catalytic systems, the

Table 1
Asymmetric 1,4-addition of diethylzinc to 2-cyclohexenone[a]

Entry	L^*	Solvent	T (°C)	Conversion (%)[b]	ee (%)[c]
1	**1a**	Toluene	0	62	17 (R)
2	**1a**	CH$_2$Cl$_2$	0	93	18 (R)
3	**1a**	THF	0	89	11 (R)
4	**1a**	CH$_2$Cl$_2$	25	100	15 (R)
5	**1a**	CH$_2$Cl$_2$	−20	38	13 (R)
6	**1a**	CH$_2$Cl$_2$	−40	12	9 (R)
7[d]	**1a**	CH$_2$Cl$_2$	0	91	17 (R)
8	**1b**	CH$_2$Cl$_2$	0	100	9 (R)
9	**1c**	CH$_2$Cl$_2$	0	93	11 (R)
10	**1d**	CH$_2$Cl$_2$	0	74	27 (R)
11	**1e**	CH$_2$Cl$_2$	0	64	41 (R)
12	**2a**	CH$_2$Cl$_2$	0	100	12 (S)
13	**2b**	CH$_2$Cl$_2$	0	65	19 (S)
14	**2c**	CH$_2$Cl$_2$	0	61	10 (R)
15	**2d**	CH$_2$Cl$_2$	0	63	9 (S)

[a] Reaction conditions: Cu(OTf)$_2$ (0.025 mmol), ligand (0.025 mmol), ZnEt$_2$ (3.5 mmol), substrate (2.5 mmol), solvent (6 ml).

[b] Conversion % determined by GC using undecane as internal standard after 5 min.

[c] Enantiomeric excess measured by GC using Lipodex-A column.

[d] 0.05 mmol of ligand was used.

best enantioselectivities were achieved at 0 °C (entry 2). Enantioselectivities decreased when the reaction temperature was either raised or lowered (entries 2, 4–6).[1]

Varying the ligand-to-copper ratio showed that excess ligand did not affect the activity and the stereos-

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[1] Preliminary characterization results suggest that the presence of several species in dynamic equilibrium may account for this interesting temperature phenomenon. A detailed mechanistic study is underway and the results will be published in due course.

electivity of the reaction (entries 2 and 7). Within the accuracy of these experiments, there was no change in the enantioselectivities over time. This agrees with the presence of the same aggregates during the reaction time.

Comparing the results using thioether-phosphite ligands **1a**–**c**, which have different substituents in the thioether moeity, we can conclude that changing the substituent in the thioether moiety produces an effect both on rate and stereoselectivity. Reaction rates were therefore higher for the catalyst precursor containing electron-rich ligand **1b** (entry 8), while enantioselectivities were better with the catalyst precursor containing ligand **1a** (entry 2).
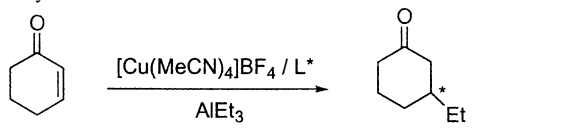
The use of thioether-phosphite ligands **1d** and **1e**, whose bulky *tert*-butyl groups at the *ortho* and *para* positions of the biphenyl moiety had been removed (Fig. 1), produced higher enantioselectivities but the reaction was slower (entries 10 and 11).

The use of phosphine-phosphite ligands **2a** and **2b**, which have different substituents in the biphenyl moieties, followed the same trend as the thioether-phosphite ligands. The presence of bulky *tert*-butyl substituents in the biphenyl moiety had a positive effect on activity and a negative effect on enantiodiscrimination. Comparing these results with those with the thioether-phosphite ligands **1**, we can conclude that activities were similar to those with ligands **1** but enantioselectivity was lower. Interestingly, the sense of the enantioselectivity was also affected. Thus, the use of ligands **1**, which contain a thioether moiety attached to carbon atom C-5, gave the (*R*)-product (entries 1–11), while the use of ligands **2a** and **2b**, with a phosphine moiety attached to C-5, preferentially produced the (*S*)-enantiomer (entries 12 and 13).

The influence of the phosphite moiety in ligands **2** was studied using ligands **2c** and **2d**, which have enantiomerically pure binaphthyl groups. These ligands led to low ee (entries 14 and 15). Interestingly, the sense of the asymmetric induction was reversed. This indicates that the absolute stereochemistry of the binaphthyl in the phosphite moiety plays an important role in the asymmetric induction.

Bearing in mind the positive effect when we recently used triethylaluminium rather than diethylzinc as the alkylating reagent in the copper-catalyzed 1,4-addition using phosphine-phosphite ligands as auxiliaries [32], we also studied the use of triethylaluminium in com-

Table 2

Asymmetric copper-catalyzed 1,4-addition of triethylaluminium to 2-cyclohexenone[a]

Entry	L^*	TOF[b]	Conversion (%)[c]	1,4-Product (%)[d]	ee (%)[e]
1	**2a**	>1200	100	99	7 (*R*)
2	**2b**	504	42	100	12 (*R*)
3	**2c**	972	81	100	5 (*S*)
4	**2d**	636	53	99	11 (*R*)

[a] Reaction conditions: [Cu(MeCN)$_4$]BF$_4$ (0.025 mmol), ligand (0.025 mmol), AlEt$_3$ (3.5 mmol), substrate (2.5 mmol), CH$_2$Cl$_2$ (6 ml), $T = -20\,°C$.

[b] TOF in mol product × mol Cu^{-1} × h^{-1} determined after 5 min reaction time by GC.

[c] Conversion % determined by GC using undecane as internal standard after 5 min.

[d] Chemoselectivity in 1,4-product determined by GC using undecane as internal standard.

[e] Enantiomeric excess measured by GC using Lipodex-A column.

bination with ligands **2**. The results are summarized in Table 2. It is noteworthy that the results were better when [Cu(MeCN)$_4$]BF$_4$ rather than Cu(OTf)$_2$ was used as a catalyst precursor (data not shown). In general, reaction rates and chemoselectivity in 1,4-product were good for all ligands.

Comparing these results with those when diethylzinc was used (Table 1, entries 12–15), we can in general conclude that activity and chemoselectivity in 1,4-product were similar but enantioselectivity was lower. Interestingly, the sense of the enantioselectivity was reversed. Therefore, the nature of the alkylating reagent is also important in determining enantioselectivity.

4. Conclusions

In summary, a series of thioether-phosphite **1a**–**e** and phosphine-phosphite **2a**–**d** ligands with xylofuranoside backbone have been tested in the Cu-catalyzed asymmetric 1,4-addition to 2-cyclohexenone. These ligands produce excellent reaction rates (TOF > 1200 h^{-1}) among with high chemo- and regioselectivity in 1,4-product. The systematic variation of

different functional groups at C-5 position (thioether and phosphine) and different substituents in the phosphite moiety at C-3 had a strong effect on rate and enantioselectivity. Enantioselectivity was best with the catalyst precursor containing thioether-phosphite ligand **1e**, which has a phenyl substituent in the thioether moiety and a non-substituted biphenyl phosphite moiety. The results also showed that the nature of alkylating agent also plays an important role in determining the enantioselectivity.

Acknowledgements

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