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Easily accessible chiral amino-phosphinite ligands for highly enantioselective palladium-mediated allylic alkylation

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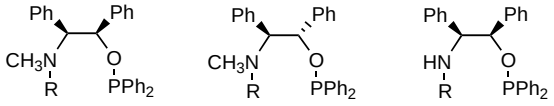
Abstract—Palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with the dimethyl malonate–BSA–LiOAc system has been successfully carried out in the presence of easily prepared new chiral amino-phosphinite ligands such as **3b** and **3c** to result in good yields and excellent enantioselectivities of up to 95% e.e. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Palladium-catalyzed allylic alkylation is known as a very useful synthetic method for the formation of carbon–carbon bonds.[1,2] The selection of chiral ligands for highly enantioselective allylic substitution has focused on the use of mixed bidentate donor ligands such as phosphorus–nitrogen[2] or sulfur–nitrogen,[3] and phosphorus–sulfur,[4] which have shown excellent levels of stereochemical control. Most of these chiral bidentate ligands were equipped with strong and weak donor heteroatom pairs (e.g. PR_3/NR_3 or PR_3/SR_2). The electronic effects have the potential to influence both the stability and reactivity of the intervening diastereomeric reaction intermediates in the catalytic cycle. Bidentate aminophosphine ligands of this type have been applied in the enantioselective palladium-catalyzed nucleophilic alkylation of allylic esters, and shown similar stereocontrol properties to phosphine-oxazolines.[5] Generally, palladium complexes of mixed donor ligands with six-membered rings deliver higher enantioselectivity than those with five-membered rings.[6] Upon coordination chiral amino-phosphinite ligands **1**–**3** would form six-membered ring complexes with palladium, thus it was thought that they could induce high enantioselectivity in the allylic alkylation reaction. To the best of our knowledge, only a few examples of phosphinite-amine type ligands have been successfully involved in this area.[7] Herein we would like to describe the application of phosphinite-amines **1**–**3** as chiral ligands in palladium-catalyzed asymmetric allylic alkylation reactions (Fig. 1).

2. Results and discussion

N,*N*-Dialkyl-1,2-diphenyl-2-aminoethanols, derived from (1*R*,2*S*)- and (1*S*,2*S*)-1,2-diphenyl-2-aminoethanol, have exhibited powerful enantioselective control properties in many reactions, and have been proven to be good chirality sources for the derivation of new chiral ligands.[8] The amino-phosphinites **1**–**3** were synthesized by reaction of the corresponding *N*,*N*-dialkyl-1, 2-diphenyl-2-aminoethanols and *N*-alkyl-1,2-diphenyl-2-aminoethanols with 1 equiv. of chlorodiphenylphosphine in the presence of Et_3N and



1a. R =Me
1b. R = Et,
1c. R = i-Pr,
1d. R = Bn

2. R =Bn

3a. R= Bn
3b. R= n-Bu
3c. R= ^{i}Pr

Figure 1. Chiral ligands studied in the titled reaction.

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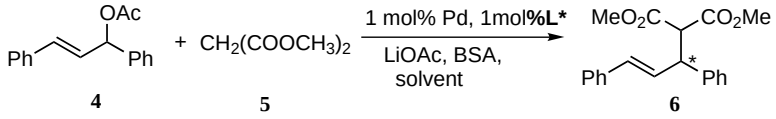
catalytic DMAP in toluene followed by filtration through a plug of Al_2O_3 to remove the catalyst and triethylamine hydrochloride.[9] The free amine groups in **3a**–**c** were unreactive toward further phosphinylation due to the bulky R group.

The efficiency of *N*,*N*-disubstituted amino phosphinites **1a**–**d** and **2** was first investigated using the standard procedure for the palladium-catalyzed substitution of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate. The acetate **4** was reacted with the nucleophile in situ generated from dimethyl malonate (3 equiv.) and *N*,*O*-bis(trimethylsilyl)acetamide (BSA, 3 equiv.) in the presence of 1 mol% catalyst, which was formed in situ from allyl palladium chloride dimer with two molar equivalents of the chiral ligands in the reaction solvent for 20 min at room temperature. The results are summarized in Table 1. The enantioselectivity was strongly dependent on the nitrogen substituent: maintaining a methyl group bonded to nitrogen while changing the other nitrogen substituent in substrates **1a** and **1c**–**e** led to a pronounced trend that increasing steric hindrance from the *N*-substituent resulted in a decrease in the ratio of the major (*R*)-enantiomeric products. Thus, changing the *N*-R group from Me (**1a**) to Et (**1b**), ^{i}Pr (**1c**) and Bn (**1d**) led to a change in the e.e. values from (*R*)-enantioenrichments of 46 and 40% with ligands **1a** and **1b**, to (*S*)-enantioenrichments of 8%, 22% e.e. with ligands **1c** and **1d**, respectively. Thus, the configuration of the major product could be inverted simply by changing the second nitrogen substituent of the ligand. The ligands (1*R*,2*S*)-**1d** and (1*S*,2*S*)-**2** showed comparable enantioselectivities and gave similar enantiomer-rich products (entries 4 and 5), which indicates that the chirality of the carbon bonded to nitrogen plays an important role in the stereochemical discrimination. This result is consistent with the findings for palladium complexes in traditional *P*,*N*-ligand-catalyzed allylic alkylation.[5]



4 **5** **6**

The dramatic substituent effects on the stereochemical outcome prompted us to fine tune the structure of the ligands for the allylic alkylation reaction. It is encouraging that the enantioselectivity of the allylic alkylation was dramatically improved to 87% e.e. when **3a** (Table 2, entry 1) was used as a chiral ligand from the 22% e.e. achieved with the *N*-methylated analogue **1d** (Table 1, entry 4). This result implies that *N*-monosubstituted amino-phosphinites might give better enantioselectivity than *N*,*N*-disubstituted ones. As the best chiral ligands could be found by screening the nitrogen substituent on the ligands, the *N*-butyl and *N*-isopropyl analogues **3b**

Table 1. Allylic alkylation of **4** with dimethyl malonate catalyzed by the complexes of $[Pd(allyl)Cl]_2$ with *N*,*N*-disubstituent amino-phosphinites

Entry	Ligand	Temp. (°C)	Time (h)	Yield[a] (%)	E.e.[b] (%)	Config.[c]
1	**1a**	25	6	95	46	*R*
2	**1b**	25	10	98	40	*R*
3	**1c**	25	10	98	8	*S*
4	**1d**	25	10	98	22	*S*
5	**2**	30	5	90	28	*S*

[a] Isolated yield.
[b] Measured by HPLC (chiral OD, *n*-hexane:isopropanol = 99:1).
[c] The absolute configuration was determined by comparing the specific rotation with the literature value.[5c]

Table 2. Allylic alkylation of **4** with dimethyl malonate catalyzed by palladium complexes of *N*-monosubstituent amino-phosphinites

Entry	Palladium	Ligand	Solvent	Temp. (°C)	Time (h)	Yield[a] (%)	E.e.[b] (%)
1	$[Pd(allyl)Cl]_2$	**3a**	Toluene	20	12	88	87
2	$[Pd(allyl)Cl]_2$	**3b**	Toluene	30	6	98	73
3	$[Pd(allyl)Cl]_2$	**3c**	Toluene	20	10	98	91
4	$Pd(dba)_2$	**3b**	Toluene	30	3	98	53
5	$[Pd(allyl)Cl]_2$	**3b**	CH_2Cl_2	25	15	47	82
6	$[Pd(allyl)Cl]_2$	**3b**	Toluene	0	24	96	75
7	$[Pd(allyl)Cl]_2$	**3b**	Toluene	−20	36	90	84
8	**$[Pd(allyl)Cl]_2$**	**3b**	**Toluene**	**−78**	**72**	**84**	**95**
9	$[Pd(allyl)Cl]_2$	**3c**	Toluene	0	36	88	93
10	**$[Pd(allyl)Cl]_2$**	**3c**	**Toluene**	**−20**	**48**	**75**	**95**

[a] Isolated yield.
[b] Measured by HPLC (chiral OD, *n*-hexane:isopropanol = 99:1), and the absolute configuration is *R*.

and **3c** were prepared. Both of these ligands provided high enantioselectvities of 73% (entry 2) and 91% e.e. (entry 3), respectively. A further improvement in the enantioselectivity was realized by lowering the reaction temperature. When the reaction was run at −78°C, **3b** gave 84% yield and 95% e.e. (entry 8). The same enantioselectivity of 95% e.e. was provided using ligand **3c** at −20°C (entry 10). These results demonstrated that the amine proton in the ligand plays a dominant role in the enantioselection. The reason that the *N*-monosubstituted amino-phosphinite ligands induced better enantioselectivity is not really clear. We propose that such a phenomenon probably results from the second interaction between the N–H proton in the ligand (for example, in **3c**) and the nucleophile.[10]

3. Conclusion

In summary, we have investigated the applications of *N*,*N*-disubstituted and *N*-monosubstituted amino phosphinites, which were readily derived from (1*R*,2*S*)- and (1*S*,2*S*)-1,2-diphenyl-2-aminoethanol, in the palladium-catalyzed allylic alkylation with excellent enantioselectivities of up to 95% e.e. The results show that *N*-monosubstituted amino phosphinites had better asymmetric induction properties than the *N*,*N*-disubstituted ones. For *N*,*N*-disubstituted amino phosphinite **1**, the configuration of the product could be reversed by variation of the substituent bonded to the nitrogen of the ligands. Investigations into the uses of such facile chiral ligands for other asymmetric transformations are now in progress.

4. Experimental

4.1. General

Palladium complexes are gifts from Professor Yoshinori Yamamoto at Tohuku University in Japan. Melting points were measured on a digital melting point apparatus and were uncorrected. Mass spectra were recorded on Finnigan LCQ DECA instrument. IR spectra were obtained on a Nicolet 200SXV spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-E 300 and Bruker AC-E 400 instrument. ^{31}P NMR spectra were recorded on Bruker AC-E 400. The e.e. was determined by HPLC on a Beckman-110A chromatography with a Beckman 165 variable wavelength detector. The Chiralcel OD column was purchased from Daicel Chemical Industries Ltd. Optical rotations were recorded on a Perkin–Elmer 341 polarimeter. Toluene was distilled from sodium under a nitrogen atmosphere.

4.2. *N*-Alkyl-1,2-diphenyl-2-aminoethanols

N-Alkyl-1,2-diphenyl-2-aminoethanols were prepared according to the literature method.[11]

4.3. *N*-Methyl-*N*-alkyl-1,2-diphenyl-2-aminoethanols

A typical procedure for the preparation of *N*-methyl-*N*-alkyl-1,2-diphenyl-2-aminoethanols is as follows: the 1,2-diphenyl-2-aminoethanol (1.3 mmol) was treated with the corresponding aldehyde or ketone (1.5 mmol) in anhydrous ethanol (5 mL) for 3 h at room temperature, followed by reduction with $NaBH_4$ (0.1 g, 2 mmol). The mixture was stirred for 1 h and adjusted to pH 1 with aqueous HCl (2N). After removal of the solvent, the residue was dissolved in water (5 mL) and basified with aqueous NaOH (2N) to pH 10, the aqueous layer was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent gave *N*-alkyl-aminoethanol, which was stirred with formic acid (5 mL) for 0.5 h and then treated with formaldehyde (5 mL) and heated under reflux for about 8 h. The excess formaldehyde was removed. The residue was cooled to room temperature, water (10 mL) was added and the mixture was basified to pH 10 and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. Removal of the solvent yielded a white solid, which was recrystallized from petroleum ether (60–90°C) to give the desired products.

4.4. *N*,*N*-Dialkyl-*O*-diphenylphosphino-1,2-diphenyl-2-aminoethanol

To a solution of *N*,*N*-dialkyl-1,2-diphenyl-2-aminoethanol or *N*-alkyl-1,2-diphenyl-2-aminoethanol (0.5 mmol), a catalytic amount of DMAP (10 mg) in dry toluene (5 mL) under nitrogen was added chlorodiphenylphosphine (0.5 mmol). After stirring at room temperature for 24 h, the resulting mixture was filtered, concentrated and purified by chromatography (toluene as eluent) to afford the products.

Compound 1a: White powder, yield: 87%, mp 116–117°C. $[\alpha]_D^{20}=-14.5$ ($c=0.2$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.14 (s, 6H), 3.68 (d, $J=7.6$ Hz, 1H), 5.37 (t, $J=8.0$ Hz, 1H), 7.08–7.29 (m, 20 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 42.69, 75.89 (d, $J=7.5$ Hz), 82.36 (d, $J=20.0$ Hz), 127.00, 127.39, 127.55, 127.60, 127.67, 127.75, 127.77, 127.83, 128.64, 128.79, 130.11, 130.26, 130.47, 130.57, 130.79. ^{31}P NMR ($CDCl_3$): δ (ppm) 112.03.

Compound 1b: Yield: 75%, $[\alpha]_D^{20}=+38.7$ ($c=0.7$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.14 (d, $J=$ Hz, 3H), 2.22 (m, 5H), 2.94 (m, 1H), 4.99 (q, $J=8.8$ Hz, 5.2 Hz, 1H), 7.23–7.61 (m, 18H), 7.60–7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 9.28, 41.47, 65.38, 83.68 (d, 18.2 Hz), 127.12, 127.28, 127.92, 128.10, 128.16, 128.76, 129.29, 130.29, 130.51, 131.07, 131.29. ^{31}P NMR ($CDCl_3$): δ (ppm) 110.08.

Compound 1c: Viscous oil, yield: 87%, $[\alpha]_D^{20}=-39.2$ ($c=0.36$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.76 (d, $J=6.4$ Hz, 3H), 0.91 (d, $J=6.4$ Hz, 3H), 2.22 (s, 3H), 2.36 (q, $J=9.2$ Hz, 1H), 2.98 (m, 1H), 3.87 (d, $J=5.6$ Hz, 3H), 5.47 (q, $J=6.0$ Hz, 8.8 Hz, 1H), 6.99–7.40 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 17.30, 19.22, 32.00, 50.53, 73.63 (d, $J=6.8$ Hz),

82.42 (d, $J=20.5$ Hz), 126.76, 127.07, 127.28, 127.54, 127.82, 128.61, 128.90, 130.28, 130.76, 130.99, 131.61. ^{31}P NMR ($CDCl_3$): δ (ppm) 111.60.

Compound 1d: Viscous oil, yield: 84%, $[\alpha]_D^{20}=+3.0$ ($c=3.1$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.28 (s, 3H), 3.22 (d, $J=13.6$ Hz, 1H), 3.52 (d, $J=13.2$ Hz, 1H), 4.01 (d, $J=9.2$ Hz, 1H), 5.45 (t, $J=8.8$ Hz, 1H), 6.84–7.39 (m, 25H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 38.10, 59.00, 72.84 (d, $J=7.7$ Hz), 82.78 (d, $J=20.0$ Hz), 126.59, 127.10, 127.61, 127.72, 127.93, 127.99, 128.54, 128.83, 129.96, 130.19, 130.40, 130.64, 130.87. ^{31}P NMR ($CDCl_3$): δ (ppm) 110.92.

Compound 2: Viscous oil, yield: 94%, $[\alpha]_D^{20}=-24.9$ ($c=0.86$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.27 (s, 3H), 3.50 (d, $J=13.2$, 1H), 3.79 (d, $J=5.6$ Hz, 1H), 4.27 (dd, $J=5.2$ Hz, 4.0 Hz, 1H), 5.45 (m, 1H), 7.00–7.38 (m, 25H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 37.26, 59.70, 73.05 (d, $J=5.5$ Hz), 81.85 (d, $J=19.5$ Hz), 125.25, 125.97, 126.59, 126.85, 127.39, 127.61, 127.78, 127.84, 127.99, 128.10, 128.18, 128.63, 128.88, 129.04, 129.77, 130.16, 130.38, 130.80, 131.02. ^{31}P NMR ($CDCl_3$): δ (ppm) 110.62.

Compound 3a: Viscous oil, yield: 91%, $[\alpha]_{20}=-20.7$ ($c=3.8$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.35 (d, $J=13.6$ Hz, 1H), 3.58 (d, $J=13.8$ Hz, 1H), 4.01 (d, $J=6.8$ Hz, 1H), 4.92 (t, $J=7.6$ Hz, 1H), 6.99–7.32 (m, 25H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 50.79, 67.61 (d, $J=5.9$ Hz), 86.16 (d, $J=19.5$ Hz), 126.61, 127.32, 127.83, 127.92, 127.99, 128.11, 128.80, 128.96, 130.41, 130.47, 130.69, 130.82. ^{31}P NMR ($CDCl_3$): δ (ppm) 110.63.

Compound 3b: Viscous oil, yield: 79%, $[\alpha]_D^{20}=-37.0$ ($c=1.94$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.74 (t, $J=7.2$ Hz, 3H), 1.04 (m, 2H), 1.26 (m, 2H), 2.26 (m, 2H), 3.95 (d, $J=6.8$ Hz, 1H), 4.92 (dd, $J=6.8$ Hz, 2.4 Hz, 1H), 7.09–7.29 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.82, 20.08, 31.87, 46.93, 68.93 (d, $J=6.7$ Hz), 86.07 (d, $J=19.1$ Hz), 127.13, 127.74, 127.85, 127.91, 127.98, 128.08, 128.75, 128.82, 129.07, 130.11, 130.33, 130.60, 130.82. ^{31}P NMR ($CDCl_3$): δ (ppm) 110.63.

Compound 3c: Viscous oil, yield: 89%, $[\alpha]_D^{20}=-13.9$ ($c=0.6$, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.25 (s, 3H), 1.56 (s, 3H), 2.46 (d, $J=6.0$ Hz, 1H), 4.42 (dt, $J=6.0$ Hz, 2.8 Hz, 1H), 4.92 (dd, $J=5.6$ Hz, 4.0 Hz, 1H), 6.94–7.30 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.60, 24.03, 51.06, 66.18 (d, $J=6.4$ Hz), 86.30 (d, $J=19.6$ Hz), 127.19, 127.80, 127.87, 127.99, 128.05, 128.22, 128.86, 129.10, 129.35, 130.18, 130.40, 130.93, 131.16. ^{31}P NMR ($CDCl_3$): δ (ppm) 110.62.

4.5. Typical procedure for asymmetric allylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate

To an oven dried Schlenk flask charged with [Pd(allyl)Cl]$_2$ (3.8 mg, 0.01 mmol) was added a solution of chiral ligand **3c** (0.02 mmol) in toluene (4 mL), the mixture was stirred at room temperature for about 20 min. 1,3-Diphenyl-2-allyl acetate (160 mg, 0.6 mmol), dimethyl malonate (0.21 mL, 1.8 mmol), BSA (0.44 mL, 1.8 mmol) and LiOAc (5.0 mg, 0.072 mmol) were added sequentially. After stirring the mixture at room temperature for about 10 h (monitored by TLC), the mixture was filtered and the filtrate was concentrated and purified by chromatography (petroleum:ethyl acetate, 8:1) to give the desired product (188 mg).

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