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C_2-Symmetric bisphosphinites and a bisaminophosphine as new chiral ligands for Pd-catalyzed asymmetric allylic substitution

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Abstract

A family of C_2-symmetric bisphosphinites **3**, **5**, **7**, **9** and bisaminophosphine **11** were prepared and were probed in the prototypical reaction system of palladium-catalyzed asymmetric allylic substitution. The highest ee of 86% was achieved by employing ligand **3**.

1. Introduction

Asymmetric synthesis and reactions based on transition metal-catalyzed processes have attracted rapidly increasing interest because of their high efficiency for the construction of carbon–carbon bonds.[1] Asymmetric allylic alkylation catalyzed by chiral palladium complex is representative of this reaction class. Since the first example of an enantioselective palladium-catalyzed allylic substitution reaction was reported in 1977, much work has been done to harness the asymmetric potential of allylic alkylation.[2] But only recently has this reaction developed into processes where high enantioselection may be realized with a wide range of ligands.[3–6]

The popularity of phosphine ligands in transition metal chemistry stems from their ability to stabilize the metal complex. The early success of C_2-symmetric diphosphine ligands in asymmetric hydrogenations led to their direct application in the asymmetric allylic alkylation reaction, good to excellent results were obtained by choosing appropriate substrates or palladium catalysts.[7,8] In contrast to phosphines, phosphinites have not been well developed as ligands in this type of reaction, especially in the prototypical testing system with *rac*-1,3-diphenyl-2-propenyl acetate as the substrate, dimethylmalonate/BSA as nucleophile and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as the catalyst.[9] Seebach and co-workers first prepared C_2-symmetric bisphosphinite (TADDOP) from TADDOL and tested it in the asymmetric allylic substitution, up to 76% ee was obtained in 1995.[9a] In 1999,

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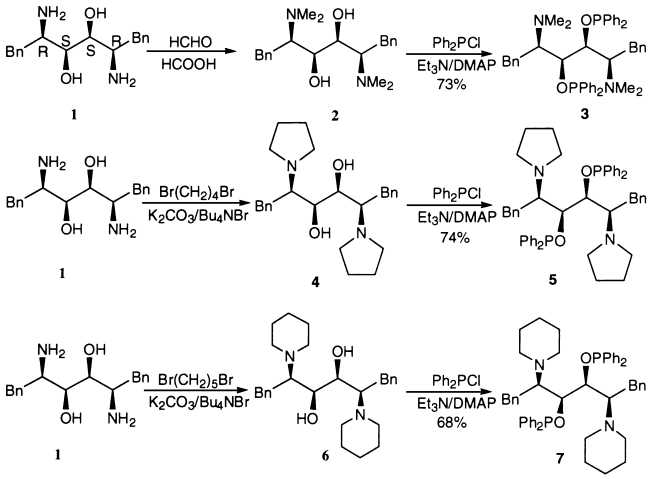
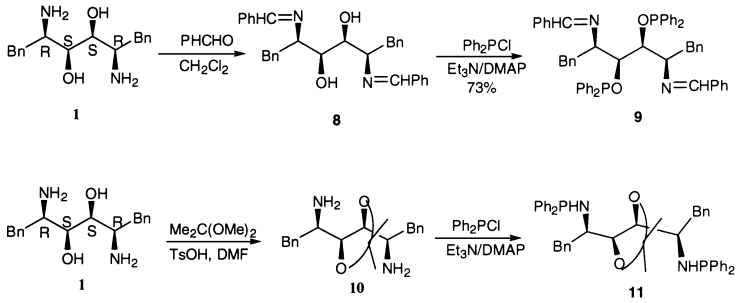
RajanBabu prepared a series of C_2-symmetric bisphosphinites and systematically studied their effects in this reaction.[9b] In RajanBabu's studies, the bisphosphinites (BINAPO) based on (*R*)- and (*S*)-binaphthol gave the best ee of 63 and 64% in the standard allylic substitution system at room temperature although 87% ee could be obtained by introducing the reaction at –30°C, and diethyl tartrate based bisphosphinite only gave 13% ee. Recently, we developed a new family of C_2-symmetric bisphosphinites **3**, **5**, **7**, **9** and C_2-symmetric bisaminophosphine **11**, and investigated their applications in the prototypical allylic substitution reaction. Here we reported our preliminary results.

2. Results and discussion

Our work started from the C_2-symmetric (2*R*,3*S*,4*S*,5*R*)-2,5-diamino-1,6-diphenyl-3,4-hexanediol **1**,[10] which could be produced in kilogram quantities. First, we reacted diol **1** with formaldehyde (37% in water) and formic acid under reflux, and (2*R*,3*S*,4*S*,5*R*)-2,5-bis(dimethylamino)-1,6-diphenyl-3,4-hexanediol **2** was obtained in 90% yield. Treatment of diol **2** with 2.2 equivalents of chlorodiphenylphosphine in the presence of pyridine and a catalytic amount of DMAP afforded C_2-symmetric bisphosphinite **3** in 73% yield (Scheme 1). Ligands **5** and **7** were obtained by similar procedures, in which treatment of compound **1** with 1,4-dibromobutane or 1,5-dibromopentane in the presence of anhydrous K_2CO_3 and a catalytic amount of Bu_4NBr gave (2*R*,3*S*,4*S*,5*R*)-2,5-di(1-pyrrolidinyl)-1,6-diphenyl-3,4-hexanediol **4** and (2*R*,3*S*,4*S*,5*R*)-2,5-di(1-piperidyl)-1,6-diphenyl-3,4-hexanediol **6**, respectively, which were then treated with 2.2 equivalents of chlorodiphenylphosphine in the presence of pyridine and a catalytic amount of DMAP. Ligand **9** was also easily prepared by the condensation of the amino group in compound **1** with benzaldehyde, and then attachment of the diphenylphosphino group to the hydroxy group. Bisaminophosphine **11** was obtained by first protecting both of the hydroxy groups with the *iso*-propylene group to give diamine **10**, then reacting diamine **10** with 2.2 equivalents of chlorodiphenylphosphine in the presence of pyridine and DMAP (Scheme 2).



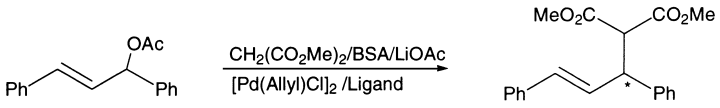
Scheme 1.



Scheme 2.

Then compound **3** was chosen as ligand to test the efficiency of the prototypical reaction of 1,3-diphenyl-2-propen-1-yl acetate with dimethyl malonate by using $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as the catalyst. A brief screening revealed that the substitution was complete in 10 hours in CH_2Cl_2, and 2 days in THF, while it was sluggish and incomplete in other solvents (Table 1, entries 4–6). As to the enantioselection, the highest was observed in THF; the ee can reach to 70% by addition of a small amount of LiOAc (entry 2). The ee did not improve at elevated temperatures, but the reaction time was shorter (entry 1). Altering the loading of ligand resulted in lower selectivity and yield (Table 1, entries 7–8). Finally, we used a small amount of KOAc as the additive instead of LiOAc, and the ee of the product rose to 86% (Table 2, entry 2), which was comparable with the best value in the prototypical allylic substitution reaction so far reported for a C_2-symmetric bisphosphinite ligand.

Table 1
Asymmetric allylic substitution using compound **3** coordinated with palladium



Entry	Solvent	T	L*/[Pd]	%ee[a]	Yield (%)[b]
1	THF	50°	5	61	74
2	THF	r.t.	5	70	73
3	CH_2Cl_2	r.t.	5	11	84
4	Et_2O	r.t.	5	5	69
5	Tolu.	r.t.	5	59	33
6	CH_3CN	r.t.	5	32	22
7	THF	r.t.	2.5	21	12
8	THF	r.t.	10	60	30

[a] Determined by chiral HPLC analysis (Daicel chiralcel OD-H).
[b] Isolated yields.

Under the same reaction conditions, compounds **5** and **7** were examined as ligands; an ee of 79% was obtained in both cases (Table 2, entries 3 and 4), slightly lower than for ligand **2**.

Next, compound **9** was examined as ligand following the optimum reaction conditions. But unfortunately, the reaction proceeded very slowly, with nearly no stereoselection (Table 2, entry 5).

Table 2
Asymmetric palladium catalyzed allylic substitution of 1,3-diphenyl-2-propenyl acetate at room temperature[a]

Entry	Solvent	L	Additive	%ee[b]	Conf.[c]	Yield%[d]
1	THF	**3**	LiOAc	70	S	73
2	THF	**3**	KOAc	86	S	68
3	THF	**5**	KOAc	79	S	74
4	THF	**7**	KOAc	79	S	78
5	THF	**9**	KOAc	4	R	31
6	THF	**11**	KOAc	13	R	47
7	CH_2Cl_2	**11**	KOAc	28	R	77

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/Ligand/KOAc/$CH_2(CO_2Me)$/BSA=1/10/2.4/183/183.
[b] Determined by chiral HPLC analysis (Daicel chiralcel OD-H).
[c] Assigned by comparison of its sign of the optical rotation with literature data.[6c]
[d] Isolated yields.

Lastly, bisaminophosphine **11** was employed as the ligand; the allylic substitution reaction occurred readily in CH_2Cl_2 in good yield with only 28% ee, while the reaction proceeded slowly in THF with 13% ee (Table 2, entries 6–7).

As to the stereochemistry, the *S*-configured product was obtained using compounds **3**, **5**, or **7** as the ligand, while application of ligands **9** or **11** resulted in a *R*-configured product.

In summary, a C_2-asymmetric bidentate phosphine ligand family was prepared from C_2-symmetric (2*R*,3*S*,4*S*,5*R*)-2,5-diamino-1,6-diphenyl-3,4-hexanediol **1**, and their inducing effect in the prototypical asymmetric allylic substitution reaction system was investigated. The highest enantioselectivity of 86% was obtained by using ligand **3**, while ligands **5** and **7** both gave the product with 79% ee. Employing ligands **9** and **11** resulted in lower stereoselection.

3. Experimental

3.1. General methods

All anaerobic reactions were carried out under an inert atmosphere of argon in a Vacuum Atmospheres drybox, or using Schlenk techniques. NMR spectra were recorded as $CDCl_3$ solutions on a VXL-300 instrument. The ^1H NMR (300 MHz) chemical shifts are reported as δ values in ppm relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin–Elmer 983 FT-IR spectrometer. Mass spectral measurements were performed on a Fining 4021 or Fining MAT 8403 gas chromatography/mass spectrometer at 70 eV. Elemental analyses were carried out on a MOD-1106 elemental analyzer. All solvents were purified and dried by standard techniques just before use. All reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. Products were purified by chromatograghy on silica gel manufactured by the Qingdao Marine Chemical Factory. Optical rotations were measured in a solution of $CHCl_3$ by using a Shanghai WZZ-1S automatic polarimeter. Melting points were determined on a Digital Melting Apparatus WRS-1A.

3.2. (2R,3S,4S,5R)-2,5-Bis(dimethylamino)-1,6-diphenyl-3,4-hexanediol **2**

Diamino diol **1** (1.2 g, 4.0 mmol) in formic acid (6 mL, 0.16 mol) was heated with a 37% formaldehyde (3.2 mL) solution under reflux for 8 h. The solvent was removed under reduced pressure. The residue was neutralized with 3N NaOH and extracted with diethyl ether and dried over anhydrous Na_2SO_4. Then the solvent was removed and the residue was purified by flash chromatography (CH_2Cl_2:MeOH = 5:1) to give **2** (1.28 g, 89.9%) as a colorless solid. $[\alpha]_D = -4.2$ (*c* 2.4, $CHCl_3$); IR (KBr) 3431, 2943, 2833, 1600, 1491, 1124, 1028, 736 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30–7.17 (m, 10H), 3.38 (d, J = 2.2 Hz, 2H), 3.00 (dd, J = 10.4, 12.9 Hz, 2H), 2.81 (dd, J = 3.7, 12.9 Hz, 2H), 2.67 (m, 2H), 2.50 (s, 12H); MS (EI) *m*/*z* 357 (M^++1, 14.1), 209 (7.8), 208 (46.4), 178 (13.8), 149 (19.3), 148 (100), 133 (13.6), 91 (10.1). Anal. calcd for $C_{22}H_{32}N_2O_2$: C, 74.10; H, 9.05; N, 7.85. Found: C, 74.32; H, 9.06; N, 7.91.

3.3. General procedure for preparation of (2R,3S,4S,5R)-2,5-di(1-pyrrolidinyl)-1,6-diphenyl-3,4-hexanediol **4** or (2R,3S,4S,5R)-2,5-di(1-piperidyl)-1,6-diphenyl-3,4-hexanediol **6**

To a suspension solution of **1** (2 g, 6.7 mmol) in THF (100 mL) was added 1,4-dibromobutane or 1,5-dibromopentane (13.4 mmol), K_2CO_3 (1.9 g, 13.7 mmol) and a catalytic amount of tetra-*n*-butylammonium iodide (53 mg, 0.14 mmol). The resulting mixture was refluxed for 7 days, then the solid was filtered. The filtrate was concentrated under reduced pressure. The residue was subjected to flash chromatography to give the products **4** or **6**.

Compound **4**: (1.69 g, 62%). $[\alpha]_D = -49.0$ (*c* 1.0, $CHCl_3$); IR (KBr) 2966, 2839, 1601, 1494, 1140, 1091, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.20 (m, 10H), 3.41 (s, 2H), 2.69–3.07 (m, 14H), 1.80 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.17, 129.48, 128.33, 125.79, 72.16, 66.43, 49.61, 29.25, 23.71; MS (EI) *m*/*z* 409 (M^++1, 18.1), 408 (61.4), 234 (15.4), 204 (4.2), 174 (100). Anal. calcd for $C_{26}H_{36}N_2O_2$: C, 76.43; H, 8.88; N, 6.86. Found: C, 76.27; H, 8.89; N, 6.74.

Compound **6**: (1.81g, 63%). $[\alpha]_D = -182.0$ (*c* 0.265, $CHCl_3$); IR (KBr) 3027, 2934, 1604, 1495, 1196, 1094, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.20 (m, 10H), 3.40 (s, 2H), 2.85–3.10 (m, 10H), 2.40–2.60 (m, 4H), 1.40–1.70 (m, 12H); MS (EI) *m*/*z* 437 (M^++1, 1.8), 435(0.4), 248 (58), 218 (12.5), 188 (100). Anal. calcd for $C_{28}H_{40}N_2O_2$: C, 77.06; H, 9.17; N, 6.42. Found: C, 76.93; H, 9.00; N, 6.09.

3.4. Preparation of compound **8**

Benzaldehyde (850 mg, 8.01 mmol) and anhydrous magnesium sulfate (1g, 8.3 mmol) were added to a solution of diamino diol **1** (1.2 g, 4.0 mmol) in CH_2Cl_2 (20 mL) and the mixture was stirred overnight. The solid was filtered through a pad of Celite and the solvent was removed. The residue was purified by flash chromatography (petroleum:ethyl acetate = 10:1) to give **8** (1.6 g, 80.2%) as a colorless solid. IR (KBr) 3310, 3028, 2977, 2845, 1602, 1494, 1454, 1131, 1009, 744 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.70 (m, 4H), 7.40–7.45 (m, 6H), 7.15–7.25 (m, 10H), 5.25 (s, 2H), 3.20–3.25 (m, 4H), 2.90–2.98 (m, 4H), 2.11 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.77, 138.56, 129.49, 128.43, 128.35, 128.20, 126.31, 126.05, 87.58, 69.71, 60.30, 37.32; MS (EI) *m*/*z* 477 (M^++1, 11.3), 478 (4.2), 385 (11.4), 268 (22.1), 238 (22.4), 91 (100). Anal. calcd for $C_{32}H_{32}N_2O_2$: C, 80.67; H, 6.72; N, 5.88. Found: C, 80.71; H, 6.90; N, 5.90.

3.5. Preparation of compound **10**

This compound was prepared according to the literature procedure[11] by the reaction of diamino diol **1** with 2,2-dimethoxypropane and *p*-methylbenzene sulfonic acid. $[\alpha]_D = -25.5$ (*c* 4.0, $CHCl_3$); IR (KBr) 3381, 2986, 2933, 1604, 1495, 1455, 1379, 1246, 1054 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.32–7.17 (m, 10H), 4.06 (s, 2H), 3.07 (m, 2H), 2.83 (dd, J = 5.0, 13.3 Hz, 2H), 2.64 (dd, J = 9.3, 13.3 Hz), 2.4 (brs, 4H), 1.46 (s, 6H); MS (EI) *m*/*z* 341 (M^++1, 100), 342 (M^++2, 31.6), 249 (51.0), 174 (25.4), 130 (19.6), 120 (63.3), 91 (40.4), 72 (23.8). Anal. calcd for $C_{21}H_{28}N_2O_2$: 340.3720. Found: 340.3709.

3.6. Typical procedure for the preparation of bisphosphinites **3**, **5**, **7**, **9** and bisaminophosphine **11**

To 1.0 equiv. of the corresponding diol **2**, **4**, **6**, **8** or diamine **10** (1.9 mmoL) in CH_2Cl_2 (20 mL) were added pyridine (5 mL) and a catalytic amount of DMAP under an argon atmosphere. After the reaction system was cooled to 0°C, a solution of chlorodiphenylphosphine (937 mg, 4.25 mmoL) in CH_2Cl_2 (10 mL) was added dropwise. The reaction mixture was stirred at room temperature overnight and filtered through basic Al_2O_3 under an argon atmosphere, and the filtrate was evaporated in vacuo to afford bisphosphinites **3**, **5**, **7**, **9** or bisaminophosphine **11** as a viscous solid (68–80% yield).

Bisphosphinite ***3***: 73% yield; $[\alpha]_D = -12.4$ (*c* 0.5, benzene); ESI (M+1) 726; ν_{max} (neat)/cm^{-1}: 3053, 2966, 2831, 1496, 1479, 1454, 1434, 1097, 1027, 736, 697; ^1H NMR ($CDCl_3$) δ 7.25 (m, 30H), 3.92 (m, 2H, OCH), 3.40 (dd, 2H, J = 8.1, 14.2 Hz, NCH), 2.70 (dd, 2H, J = 7.8, 14.0 Hz, CH_2Ph), 2.50 (dd, 2H, J = 5.4, 14.0 Hz, CH_2Ph), 1.67 (s, 12H, NCH_3); ^{31}P {^1H} NMR δ 101.60 (s).

Bisphosphinite ***5***: 74% yield; $[\alpha]_D = -5.8$ (*c* 0.85, benzene); ESI (M+1) 777; MS (EI) *m*/*z* 778 (M^++2, 0.67), 591 (M^+–PPh_2, 1.5), 516 (3.1), 441 (12.4), 400 (11.6), 370 (23.1), 217 (53.4), 200 (20.1), 174 (100); ν_{max} (neat)/cm^{-1}: 2932, 2852, 1602, 1453, 1435, 1262, 1100, 1030, 802, 736, 697; ^1H NMR ($CDCl_3$) δ 7.20 (m, 30H), 4.1 (dd, 2H, J = 8.47, 8.77, OCH), 3.60 (m, 2H, NCH), 2.70 (dd, 2H, J = 6.56, 13.87 Hz), 2.55 (dd, 2H, J = 5.6, 14.0 Hz), 2.2 (m, 8H), 1.1 (s, 8H); ^{31}P {^1H} NMR δ 101.57 (s).

Bisphosphinite ***7***: 68% yield; $[\alpha]_D = -21.6$ (*c* 2.6, benzene); ν_{max} (neat)/cm^{-1}: 3054, 2932, 2852, 1600, 1453, 1435, 1262, 1100, 1030, 802, 736, 697; ^1H NMR ($CDCl_3$) δ 7.25 (m, 30H), 4.15 (t, 2H, J = 9.14), 3.30 (dd, 2H, J = 6.58, 14.38 Hz), 2.80 (dd, 2H, J = 7.37, 14.19 Hz), 2.45 (dd, 2H, J = 5.61, 14.16 Hz), 2.30 (m, 2H), 2.15 (m, 2H), 0.9 (m, 8H), 0.7 (m, 4H); ^{31}P {^1H} NMR δ 101.97 (s); MS (EI) *m*/*z* 806 (M^++2, 0.5), 619 (M^+–PPh_2, 0.3), 458 (21.4), 325 (10.8), 242 (16.1), 217 (50.9), 188 (100), 108 (80.8). Anal. calcd for $C_{40}H_{48}N_2O_2P_2$ (M^+–PPh_2): 619.3461. Found: 619.3457.

Bisphosphinite ***9***: 73% yield; $[\alpha]_D = -85.1$ (*c* 2.65, benzene); ν_{max} (neat)/cm^{-1}: 3054, 2932, 2852, 1600, 1453, 1435, 1262, 1100, 1030, 802, 736, 697; ^1H NMR ($CDCl_3$) δ 7.50 (m, 40H), 5.25 (s, 2H), 3.10 (m, 4H), 2.95 (m, 4H); MS (EI) *m*/*z* 844 (M^+, 0.3), 567 (M^+–PPh_2 5.5), 477 (94.2), 385 (58.7), 282 (28.3), 268 (67.3), 238 (51.5), 208 (51.2), 91 (100). Anal. calcd for $C_{32}H_{31}N_2O_2$ (M^+–2×PPh_2): 475.2395. Found: 475.2390.

Bisaminosphosphine ***11***: 80% yield; $[\alpha]_D = 37.0$ (*c* 2.17, benzene); ν_{max} (neat)/cm^{-1}: 3375, 3025, 2985, 1568, 1496, 1434, 1260, 1094, 741, 697; ^1H NMR ($CDCl_3$) δ 7.20 (m, 30H), 3.85 (m, 2H), 3.45 (m, 2H), 2.75 (dd, 2H, J = 8.1, 13.7 Hz), 2.55 (dd, 1H, J = 7.0, 13.7 Hz), 2.15 (t, 2H, 10.97), 1.15 (s, 6H); ^{31}P {^1H} NMR δ 42.12 (s); MS (EI) *m*/*z* 708 (M^+, 2.8), 709 (2.6), 617 (6.7), 523 (63.1), 358 (100), 304 (53.71), 201 (38.6), 185 (100), 108 (49.1).

3.7. General procedure for the palladium-catalyzed allylic substitution of rac-1,3-diphenyl-2-propenyl acetate

A flame-dried Schlenk tube was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.5 mg, 0.0041 mmol) and the corresponding ligand (0.041 mmol) under a stream of argon and dry THF (2 mL) was added. The mixture was stirred for 1 hour at room temperature. To this solution were successively added *rac*-1,3-diphenyl-2-propenyl acetate (63 mg, 0.25 mmol), dimethyl malonate (99 mg, 0.75 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (153 mg, 0.75 mmol), and potassium acetate (1 mg, 0.01 mmol). The reaction mixture was stirred overnight at room temperature, then diluted with diethyl ether (20 mL). The isolated organic phase was washed twice with ice-cold saturated aqueous ammonium chloride, dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum:ethyl acetate = 10:1) to give the pure product. The enantiomeric purities were determined by HPLC (Chiralcel OD column).

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