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Chiral diphenylthiophosphoramides: a new class of chiral ligands for the silver(I)-promoted enantioselective allylation of aldehydes

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Abstract

Chiral C_2-symmetric diphenylthiophosphoramides **1** and **2** were prepared in high yields from the reaction of diphenylthiophosphinic chloride with (1*R*,2*R*)-(−)-1,2-diaminocyclohexane and (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine, respectively. Another novel chiral ligand **4** was prepared from reaction of diphenylthiophosphinic chloride with (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine using butyllithium as a base. They were used as catalytic chiral ligands in the silver(I)-promoted enantioselective allylation reaction of aldehydes with allyltributyltin. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Catalytic asymmetric synthesis is a valuable method for the preparation of optically active substances.[1] In this context, the stereoselective addition of organometallics to one of the two heterotopic faces of a carbonyl group has been extensively studied. In particular, the enantioselective allylation of carbonyl compounds is a challenging problem in organic synthesis. Although numerous important examples of the reaction using a stoichiomeric amount of chiral Lewis acids have been reported,[2] there are only a few methods available for a catalytic process including chiral (acyloxy)borane (CAB) complex/allylic silanes[3] or allylic stannanes[4] and binaphthol-derived chiral titanium complexes/allylic stannanes.[5] Recently Yamamoto reported a new catalytic enantioselective allylation reaction of aldehydes with allyltributyltin using a BINAP·silver(I) complex as a catalyst.[6] To the best of our knowledge, this is the only case using a chiral silver(I) complex in a catalytic asymmetric reaction. This interesting result prompted us to design and synthesize other chiral ligands which are suitable for making chiral silver(I) complexes for catalytic asymmetric reactions. We wanted to try some chiral ligands containing

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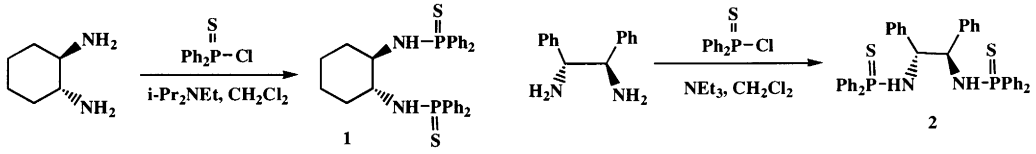
a sulfur atom because it is well known that sulfur can easily coordinate to various metals such as Co, Cu and Zn giving stable chiral metal complexes.[7] Based on this concept, we started to prepare the chiral C_2-symmetric diphenylthiophosphoramides **1** and **2** from (1*R*,2*R*)-(−)-1,2-diaminocyclohexane and (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine, respectively. Moreover, using (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine as a chiral scaffold we also prepared a novel chiral ligand **4**. In this paper, we wish to report the results using them as catalytic chiral ligands for silver(I)-promoted enantioselective allylation reaction of various aldehydes with allyltributyltin.

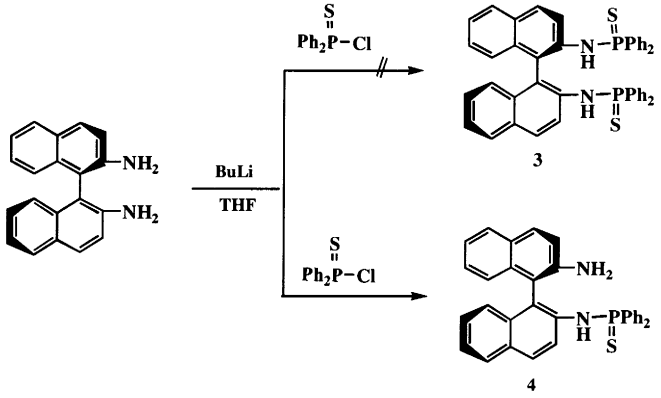
2. Results and discussion

Diphenylthiophosphoramides **1** and **2** were synthesized from the reaction of diphenylthiophosphinic chloride with (1*R*,2*R*)-(−)-1,2-diaminocyclohexane and (1*S*,2*S*)-(−)-1,2-diphenylethylenediamine, respectively, in the presence of diisopropylethylamine in dichloromethane (Scheme 1). After usual workup and purification by silica gel column chromatography or recrystallization, compounds **1** and **2** were obtained as colorless solids in over 90% yield.[8] In addition, using C_2-symmetric (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine as a chiral scaffold, we tried to synthesize the novel chiral ligand **3**. No reaction took place between (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine and diphenylthiophosphinic chloride using diisopropylethylamine or triethylamine as a base in dichloromethane. Thus, we selected butyllithium as a base to prepare the corresponding lithium amide and then react with diphenylthiophosphinic chloride (Scheme 2). This synthetic method was used for the preparation of (*R*)-2,2′-bis(diphenylphosphinamino)-1,1′-binaphthyl.[9] But surprisingly we found that the compound **4** was formed as the only product (Scheme 2). Namely, only one diphenylthiophosphinyl group could be introduced into the 1,1′-binaphthyl-2,2′-diamine chiral scaffold. This may be due to the steric hindrance of the diphenylthiophosphinyl group. Their structures were confirmed by spectral data and microanalysis. Moreover, the structures of **2** and **4** were established by X-ray analysis (Figs. 1 and 2).[10] Interestingly, one dichloromethane molecule was included into the crystal lattice of **2** during the recrystallization from dichloromethane.[10] Those chiral ligands were used for the silver(I)-promoted enantioselective allylation reaction of aldehydes with allyltributyltin. The ees of the products were determined by HPLC analysis using a chiral stationary-phase column (Chiralcel OD and OJ) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation. Of silver(I) salts, silver(I) triflate is a good catalyst for allylation of aldehydes, but the reaction is sluggish using $AgNO_3$ and $AgBF_4$. Utilizing **1** and **2** as chiral ligands, the ees of *sec*-alcohol are very low in THF or dichloromethane. The results are shown in Table 1. By means of the novel chiral ligand **4**, the ee can reach 52% in THF and 50% in dichloromethane at −20°C. In DMF, obviously the silver(I) complex decomposed with the precipitation of black solid. In addition, if the reaction was carried out below −20°C, the reaction proceeded very slowly. The best result is shown in Table 1, entry 4. By means of these optimized reaction conditions, various aldehydes were used as substrates for this addition reaction and the corresponding *sec*-alcohol could be obtained in 65–85% yield and 54–63% ee with *R*-configuration. These results are summarized in Table 2. It should be emphasized that the chiral phosphoramide ligands **1**, **2** and **4** could be recovered from the reaction mixture in 90% yield after usual workup and can be used again in the asymmetric reaction without loss of enantioselectivity. Thus, the chiral phosphoramides **1**, **2** and **4** are quite stable chiral ligands. For chiral ligands **1** and **2**, as expected the phosphoryl sulfur atoms can coordinate to the silver(I) metal center to some extent giving a chiral environment, although the achieved ee is low. We also found that this allylation reaction takes place only when the heteroatom on the phosphorus atom is sulfur; if it is an oxygen or selenium atom no reaction occurs. This result strongly suggests that the coordination between

the sulfur atom and silver(I) metal plays an important role in this reaction. Thus, we believe that chiral ligand **4** is a bidentate chiral ligand, namely, the nitrogen and phosphoryl sulfur atoms can coordinate to the silver(I) metal affording a chiral silver(I) Lewis acid. In order to verify this speculation, we attempted to obtain a single crystal of the catalyst to confirm its structure. But despite extensive efforts, we could not obtain a single crystal of chiral silver(I) complex which could be subjected to X-ray crystal analysis.



Scheme 1.



Scheme 2.

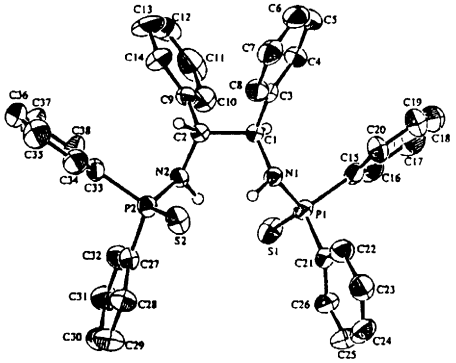


Fig. 1. The crystal structure of **2**

In conclusion, the chiral bidentate phosphoramide **4** prepared from C_2-symmetric (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine was found to be a new class of relatively effective chiral ligands for the silver(I)-promoted enantioselective allylation reaction of aldehydes with allyltributyltin, although they are not as effective as BINAP·silver(I) complex.[6] This paper, for the first time, discloses that chiral phosphoryl sulfide can catalyze the enantioselective allylation reaction using silver(I) salt. These results open a new way to design and synthesize new chiral ligands for asymmetric reactions. Efforts are underway to elucidate the mechanistic details of this addition reaction and to disclose the exact structure of the active species. Moreover, we are planning to synthesize similar bidentate chiral phosphoramides embedded into a C_2-symmetric chiral scaffold in order to find more effective and stereoselective chiral ligands and to utilize these novel chiral ligands with regard to other catalytic asymmetric reactions.

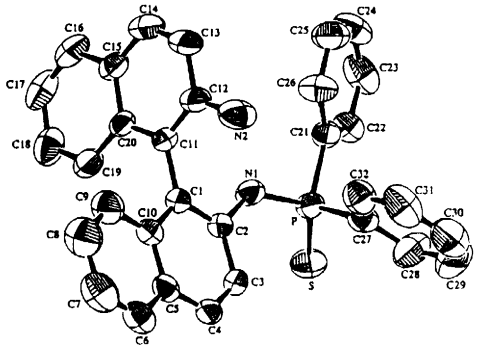
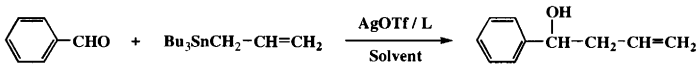


Fig. 2. The crystal structure of **4**

Table 1
Enantioselective allylation reaction of benzaldehyde in the presence of chiral ligands **1**, **2**, **4** and silver(I) triflate under different reaction conditions



Entry	Ligand	Solvent	Temp. [°C]	Time [h]	Yield[a] [%]	ee[b] [%]	Config.
1	1	THF	-20	48	68	9	R
2	2	THF	-20	48	70	15	R
3	2	CH_2Cl_2	-20	48	40	12	R
4	4	THF	-20	48	70	52	R
5	4	CH_2Cl_2	-20	48	30	50	R
6	4	DMF	-20	48	-	-	

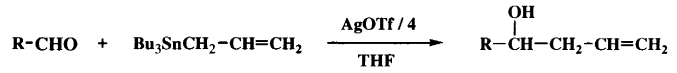
[a] Isolated yields. [b] Determined by chiral HPLC.

3. Experimental

3.1. General

Melting points were obtained with a Yanagimoto micro melting point apparatus and remain uncorrected. Optical rotations were determined in a solution of $CHCl_3$ at 20°C using a Perkin–Elmer 241 MC polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J* values are given in hertz. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured using a Finnigan MA+ mass spectrometer. The organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses with an Italian Carlo–Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai $60F_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. All allylation experiments were performed under argon using standard Schlenk techniques. The enantiomeric excesses of *sec*-alcohols were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. Chiralcel OD and OJ; eluent, 100:0.5 2 hexane:2-propanol mixture;

Table 2
Enantioselective allylation reaction of aldehyde in the presence of chiral ligand **4** and silver(I) triflate under different reaction conditions



R	Temp. [°C]	Time [h]	Yield[a] [%]	ee[b] [%]	Config.[c]
p-ClPh	-20	48	72	54	R
p-MePh	-20	48	70	60	R
p-MeOPh	-20	48	65	62	R
1-Naphthyl	-20	48	80	63	R
Ph-CH=CH-	-20	48	84	55	R
n-C_4H_9	-20	48	82	58	R

[a] Isolated yield. [b] Determined by chiral HPLC. [c] Determined by the sign of the specific rotation.

flow rate, 1.0 ml min^{-1}; detection, 254 nm light) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation. The preparation of chiral ligand **1** has been reported previously.[8]

3.2. Preparation of chiral phosphoramide *2*

To a solution of (1*S*,2*S*)-(−)-1,2-diphenylethylenediamine (214 mg, 1.0 mmol) and triethylamine (300 mg, 3.0 mmol, 0.42 ml) in dichloromethane (20 ml) was added diphenylthiophosphinic chloride (504 mg, 2.0 mmol) at 0°C. After stirring of the reaction mixture for 10 h, the solvent was removed under reduced pressure. The crude product was extracted with ether and washed with water (3×50 ml), 10% Na_2CO_3 (50 ml) and brine. The organic layer was dried over anhydrous Na_2SO_4 and then evaporated under reduced pressure. The residue was recrystallized from dichloromethane and hexane (4:1) to give **2** as colorless crystals (680 mg, 95%). Mp 178–180°C (dec.); $[\alpha]_D$ −63.4 (c 1.16, $CHCl_3$); δ_H ($CDCl_3$) 4.40–4.65 (2H, m, CH), 5.56–5.76 (2H, m, NH), 6.80–6.95 (4H, dd, *J* 7.4, 1.3 Hz, Ar), 7.0–7.20 (8H, m, Ar), 7.24–7.50 (10H, m, Ar), 7.55–7.75 (4H, m, Ar), 7.75–8.0 (4H, m, Ar); MS (EI) *m/z* (%) 645 (MH^+, 10.3), 322 (100), 290 (4.7), 217 (97.7), 139 (46.4); [found: C, 64.17; H, 4.90; N, 3.80%. HRMS (EI) *m/z* 644.1628 (M^+); $C_{38}H_{34}N_2S_2P_2 \cdot CH_2Cl_2$ requires: C, 64.19; H, 4.97; N, 3.84%; M, 644.1639].

3.3. Preparation of chiral thiophosphoramide *4*

To a solution of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (148 mg, 0.5 mmol) in THF (10 ml) was added dropwise 2.0 M *n*-butyllithium in cyclohexane (0.70 ml, 1.4 mmol) at −40°C over 40 min and the reaction mixture was stirred for 1 h. Then diphenylthiophosphinic chloride (440 mg, 1.8 mmol, 0.344 ml) was added dropwise and the reaction solution was stirred for a further 10 h at −40°C to room temperature. The mixture was filtered to remove the solid and the THF was removed under reduced pressure. The organic product was extracted with ether and the organic layer was washed with water, 10% Na_2CO_3 and brine. The extract was dried over $MgSO_4$ and then evaporated under reduced pressure. The residue was

purified by alumina (Al_2O_3) column chromatography to give the compound **4** as a colorless solid (264 mg, 97%). Mp 80–81°C (dec.); $[\alpha]_D$ −4.4 (c 1.20, $CHCl_3$); δ_H ($CDCl_3$) 4.10 (2H, s, br., NH_2), 5.12 (1H, d, *J* 7.4 Hz), 7.0–7.50 (10H, m, Ar), 7.50–7.70 (4H, m, Ar), 7.70–8.0 (8H, m, Ar); MS (EI) *m/z* (%) 500 (M^+, 3.6), 559 (0.6), 467 (100), 371 (0.7); [found: C, 76.65; H, 5.07; N, 5.74%. HRMS (EI) *m/z* 500.1458 (M^+). $C_{32}H_{25}N_2PS$ requires: C, 76.78; H, 5.03; N, 5.60%; M, 500.1467].

3.4. Typical reaction procedure

To a solution of phosphoramide **4** (50.0 mg, 0.1 mmol) and AgOTf (25.7 mg, 0.1 mmol) in THF (2 ml) was added benzaldehyde (53 mg, 0.5 mmol, 50 μl) at room temperature. After stirring the reaction mixture for 0.5 h, allyltributyltin (199 mg, 0.6 mmol, 186 μl) was added into the reaction solution at −20°C and the reaction mixture was stirred at −20°C for 8 h. The reaction was quenched by a mixture of 15% aq. HCl (5 ml) and solid KF (1 g) at ambient temperature for 30 min. The resulting precipitate was filtered off, and the filtrate was dried over $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the homoallylic alcohol as a colorless oil (52 mg, 70%).

Acknowledgements

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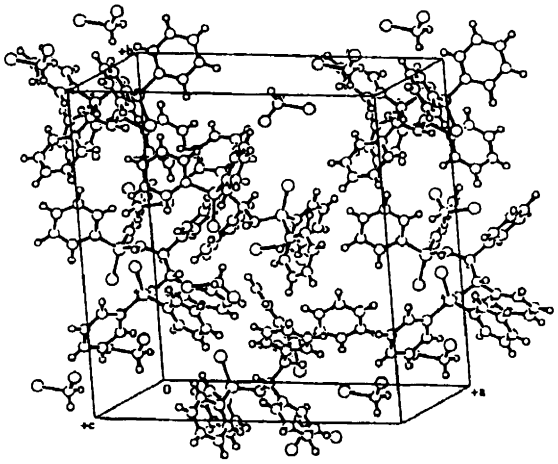
10. (a) The crystal data of **2**. Empirical formula: $C_{39}H_{36}N_2S_2P_2Cl_2$; formula weight: 729.70; crystal color, habit: colorless, prismatic; crystal dimensions: 0.20×0.20×0.30 mm; crystal system: orthorhombic; lattice type: primitive; lattice parameters: a=19.715(2) Å, b=20.071(2) Å, c=9.453(1) Å, V=3740.6(7) Å^3; Space group: $P2_12_12_1$(#19); Z value=4; D_{calcd}=1.296 g cm^{-3}; F_{000}=1520.00; μ(MoKα)=4.01 cm^{-1}; diffractometer: Rigaku AFC7R; temperature: 20°C; scan type: ω-2θ.



(b) The crystal data of **4**. Empirical formula: $C_{32}H_{25}N_2SP$; formula weight: 500.60; crystal color, habit: colorless, prismatic; crystal dimensions: 0.20×0.20×0.30 mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: a=9.267(4) Å, b=14.554(3) Å, c=10.404(2) Å, β=113.04(3)°, V=1291.2(9) Å^3; space group: $P2_1$(#4); Z value=2; D_{calcd}=1.288 g cm^{-3}; F_{000}=524.00; μ(MoKα)=2.11 cm^{-1}; diffractometer: Rigaku AFC7R; temperature: 20°C; scan type: ω-2θ.