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Furanoside thioether–phosphinite ligands for Rh-catalyzed asymmetric hydrosilylation of ketones

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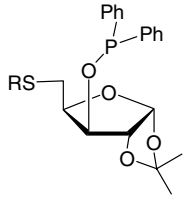
Abstract—A series of thioether–phosphinite ligands, easily prepared in a few steps from inexpensive D-(+)-xylose, were tested in the Rh-catalyzed hydrosilylation of ketones. Systematic variation of the electronic and steric properties of the thioether moiety provided useful information about the ligand parameters which control enantiodiscrimination. The results show that the enantiomeric excesses are strongly dependent on the steric properties of the substituent on the thioether moiety and on the steric properties of the substrate. High activities and good enantiomeric excesses (up to 90%) were obtained in the hydrosilylation of several aryl ketones.

1. Introduction

Over the last few decades, the asymmetric rhodium-catalyzed hydrosilylation of ketones has been recognized as a versatile method for obtaining optically active secondary alcohols.[1] Most of the chiral ligands developed for the asymmetric hydrosilylation of ketones are N- and P-containing compounds, possessing either *C*1 or *C*2-symmetry. Mixed P–N and N–N′ ligands have played a dominant role amongst the heterodonor ligands.[1] Phosphorus–thioether ligands have scarcely been used in this process, possibly because the first applications of these systems generally only produced moderate enantioselectivity.[2] However, more recently, Evans et al. developed a family of thioether–phosphinite ligands, which proved to be effective.[3] Despite this success, the use of other thioether–phosphinite ligands in metal-catalyzed hydrosilylation is yet to be reported. More research is therefore needed to study the possibilities offered by thioether–phosphinites as a new class of ligands for this process. For this purpose, carbohydrates are particularly advantageous due to them being inexpensive and the ease of modular construction. Although they have successfully been used in other enantioselective reactions,[4] there have only been a few reports of highly enantioselective hydrosylilylation using these systems.[5] To the best of our knowledge, carbohydrate-based thioether–phosphinite ligands have not been tested in this process.

Following our interest in carbohydrates as an inexpensive and highly modular chiral sources for preparing ligands[4,6] and encouraged by the results of Evans' thioether–phosphinite ligands in asymmetric hydrosilylation, we applied furanoside thioether–phosphinite ligands **1**–**7** (Fig. 1) in the Rh-catalyzed enantioselective hydrosilylation of several ketones. These ligands contain thioether moieties with different electronic and steric properties, whose effects on catalytic performance have been studied.



1 R = Ph **5** R = 4-Me-C_6H_4
2 R = Me **6** R = 4-CF_3-C_6H_4
3 R = ^{i}Pr **7** R = 2,6-diMe-C_6H_3
4 R = ^{t}Bu

Figure 1. Thioether-phosphinite ligands **1**–**7**.

2. Results and discussion

2.1. Synthesis of the chiral thioether–phosphinite ligands

Ligands **1**–**7** consist of a chiral 3-diphenylphosphinite-1,2-O-protected xylofuranoside backbone, which

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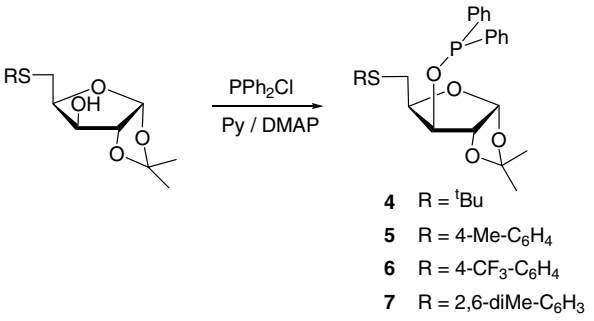


Scheme 1. Synthesis of the new ligands **4**–**7**.

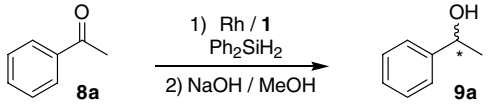
determines their underlying structure to which several thioether moieties at the C-5 position were attached (Fig. 1). The new ligands **4**–**7**[7] were synthesized very efficiently in one step by the reaction of the corresponding thioether-alcohols[8] with 1 equiv of chlorodiphenylphosphine in dry THF, under nitrogen, and in the presence of pyridine and 4-(dimethylamino)-pyridine (DMAP) (Scheme 1). All ligands were stable during purification on neutral alumina under an argon atmosphere and were isolated as colorless oils. The ^{1}H, ^{31}P and ^{13}C NMR spectra were as expected for these C_1 ligands (see Experimental).

2.2. Asymmetric hydrosilylation of ketones

We first investigated the Rh-catalyzed hydrosilylation of acetophenone **8a**, which is widely used as a model substrate.[1] The catalysts were generated in situ by adding the corresponding ligand to the catalyst precursor.

The effect of the solvent, catalyst precursor and the ligand-to-rhodium ratio were investigated using the catalyst precursor containing ligand **1**. The results are summarized in Table 1.

Table 1. Effect of the solvent, catalyst precursor and ligand-to-rhodium ratio on the hydrosilylation of acetophenone **8a** using ligand **1**[a]



Entry	Precursor	Solvent	% Conv.[b]	% ee[c]
1	$[Rh(cod)_2]BF_4$	THF	75	30 (*R*)
2	$[Rh(cod)_2]BF_4$	CH_2Cl_2	5	<5 (*R*)
3	$[Rh(cod)_2]BF_4$	Toluene	70	32 (*R*)
4	$[Rh(\mu\text{-Cl})(cod)]_2$	THF	73	29 (*R*)
5	$[Rh(\mu\text{-Cl})(cod)]_2$	CH_2Cl_2	0	—
6	$[Rh(\mu\text{-Cl})(cod)]_2$	Toluene	68	38 (*R*)
7[d]	$[Rh(\mu\text{-Cl})(cod)]_2$	Toluene	87	25 (*R*)

[a] Reaction conditions: **8** (1 mmol), Ph_2SiH_2 (1.1 mmol), **1** (0.011 mmol), **1**/Rh = 1.1, solvent (2 mL), room temperature.
[b] Conversion after 30 min. Determined by GC using undecane as internal standard.
[c] Enantiomeric excess determined by GC.
[d] **1**/Rh = 2.

Our results indicate that both solvent and catalyst precursors affected catalytic performance. Toluene as the solvent and $[Rh(\mu\text{-Cl})(cod)]_2$ (cod = 1,5-cyclooctadiene) as the catalyst precursor provided the best combination of activity and enantioselectivity (entry 6 vs 1–5). Adding a one-fold excess of ligand had a positive effect on activity but the enantioselectivity decreased (entry 6 vs 7).

We next studied, with ligands **1**–**7**, how the electronic and steric properties of the thioether substituents affect the catalytic performance under the conditions, which gave an optimum trade-off between enantioselectivity and reaction rates, that is, a ligand-to-rhodium ratio of 1.1, using $[Rh(\mu\text{-Cl})(cod)]_2$ as a catalyst precursor and toluene as solvent (Table 2). Our results show that the enantiomeric excesses are mainly dependent on the steric properties of the substituents in the thioether moiety.

Table 2. Rh-catalyzed asymmetric hydrosilylation of acetophenone **8a** using thioether–phosphinite ligands **1**–**7**[a]

Entry	Ligand	% Conv.[b]	% ee[c]
1	**1**	68	38 (*R*)
2	**2**	93	25 (*R*)
3	**3**	97	47 (*R*)
4	**4**	90	76 (*R*)
5	**5**	82	41 (*R*)
6	**6**	94	37 (*R*)
7	**7**	92	44 (*R*)
8[d]	**4**	90	86 (*R*)
9[e]	**10**	100	88 (*S*)

[a] Reaction conditions: **8** (1 mmol), Ph_2SiH_2 (1.1 mmol), **1** (0.011 mmol), **1**/Rh = 1.1, toluene (2 mL), room temperature.
[b] Conversion after 30 min determined by GC using undecane as internal standard.
[c] Enantiomeric excess determined by GC.
[d] $T = -15$ °C, conversion after 1 h determined by GC using undecane as internal standard.
[e] Reaction conditions: **8** (0.5 mmol), Ph_2SiH_2 (0.75 mmol), [Rh(nbd)(**10**)]OTf (0.005 mmol), THF (2.5 mL), room temperature.

With ligands **1**–**4** and **7**, we next studied how the steric properties of the ligand affected the product outcome. If we compare the results obtained with these ligands, it can be concluded that the best enantioselectivities can be achieved when bulky thioether substituents are present (entries 1–4 and 7). The use of ligand **4** with bulky *tert*-butyl groups in the thioether moiety, therefore, provided **9a** in 76% ee (entry 4), while ligand **2** with a sterically undemanding methyl substituent, yielded **9a** in only 25% ee (entry 2).

Using ligands **1**, **5** and **6** with different substituents at the *para*-positions of the thiophenyl group, we studied how the electronic properties of the ligand affects enantioselectivity. The results indicated that enantioselectivity was hardly affected by the electronic properties of the thioether moiety (entries 1, 5 and 6).

Finally, we studied how the temperature affected the outcome of the reaction with ligand **4**. By lowering the temperature to −15 °C, the enantioselectivity increased to 86 % (entry 4 vs 8). This result is similar to that obtained by Evans (ligand **10**, Fig. 2) using diphenylsylane as a silylating agent (entry 9).[3]

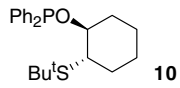
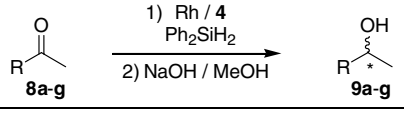


Figure 2. Thioether-phosphinite ligand developed by Evans et al.

We next studied how the steric and electronic properties of the ketone affected the outcome of the reaction. For this purpose, a series of substituted benchmark aryl ketones **8a**–**g** were tested using the catalyst containing ligand **4** at −15 °C. The results are summarized in Table 3. We found that *ortho*-substitution (substrate **8f**) resulted in higher selectivities in the hydrosilylation (entry 6 vs 1), while *para* substitution (substrate **8b**–**d**) gave lower selectivities (entries 2–4 vs 1).[9] As expected when 2-naphthtylmethyl ketone **8g** is used, the enantioselectivity was similar to that seen when acetophenone **8a** was used (entry 1 vs 7).

Table 3. Rh-catalyzed asymmetric hydrosilylation of ketones **8a**–**g** using thioether–phosphinite ligand **4**[a]



Entry	Ketone	R	% Conv.[b]	% ee[c]
1	**8a**	C_6H_5	90	86 (*R*)
2	**8b**	4-F-C_6H_4	72	84 (*R*)
3	**8c**	4-OMe-C_6H_4	98	78 (*R*)
4	**8d**	4-CF_3-C_6H_4	98	72 (*R*)
5	**8e**	3-OMe-C_6H_4	95	87 (*R*)
6	**8f**	2-OMe-C_6H_4	82	90 (*R*)
7	**8g**	2-Naphthyl	85	88 (*R*)

[a] Reaction conditions: **8** (1 mmol), Ph_2SiH_2 (1.1 mmol), **1** (0.011 mmol), **1**/Rh = 1.1, solvent (2 mL), $T = -15$ °C.
[b] Conversion after 1 h determined by GC using undecane as internal standard.
[c] Enantiomeric excess determined by GC.

3. Conclusion

Thioether–phosphinite ligands **1**–**7** bearing substituents with different steric and electronic demands on the sulfur center have been developed and tested in the Rh-catalyzed asymmetric hydrosilylation of aryl ketones. High activities and good enantiomeric excesses (ees up to 90%) were obtained. Our results show that enantiomeric excesses depend strongly on the steric properties of the substituent on the thioether moiety and the steric properties of the substrate. A bulky group on the thioether moiety of the ligand had a positive effect on the enantioselectivity. Enantioselectivities are higher when an *ortho*-substituent in the aryl moiety of the ketone is present.

4. Experimental

4.1. General comments

All syntheses were performed using standard Schlenk techniques under an argon atmosphere. Solvents were purified by standard procedures. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^1H and ^{13}C) as the internal standard or H_3PO_4 (^{31}P) as the external standard. All assignments in NMR spectra were determined by ^1H–^1H and ^{13}C–^1H spectra. Ketones were used as commercially available. Thioether-alcohols[8] and ligands **1**–**3**[7] were prepared according to the literature procedures. Complexes $[Rh(\mu\text{-}Cl)(cod)]_2$[10] and $[Rh(cod)_2]BF_4$[11] were prepared according to the literature procedures.

4.2. Typical procedure for the synthesis of chiral thioether–phosphinite ligands 4–7

A solution of chlorodiphenylphosphine (0.64 mL, 3.5 mmol) in THF (12 mL) was slowly added at 0 °C to a solution of the corresponding thioether-alcohol (3.2 mmol) and DMAP (18.3 mg, 0.15 mmol) in pyridine (3 mL). The reaction mixture was stirred for 90 min at room temperature. Diethyl ether was then added and the pyridium salts then removed by filtration. The residue was purified by flash chromatography (eluent: toluene/Et_3N = 100:1).

4.3. 1,2-*O*-Isopropylidene-3-diphenylphosphinite-5-*tert*-butylsulfanyl-D-xylofuranose 4

Yield: 0.73 g (68%). ^{31}P NMR, δ: 117.3 (s). ^1H NMR ($CDCl_3$), δ: 1.43 (s, 9H, CH_3, *t*Bu), 1.47 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 3.03 (m, 2H, H-5 and H-5′), 4.59 (m, 1H, H-4), 4.70 (dd, 1H, H-3, $^3J_{3\text{-}P} = 12.8$ Hz, $^3J_{3\text{-}4} = 2.8$ Hz), 4.80 (d, 1H, H-2, $^3J_{2\text{-}1} = 4.4$ Hz), 6.15 (d, 1H, H-1, $^3J_{1\text{-}2} = 4.4$ Hz), 7.3–7.8 (m, 10H, CH=). ^{13}C NMR ($CDCl_3$), δ: 26.6 (CH_3 and C-5), 27.1 (CH_3), 31.0 (CH_3, *t*Bu), 42.5 (C, *t*Bu), 80.7 (d, C-4, $^3J_{4\text{-}P} = 6.1$ Hz), 82.8 (d, C-3, $^2J_{3\text{-}P} = 20.1$ Hz), 84.1 (d, C-2, $^3J_{2\text{-}P} = 6.1$ Hz), 105.1 (C-1), 112.1 (CMe_2), 125–142 (aromatic carbons). Anal. Calcd (%) for $C_{24}H_{31}O_4PS$: C, 64.55; H, 7.00; S, 7.18. Found: C, 64.51; H, 6.94; S, 7.24.

4.4. 1,2-*O*-Isopropylidene-3-diphenylphosphinite-5-(4-methylphenyl)sulfanyl-D-xylofuranose 5

Yield: 1 g (75%). ^{31}P NMR, δ: 116.3 (s). ^1H NMR ($CDCl_3$), δ: 1.28 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 2.33 (CH_3-Ph), 3.08 (dd, 1H, H-5, $^3J_{5\text{-}5'} = 12.8$ Hz, $^3J_{5\text{-}4} = 5.6$ Hz), 3.20 (dd, 1H, H-5′, $^3J_{5'\text{-}5} = 12.8$ Hz, $^3J_{5'\text{-}4} = 8.4$ Hz), 4.36 (m, 1H, H-4), 4.56 (dd, 1H, H-3, $^3J_{3\text{-}P} = 9.6$ Hz, $^3J_{3\text{-}4} = 2.8$ Hz), 4.62 (d, 1H, H-2, $^3J_{2\text{-}1} = 3.6$ Hz), 5.96 (d, 1H, H-1, $^3J_{1\text{-}2} = 3.6$ Hz), 7.0–7.6 (m, 14H, CH=). ^{13}C NMR ($CDCl_3$), δ: 21.1 (CH_3-Ph), 26.5 (CH_3), 26.9 (CH_3), 32.3 (C-5), 79.4 (C-4), 82.4 (d, C-3, $^2J_{3\text{-}P} = 19.8$ Hz), 83.9 (C-2), 105.0 (C-1), 112.0 (CMe_2), 125–145 (aromatic carbons). Anal. Calcd (%) for $C_{27}H_{29}O_4PS$: C, 67.48; H, 6.08; S, 6.67. Found: C, 67.51; H, 6.04; S, 6.74.

4.5. 1,2-*O*-Isopropylidene-3-diphenylphosphinite-5-(4-trifluoromethylphenyl)sulfanyl-D-xylofuranose 6

Yield: 0.16 g (17%). ^{31}P NMR, δ: 115.3 (s). ^1H NMR ($CDCl_3$), δ: 1.26 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.09

(dd, 1H, H-5, $^3J_{5\text{-}5'} = 12.8$ Hz, $^3J_{5\text{-}4} = 8.4$ Hz), 3.25 (dd, 1H, H-5′, $^3J_{5'\text{-}5} = 12.8$ Hz, $^3J_{5'\text{-}4} = 6.4$ Hz), 4.37 (m, 1H, H-4), 4.52 (dd, 1H, H-3, $^3J_{3\text{-P}} = 10$ Hz, $^3J_{3\text{-}4} = 2.8$ Hz), 4.61 (d, 1H, H-2, $^3J_{2\text{-}1} = 4$ Hz), 5.96 (d, 1H, H-1, $^3J_{1\text{-}2} = 4$ Hz), 7.1–7.6 (m, 14H, CH=). ^{13}C NMR ($CDCl_3$), δ: 26.5 (CH_3), 27.0 (CH_3), 30.7 (C-5), 79.1 (d, C-4, $^3J_{4\text{-P}} = 6.8$ Hz), 82.7 (d, C-3, $^2J_{3\text{-P}} = 20.6$ Hz), 84.1 (d, C-2, $^3J_{4\text{-P}} = 5.5$ Hz), 105.2 (C-1), 112.4 (CMe_2), 125–132 (aromatic carbons). Anal. Calcd (%) for $C_{27}H_{26}F_3O_4PS$: C, 60.67; H, 4.90; S, 6.00. Found: C, 60.97; H, 4.92; S, 5.98.

4.6. 1,2-*O*-Isopropylidene-3-diphenylphosphinite-5-(2,6-dimethylphenyl)sulfanyl-D-xylofuranose 7

Yield: 0.67 g (68%). ^{31}P NMR, δ: 115.6 (s). ^{1}H NMR ($CDCl_3$), δ: 1.26 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 2.51 (s, 6H, CH_3-Ph), 2.82 (dd, 1H, H-5, $^3J_{5\text{-}5'} = 10.4$ Hz, $^3J_{5\text{-}4} = 6$ Hz), 2.90 (dd, 1H, H-5′, $^3J_{5'\text{-}5} = 10.4$ Hz, $^3J_{5'\text{-}4} = 7.2$ Hz), 4.13 (m, 1H, H-4), 4.46 (dd, 1H, H-3, $^3J_{3\text{-P}} = 9.2$ Hz, $^3J_{3\text{-}4} = 2.4$ Hz), 4.58 (d, 1H, H-2, $^3J_{2\text{-}1} = 3.6$ Hz), 5.91 (d, 1H, H-1, $^3J_{1\text{-}2} = 3.6$ Hz), 7.0–7.5 (m, 13H, CH=). ^{13}C NMR ($CDCl_3$), δ: 22.1 (CH_3-Ph), 26.5 (CH_3), 26.7 (CH_3), 33.0 (C-5), 79.8 (d, C-4, $^3J_{4\text{-P}} = 6.1$ Hz), 82.4 (d, C-3, $^2J_{3\text{-P}} = 18.3$ Hz), 83.9 (C-2), 104.9 (C-1), 111.9 (CMe_2), 125–144 (aromatic carbons). Anal. Calcd (%) for $C_{28}H_{31}O_4PS$: C, 68.00; H, 6.32; S, 6.48. Found: C, 67.97; H, 6.34; S, 6.53.

4.7. General procedure for asymmetric hydrosilylation reactions

To a solution of the desired catalyst precursor (0.01 mmol Rh) in the corresponding solvent (2 mL), the ligand (0.011 mmol) was added. The mixture was stirred for 30 min. Ketone (1 mmol), Ph_2SiH_2 (1.1 mmol) and undecane as the GC internal standard (0.1 mL) were then added. After the desired reaction time, the reaction mixture was quenched with methanol (7 mL) and 2.5 M aqueous NaOH (5 mL). The mixture was extracted with diethyl ether (3×5 mL), the combined ether phases were dried over Na_2SO_4 and filtered. The conversion and enantiomeric excesses were determined by GC.

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