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Application of phosphinous amide ligands in palladium complex-catalyzed asymmetric allylic alkylation: influence of steric effects on enantioselectivity

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Abstract—Phosphinous amide ligands **1**–**4** derived from 2,2′-diamino-1,1′-binaphthyl (BINAM) and 2,2′-diamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (H_8-BINAM) have been prepared and applied in palladium complex-catalyzed asymmetric allylic alkylations. The alkylations of racemic 1,3-diphenyl-2-propenyl acetate with malonate, α-substituted malonates or acetylacetone catalyzed by the palladium complexes bearing these ligands gave products in up to 96% ee.

1. Introduction

Chiral ligands bearing a 1,1′-binaphthyl backbone have been successfully applied in a variety of asymmetric reactions.[1] The highly skewed position of the naphthyl rings in the binaphthyl backbone is believed to be the determining factor for the ligands to be effective in asymmetric catalytic reactions,[2] and different dihedral angles of the axial biaryl in the backbone might consequently give better enantioselectivity of a catalyst.[3]

The dihedral angle of the axial biaryl in the binaphthyl-type chiral catalysts can either be adjusted by partially hydrogenating the naphthyl rings to H_8-naphthyls,[4] or by the introduction of bulky groups onto the binaphthyl ring adjacent of the hydroxyl group in the binaphthol molecule,[5] or by introducing bulky groups into the diaryl phosphino group.[6] Herein we report the effect of steric hindrance on the enantioselectivity of asymmetric allylic alkylation reactions catalyzed by phosphinous amide–palladium catalysts.

Allylic substitution has become one of the most important C–C bond formation reactions since its first discovery in 1965;[7] and palladium catalyzed asymmetric allylic substitution has been actively studied due to its potential application in asymmetric C–C bond formations.[8–10] Oxazoline type ligands,[11] ferrocene type ligands,[12] Trost's ligands,[13] and several other ligands[14] have shown excellent enantioselectivities in palladium-catalyzed asymmetric allylic substitutions and several applications to natural product synthesis have been reported by Trost et al.[15] On the other hand, readily available phosphinous amide ligands have not been well applied in this type of reaction. Spilling et al. prepared a series of phosphinous amide ligands derived from 1,2-cyclohexanediamine, and obtained moderate ee's in applying these ligands in asymmetric allylic substitution.[16] In this study we found the asymmetric allylic alkylation catalyzed by palladium complexes containing phosphinous amide ligands **1**–**4** derived from 2,2′-diamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl and 2,2′-diamino-1,1′-binaphthyl to be facile.

2. Results and discussion

Phosphinous amide ligand 2,2′-bis(diphenylphosphinoamino)-1,1′-binaphthyl (BDPAB) has been used in

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the asymmetric hydrogenation of dehydroamino acids, and up to 95% ee has been obtained.[17] Increasing the steric hindrance of the phosphinous amide ligand by partially hydrogenating the naphthyl ring improved the enantioselectivity of the catalyst in asymmetric hydrogenation of enamides and their derivatives.[18] Expanding the scope of these findings, it is of interest to use this class of phosphinous amide ligands in the asymmetric allylic alkylation to investigate the steric hindrances effect on the enantioselectivity of the reaction. Ligands **1**–**4** with different steric hindrance were prepared through the reaction of 2,2′-diamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (H_8-BINAM) and 2,2′-diamino-1,1′-binaphthyl (BINAM) with chlorodiarylphosphine (Fig. 1).

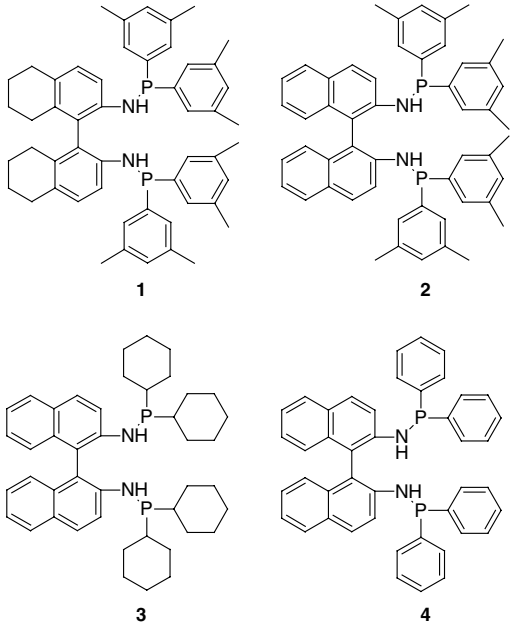


Figure 1. Phosphinous amide ligands derived from BINAM.

Initially the reaction of racemic 1,3-diphenyl-2-propenyl acetate with dimethyl malonate in the presence of base [*N*,*O*-bis(trimethylsilyl)acetamide (BSA) and LiOAc] was chosen for the examination of the efficiency of these ligands in palladium complex-catalyzed asymmetric allylic alkylations. The results shown in Table 1 revealed that the most sterically hindered ligand **1** gave the least satisfactory result in comparison to its less hindered analog **2** (Table 1, entry 1 vs entry 2). The least hindered ligand **4** (BDPAB) showed the highest efficiency among the ligands tested in this reaction, giving quantitative conversion and 75% ee at ambient temperature (Table 1, entry 4). Lowering the reaction temperature gave improved enantioselectivity; and the ee reached 87% when the reaction was carried out at 0 °C (Table 1, entry 5).

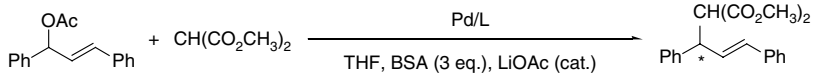
Since ligand **4** gave the best results, this ligand was chosen for the rest of the study. When acetylacetone was used as a nucleophile source in the BSA/LiOAc base system, no substitution product was detected after 4 days (Table 2, entry 1). When KOAc was used instead of LiOAc, 86% conversion and 81% ee was obtained (Table 2, entry 2) after 7 h. When a combination of LiOAc and KOAc, together with BSA, was employed, the ee was improved to 85% at ambient temperature and 94% at 0 °C (Table 2, entries 3 and 4). A variety of combinations of bases were investigated and the results are listed in Table 2. THF was found to be the best choice of solvent, giving the highest ee in the reaction.

A series of malonates were tested with this catalyst system and the results were summarized in Table 3. The reaction using the substituted malonates as nucleophiles also gave high enantioselectivities. For example, when diethyl *n*-butylmalonate was used as the nucleophile source, up to 96% ee was obtained (Table 3, entry 5). Similarly the use of diethyl benzylmalonate and diethyl formamidomalonate as nucleophile sources gave 94% ee and 90% ee, respectively (Table 3, entries 8 and 13).

3. Conclusion

In summary, a readily accessible chiral ligand derived from BINAM shows high efficiency in asymmetric catalytic alkylation. High enantioselectivities (90–96%)

Table 1. Asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with dimethyl malonate catalyzed by Pd^0/phosphinite ligands[a]



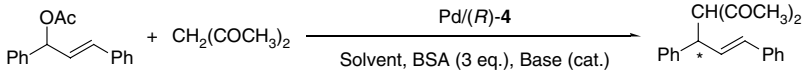
Entry	Ligand	Temperature (°C)	Time (h)	Conversion (%)[b]	Ee (%)[c]
1	(*S*)-**1**	rt	18	>99	31(*R*)
2	(*R*)-**2**	rt	18	>99	46(*R*)
3	(*S*)-**3**	rt	24	60	72(*R*)
4	(*R*)-**4**	rt	18	>99	75(*S*)
5	(*R*)-**4**	0	48	>99	87(*S*)

[a] Reaction conditions: Substrate/BSA/dimethyl malonate/ligand/Pd = 20/60/60/2/1 (molar ratio); LiOAc = 1 mg; $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ = 0.73 mg (0.002 mmol); THF solvent = 2 mL.

[b] Conversions were determined by NMR.

[c] The ee's were determined by HPLC analysis using a DAICEL Chiralpak AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min) and the absolute configurations of the product were determined by comparison with literature values.[11c]

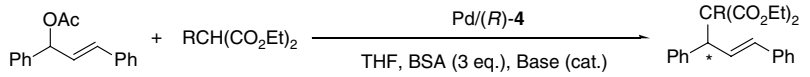
Table 2. Asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with acetylacetone catalyzed by Pd^0/ligand (*R*)-**4**[a]



Entry	Additive	Solvent	Temperature (°C)	Time (h)	Conversion (%)[b]	Ee (%)[c]
1	LiOAc	THF	rt	96	—	—
2	KOAc	THF	rt	7	86	81(*S*)
3	LiOAc + KOAc	THF	rt	7	>99	85(*S*)
4	LiOAc + KOAc	THF	0	30	93	94(*S*)
5	Cs_2CO_3 + KOAc	THF	rt	18	>99	83(*S*)
6	$SrCO_3$ + KOAc	THF	rt	18	>99	82(*S*)
7	NaOAc + KOAc	THF	rt	18	>99	82(*S*)
8	LiOAc + KOAc	Et_2O	rt	18	>99	69(*S*)
9	LiOAc + KOAc	Toluene	rt	18	>99	79(*S*)
10	LiOAc + KOAc	CH_2Cl_2	rt	18	>99	39(*S*)

[a] Reaction conditions: Substrate/BSA/acetylacetone/ligand/Pd (molar ratio) = 20/60/60/2/1; base = 1 mg LiOAc or 0.5 mg LiOAc + 0.5 mg KOAc; $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ = 0.73 mg (0.002 mmol); THF solvent = 2 mL.
[b] Conversions were determined by NMR.
[c] The ee's were determined by HPLC analysis using a DAICEL Chiralpak AD-H column (hexane/2-propanol = 97/3, 1.0 mL/min) and the absolute configurations of the product were determined by comparison with literature values.[5]

Table 3. Asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with various ester malonates catalyzed by Pd(0)-(*R*)-**4**[a]



Entry	R	Additive	Temperature (°C)	Time (h)	Conversion (%)[b]	Ee (%)[c,d]
1	H	LiOAc	rt	4	>99	68(*S*)
2	H	LiOAc	0	48	>99	80(*S*)
3	*n*-Butyl	LiOAc	rt	6	>99	94(*R*)(+)
4	*n*-Butyl	LiOAc, KOAc	rt	20	>99	91(*R*)(+)
5	*n*-Butyl	LiOAc	0	48	>99	96(*R*)(+)
6	Benzyl	LiOAc	rt	6	>99	93(*R*)(+)
7	Benzyl	LiOAc, KOAc	rt	10	>99	86(*R*)(+)
8	Benzyl	LiOAc	0	48	>99	94(*R*)(+)
9	Acetamido	LiOAc	rt	6	>99	72(*R*)
10	Acetamido	LiOAc	0	48	80	83(*R*)
11	Formamido	LiOAc	rt	6	>99	87(*R*)(+)
12	Formamido	LiOAc, KOAc	rt	6	>99	84(*R*)(+)
13	Formamido	LiOAc	0	48	80	90(*R*)(+)

[a] Reaction conditions: Substrate/BSA/various ester malonate/ligand/Pd (molar ratio) = 20/60/60/2/1; base = 1 mg LiOAc or 0.5 mg LiOAc + 0.5 mg KOAc; $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ = 0.73 mg (0.002 mmol); THF solvent = 2 mL.
[b] Conversions were determined by NMR.
[c] The ee's were determined by HPLC analysis using a DAICEL Chiralpak AD-H column.
[d] Optical rotations were measured using a Perkin–Elmer polarimeter (Model 341); the absolute configurations were determined by comparison with literature values.[19,20]

were achieved in the allylic substitution of racemic 1,3-diphenylallylic acetate using a [Pd-(*R*)-**4**] catalyst. A balanced rigidity/steric hindrance of the ligand is important for the best results. This finding is consistent with the results reported by Trost and Murphy[21] and RajanBabu and coworkers[22] that binaphthyl phosphite ligands bearing bulky groups give low enantioselectivity.

4. Experimental section

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a glove box. Flash column chromatography was performed using silica gel as adsorbent. Hexane, toluene, tetrahydrofuran, and diethyl ether were distilled from sodium or sodium benzophenone ketyl before use. Dichloromethane was distilled from CaH_2. ^1H, ^{31}P, and ^{13}C NMR were recorded on a Bruker AVANCE 400 or Varian AS 500 at RT using $CDCl_3$ as solvent. Enantiomeric excesses were determined by HPLC conducted on an Agilent 1100 series system. Optical rotations were measured on a Perkin–Elmer polarimeter. Thin layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60 F_{254} (0.25 mm, Merck).

4.1. (*R*)-2,2′-Bis[bis(3,5-dimethylphenyl)phosphinoamino]-5,5′,6,6′,7,7′,8,8′-octohydro-1,1′-binaphthyl 1

(*R*)-2,2′-diamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (292 mg, 1.0 mmol) and 4-(dimethylamino)pyridine (15 mg) were placed in a 50 mL round-bottom Schlenk flask with a stirring bar under N_2 atmosphere and dry Et_3N (0.8 mL) and CH_2Cl_2 (30 mL) were added to the mixture. The reaction mixture was cooled to 0 °C with an ice-water bath followed by dropwise addition of bis(3,5-dimethylphenyl)phosphine chloride (2.5 mmol) in 20 min. The solvent was removed under reduced pressure after the reaction mixture was stirred at ambient temperature for 3 h. The residue was re-dissolved in 15 mL toluene and was purified through a flash silica gel column (30 mL toluene as eluent). The solvent was removed to give 645 mg white solid (85% yield). Colorless crystals were obtained after recrystallization from diethylether. ^{31}P NMR (202 MHz, $CDCl_3$): δ 25.2 ppm. ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): δ 1.51–1.68 (m, 8H), 2.07 (s, 12H), 2.16–2.18 (m, 4H), 2.22 (s, 12H), 2.66–2.68 (m, 4H), 4.29 (d, 2H, $J = 9.0$ Hz), 6.74–6.75 (m, 6H), 6.90–6.91 (m, 6H), 6.96–6.99 (m, 2H), 7.26–7.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.12, 21,27, 23.19, 23.29, 27.41, 29.31, 112.23–142.16 (Ph); $[\alpha]_D^{20} = +3.3$ (*c* 1.0, THF). Anal. Calcd for $C_{52}H_{58}N_2P_2$: C, 80.80; H, 7.56; N, 3.62; P, 8.01. Found: C, 80.59; H, 7.53; N, 3.78; P, 8.10.

4.2. A typical procedure for the asymmetric allylic alkylation

In a glove box, ligand **4** (52.2 mg, 0.08 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (7.3 mg, 0.02 mmol) and 2 mL dried THF were placed in a 4 mL glass bottle, the mixture was stirred at room temperature for 1 h to prepare a stock solution of the catalyst. In a typical experiment, 200 μL (0.002 mmol) of the catalyst solution was added in a 4 mL glass bottle, to the solution were added successively racemic 1,3-diphenyl-2-propenyl acetate (0.08 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.24 mmol), catalytic amount of anhydrous lithium acetate (1 mg) and malonate ester (0.24 mmol) and then THF was added to form 2 mL solution. The reaction mixture was stirred at appropriate temperature for a given period of time. The reaction mixture was diluted with ether (20 mL), and washed with saturated aqueous ammonium chloride (3 × 20 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography and enantiomeric composition was measured by HPLC analysis using a DAICEL Chiralpak AD-H column.

4.3. Diethyl 2-benzyl-2-[(*E*)-1,3-diphenyl-2-propenyl]-malonate

Viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.01 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H), 3.09 (d, $J = 13.8$ Hz, 1H), 3.24 (d, $J = 13.8$ Hz, 1H), 3.94–3.98 (m, 2H), 4.11–4.23 (m, 2H), 4.28 (d, $J = 8.4$ Hz, 1H), 6.33 (d, $J = 15.8$ Hz, 1H), 6.75 (dd, $J = 8.4$ Hz, $J = 15.8$ Hz, 1H), 7.17–7.33 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.72, 13.94, 41.04, 54.82, 61.09, 61.15, 64.20, 126.34, 126.72, 127.22, 127.26, 127.87, 128.38, 128.43, 129.51, 129.99, 130.37, 132.14, 136.87, 137.50, 139.39, 170.18, 170.26. Anal. Calcd for $C_{29}H_{30}O_4$: C, 78.71; H, 6.83; O, 14.46. Found: C, 78.34; H, 6.93. Enantiomeric excess value was measured by HPLC (Chiral AD-H, *n*-hexane/isopropanol = 97/3): 8.83 min, 11.71 min (flow rate = 1.0 mL/min).

4.4. Diethyl 2-(*n*-butyl)-2-[(*E*)-1,3-diphenyl-2-propenyl]-malonate

Viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.82 (t, $J = 6.9$ Hz, 3H), 1.17–1.31 (m, 10H), 1.69–1.72 (m, 1H), 1.82–1.85 (m, 1H), 4.09–4.24 (m, 5H), 6.34 (d, $J = 15.7$ Hz, 1H), 6.77 (dd, $J = 7.1$ Hz, $J = 15.7$ Hz, 1H), 7.18–7.34 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.85, 14.08, 22.99, 26.79, 28.48, 34.44, 53.48, 60.99, 61.08, 61.26, 126.30, 127.08, 127.15, 128.25, 128.41, 129.28, 130.07, 131.70, 137.56, 139.62, 170.66, 170.94. Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.63; H, 7.82. The enantiomeric excess was measured by HPLC (Chiralpak AD-H, *n*-hexane/2-propanol = 97/3): 6.20 min, 7.60 min (flow rate = 1.0 mL/min).

4.5. Diethyl 2-formamido-2-[(*E*)-1,3-diphenyl-2-propenyl]-malonate

Colorless needles. ^1H NMR (400 MHz, $CDCl_3$): (ratio of NH tautomer 6/1; major tautomer) δ (ppm) 1.17 (t, $J = 7.1$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), 3.60–4.16 (m, 2H), 4.27–4.32 (m, 2H), 4.77 (d, $J = 7.1$ Hz, 1H), 6.32 (d, $J = 15.9$ Hz, 1H), 6.76 (dd, $J = 7.1$ Hz, $J = 15.9$ Hz, 1H), 6.81 (br, 1H), 7.23–7.34 (m, 10H), 8.18 (d, $J = 2.6$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.83, 14.02, 53.20, 62.64, 62.91, 68.40, 126.46, 127.25, 127.75, 128.37, 128.43, 128.47, 129.51, 132.68, 137.39, 137.88, 159.83, 166.52, 167.03. Anal. Calcd for $C_{23}H_{25}NO_5$: C, 69.86; H, 6.37; N, 3.54. Found: C, 69.63; H, 6.46; N, 3.60. The enantiomeric excess was measured by HPLC (Chiralpak AD-H, *n*-hexane/2-propanol = 90/10): 15.20 min, 21.84 min (flow rate = 1.0 mL/min); 10.10 min, 14.23 min (flow rate = 1.5 mL/min).

4.6. Determination of the configuration of new allylic alkylation products

(*R*)-Diethyl-2-[(*E*)-1,3-diphenyl-2-propenyl] malonate (82% ee, 70 mg, 0.2 mmol) and NaH (6 mg, 0.25 mmol) in 3 mL dry THF stirred for 0.5 h, followed by added in benzyl chloride (30 mg, 0.24 mmol). The mixture was stirred overnight at ambient temperature. Crude product was purified with silica gel column, (*S*)-diethyl 2-benzyl-2-[(*E*)-1,3-diphenyl-2-propenyl]malonate was obtained with 81% ee. Similarly, (*S*)-diethyl 2-(*n*-butyl)-2-[(*E*)-1,3-diphenyl-2-propenyl]malonate was obtained with 80% ee by the reaction of (*R*)-diethyl-2-[(*E*)-1,3-diphenyl-2-propenyl]malonate (82% ee) with *n*-butyl

p-toluene sulfonate when the NaH as base. The determination of the configuration of diethyl 2-formamido-2-[(*E*)-1,3-diphenyl-2-propenyl]malonate followed from the literature procedures.[20]

Acknowledgements

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