Assessment of the Activity of 8-Diphenylphosphino-8'-methoxy-1,1'-binaphthyl as a Ligand for Palladium-Catalyzed Reactions

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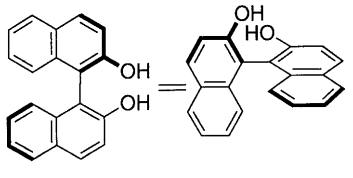
A monodentate phosphine, 8-diphenylphosphino-8'-methoxy-1,1'-binaphthyl, was shown to be active as a ligand in palladium-catalyzed reactions, including the reduction of allylic carbonates with formic acid, hydrosilylation of a terminal olefin, and hydroboration of but-1-en-3-yne, even though it has a highly hindered lone pair.

Key words phosphine ligand; palladium-catalyzed reaction; binaphthol; hydrosilylation; hydroboration

2,2'-Dihydroxy-1,1'-binaphthyl (2,2'-BINOL, **1**) and its derivatives have frequently been used for both stoichiometric[1] and catalytic[2] asymmetric syntheses. On the other hand, 8,8'-dihydroxy-1,1-binaphthyl (8,8'-BINOL, **2**) has received little attention as a chiral source. The hydroxy groups of 8,8'-BINOL (**2**) point in opposite directions, while those of 2,2'-BINOL (**1**) point in the same direction (Fig. 1). Moreover, a highly dissymmetric environment is created around the substituents at C-8 and C-8' in **2**, since one side of the substituents is completely blocked by another naphthyl ring in the molecule.[3] We previously reported the enantioselective protonation of enolates with the monocarbamate **3** of optically active 8,8'-BINOL (**2**)[4] and the highly enantioselective synthesis of ketones *via* tandem 1,4-and 1,2-addition of Gilman reagents to the half-ester **4**.[5] As a part of our investigation aimed at applying the highly dissymmetric environment of 8,8'-BINOL (**2**) for asymmetric synthesis, we attempted to synthesize optically active 8-diphenylphosphino-8'-methoxy-1,1'-binaphthyl (8-MeO-MOP, **8**) and encountered unexpected racemization of a synthetic intermediate **7**.[6] In this note, we report our assessment of the activity of racemic **8** as a ligand in palladium-catalyzed reactions.

Optically active monodentate phosphines such as 2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (2-MeO-MOP, **9**) and its analogues have been shown to be effective catalysts for the palladium-catalyzed reduction of allylic carbonates with formic acid,[7] hydrosilylation of terminal olefins,[8] and hydroboration of but-1-en-3-ynes.[9] The phosphine ligand **8** was prepared from 8,8'-BINOL (**2**) in four steps by a route similar to that reported by Hayashi and coworkers for 2-MeO-MOP (**9**).[10] Monotriflation of racemic **2** proceeded smoothly to give **5** in 79% yield. The coupling of **5** with diphenylphosphine oxide in the presence of a catalyst prepared *in situ* from palladium diacetate and 1,4-bis(diphenylphosphino)butane (dppb) gave **6** in quantitative yield. The corresponding methyl ether **7** was reduced with trichlorosilane and triethylamine to afford the desired phosphine **8**, which was slowly oxidized when kept in solution.

The most stable conformations of 8-MeO-MOP (**8**) and 2-MeO-MOP (**9**), calculated by molecular mechanics,[11] are shown in Fig. 2. The lone pair of the phosphorus atom in **9** extends parallel to the face of the naphthyl ring bearing the methoxy group (Fig. 2b), while that of **8** points almost perpendicularly to the face of the naphthyl ring due to severe steric hindrance (Fig. 2a). The X-ray crystal structure[12] shown in Fig. 3 revealed that the solid state conformation of **8** is similar to the calculated results. It is unclear whether the phosphorus compound **8** with such a highly hindered lone pair can be used as a ligand in palladium-catalyzed reactions. To assess the catalytic activity of 8-MeO-MOP (**8**), we carried out the palladium-catalyzed reduction of allylic carbonates with formic acid and the hydrosilylation of styrene with racemic **8** as a ligand. The results are shown in Tables 1 and 2, respec-



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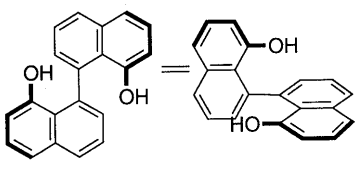

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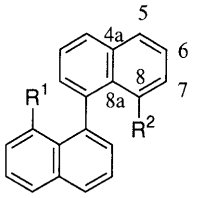
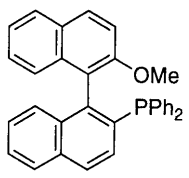
Fig. 1. Structural Features of 2,2'-BINOL (**1**) and 8,8'-BINOL (**2**)





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3: R^1 = OH, R^2 = $OCONEt_2$
4: R^1 = OH, R^2 = OCOCH=CHAr
5: R^1 = OH, R^2 = OTf
6: R^1 = OH, R^2 = $P(O)Ph_2$
7: R^1 = OMe, R^2 = $P(O)Ph_2$
8: R^1 = OMe, R^2 = PPh_2

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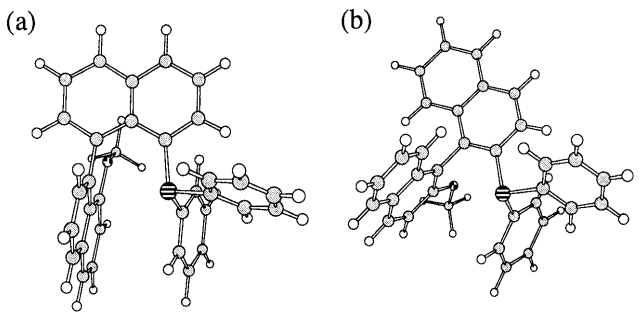


Fig. 2. The Most Stable Conformation of (a) 8-MeO-MOP (**8**) and (b) 2-MeO-MOP (**9**) Calculated by Macromodel (Version 4.5)

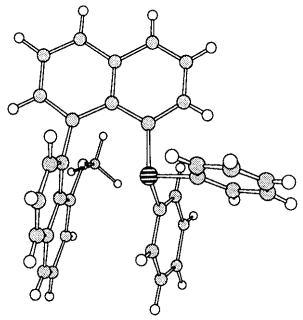
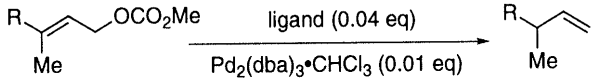


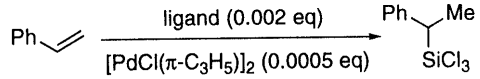
Fig. 3. Crystal Structure of 8-MeO-MOP (**8**) Generated through CS Chem3D Pro

Table 1. Evaluation of Catalytic Activity of **8** in the Palladium-Catalyzed Reduction of Allylic Carbonates with Formic Acid



Entry	R	Ligand	Reaction time, h	Yield, %
1	Me	None	143	0
2		PPh_3	37	65
3	Me	**8**	37	52
4		None	102	0
5		PPh_3	22	54
6		**8**	22	82

Table 2. Evaluation of Catalytic Activity of **8** in the Palladium-Catalyzed Hydrosilylation



Ligand	Reaction time, h	Yield, %
None	71	0
PPh_3	19	69
8	8	74

tively. Reduction of methyl carbonates without phosphine ligands gave no desired products, even after a prolonged reaction time (entries 1, 4, Table1). In contrast, the same reaction proceeded smoothly with **8** as a ligand, and the activity was similar to or even stronger than that of triphenylphosphine (compare entries 2 with 3 and 5 with 6 in Table 1). Table 2 clearly indicates that **8** has an activity equal to that of triphenylphosphine for hydrosilylation.

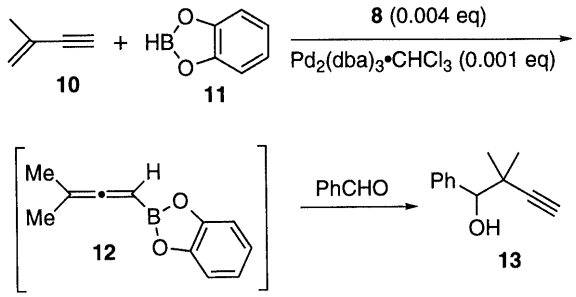


Chart 1

Table 3. Selected Torsion Angles of **7**[a] and **8**

Compound	Atom	Atom	Atom	Atom	Torsion angle
7	C-4a	C-5	C-6	C-7	6.4
7	C-5	C-6	C-7	C-8	−3.8
7	C-6	C-7	C-8	C-8a	−4.4
7	C-7	C-8	C-8a	C-4a	9.5
7	C-8	C-8a	C-4a	C-5	−7.1
7	C-8a	C-4a	C-5	C-6	−0.8
8	C-4a	C-5	C-6	C-7	0.3
8	C-5	C-6	C-7	C-8	−1.9
8	C-6	C-7	C-8	C-8a	1.7
8	C-7	C-8	C-8a	C-4a	0.1
8	C-8	C-8a	C-4a	C-5	−1.6
8	C-8a	C-4a	C-5	C-6	1.5

a) Taken from ref. 6.

Palladium-catalyzed hydroboration of 2-methyl-1-buten-3-yne (**10**) with catecholborane (**11**) gave the allene **12** in 11—13% yield in the presence of triphenylphosphine or **8** (Chart 1). The allene **12** was characterized as **13** after the reaction with benzaldehyde.[9] Hydroboration did not proceed without a phosphine ligand. These findings show that 8-MeO-MOP (**8**) can generate a catalytically active species in the palladium-catalyzed reactions even though the lone pair of the phosphorus in **8** seems to be too hindered to coordinate with palladium.

The torsion angles of the naphthyl ring with the phosphorus substituent are given in Table 3 for **7** and **8**. The striking distortion of the naphthyl ring observed in **7** is not seen in **8**. All of the torsion angles of the aromatic ring in **8** were within ±2.0 degrees, which indicates that the ring is quite planar. Thus, we can expect that the activation energy for the racemization of **8** is high enough for each enantiomer to exist at room temperature. The synthesis of optically active 8-MeO-MOP (**8**) is currently under investigation.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Varian Gemini-200 spectrometer. Data are recorded in parts per million (ppm) downfield from internal tetramethylsilane (TMS). The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). IR spectral measurements were performed on a JASCO FT/IR-300 spectrophotometer. MS and HR-MS were taken on a JEOL JMS-DX 300 mass spectrometer. Elemental analyses were measured on a Yanako CHN Corder MT-3 or MT-5. Silica Gel 60 spherical (150—325 mesh, Nakarai) was used for column chromatography.

8-Hydroxy-8′-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl (5) Triflic anhydride (1.5 ml, 8.7 mmol), 2,4,6-collidine (1.6 ml, 12 mmol), and 4-dimethylaminopyridine (43 mg, 0.35 mmol) were added to a solution

of 8,8′-BINOL (**2**) (1.0 g, 3.5 mmol) in CH_2Cl_2 (20 ml) at 0 °C, and the mixture was stirred at the same temperature for 4 h. The resulting mixture was diluted with ethyl acetate and poured into 1 N HCl. After separation, the organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane : CH_2Cl_2 = 2 : 1) to give **5** (1.2 g, 79%), which was recrystallized from hexane-isopropyl ether to afford pale yellow crystals, mp 95.5—96.5 °C. ^{1}H-NMR ($CDCl_3$) δ: 4.84 (s, 1H), 6.79 (dd, 1H, J = 1.2, 7.5 Hz), 7.23—7.67 (m, 8H), 7.90—8.04 (m, 3H). IR ($CHCl_3$) cm^{-1}: 3540, 1425, 1219, 1140, 825. MS *m/z*: 418 (M^+), 285 (base peak), 268. *Anal.* Calcd for $C_{21}H_{13}F_3O_4S$: C, 60.29; H, 3.13; F, 13.62. Found: C, 60.36; H, 2.98; F, 13.70.

8-Diphenylphosphinoyl-8′-hydroxy-1,1′-binaphthyl (6) Diphenylphosphine oxide (3.0 g, 15 mmol), palladium diacetate (0.17 g, 0.75 mmol), dppb (0.32 g, 0.75 mmol), and *N*,*N*-diisopropylethylamine (5.2 ml, 30 mmol) were added to a solution of **5** (3.1 g, 7.5 mmol) in dimethyl sulfoxide (DMSO) (31 ml) at room temperature, and the mixture was stirred at 100 °C for 30 min. After having been cooled to room temperature, the resulting mixture was diluted with ethyl acetate and poured into 1 N HCl. After separation, the organic layer was washed with water, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 2 : 1) to give **6** (3.5 g, 100%) as a yellow solid, mp 249.5—250.5 °C. ^{1}H-NMR ($CDCl_3$) δ: 6.08—6.18 (m, 2H), 7.16—7.53 (m, 18H), 7.85 (dt, 1H, J = 1.6, 8.1 Hz), 8.03—8.08 (m, 1H). IR (KBr) cm^{-1}: 3440, 1254, 1171, 1162, 772, 768, 695. MS *m/z*: 470 (M^+), 268, 201 (base peak). *Anal.* Calcd for $C_{32}H_{23}O_2P$: C, 81.69; H, 4.93. Found: C, 81.40; H, 4.85.

8-Diphenylphosphinoyl-8′-methoxy-1,1′-binaphthyl (7) Methyl iodide (4.9 ml, 78 mmol) and pulverized potassium carbonate (4.3 g, 31 mmol) were added to a solution of **6** (3.7 g, 7.8 mmol) in acetone (55 ml) at room temperature. After having been refluxed for 2 h, the mixture was cooled to room temperature. Dichloromethane was added, and the resulting mixture was filtered to remove the precipitate. After evaporation under reduced pressure, the residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 1 : 1) to give **7** (3.3 g, 87%); mp 205—208 °C (from hexane–toluene). ^{1}H-NMR ($CDCl_3$) δ: 2.88 (s, 3H), 6.35 (dd, 1H, J = 2.3, 6.4 Hz), 6.77—6.88 (m, 2H), 6.96—7.49 (m, 16H), 7.65 (dd, 1H, J = 1.3, 7.0 Hz), 7.88 (dt, 1H, J = 1.6, 8.1 Hz), 8.06—8.11 (m, 1H). IR (KBr) cm^{-1}: 1255, 1188, 1118, 823, 758, 719, 698. MS *m/z*: 484 (M^+, base peak), 282, 252, 201. HR-MS *m/z*: Calcd for $C_{33}H_{25}O_2P$ (M^+): 484.1593. Found: 484.1599.

8-Diphenylphosphino-8′-methoxy-1,1′-binaphthyl (8) Triethylamine (0.52 ml, 3.7 mmol) and trichlorosilane (0.31 ml, 3.1 mmol) were added to a suspension of **7** (0.10 g, 0.21 mmol) in xylene (1.3 ml) at 0 °C. The mixture was stirred at 140 °C for 2.5 h. After having been cooled to 0 °C, the resulting mixture was diluted with ethyl acetate, followed by the addition of a small amount of saturated aqueous $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (hexane : CH_2Cl_2 = 3 : 1) to give **8** (84 mg, 87%); mp 113.5—115.0 °C (from MeOH). ^{1}H-NMR ($CDCl_3$) δ: 3.04 (s, 3H), 6.55 (dd, 1H, J = 1.2, 7.7 Hz), 6.65—6.89 (m, 5H), 7.04—7.52 (m, 13H), 7.79 (dd, 1H, J = 1.5, 8.6 Hz), 7.87 (dt, 1H, J = 1.4, 8.0 Hz), 7.94 (dd, 1H, J = 1.4, 8.1 Hz). IR (KBr) cm^{-1}: 1253, 821, 773, 748, 698. MS *m/z*: 468 (M^+), 437 (base peak). *Anal.* Calcd for $C_{33}H_{25}OP$: C, 84.60; H, 5.38; P, 6.61. Found: C, 84.61; H, 5.35; P, 6.73.

Reduction of Allylic Carbonates with Formic Acid: Typical Procedure in Table 1 Formic acid (41 μl, 1.1 mmol) and geranyl methyl carbonate (106 mg, 0.50 mmol) in dioxane (2 ml) were added to a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (5.0 mg, 5.0 μmol), **8** (9.0 mg, 20 mmol) and proton sponge (128 mg, 0.60 mmol) in 1,4-dioxane (1 ml), and the mixture was stirred at room temperature for 37 h. The resulting mixture was poured into water and extracted with ether. The organic layer was washed successively with 1 N HCl, saturated aqueous $NaHCO_3$, and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to give 3,7-dimethylocta-1,6-diene (36 mg, 52%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.99 (d, 3H, J = 6.6 Hz), 1.31 (dt, 2H, J = 7.0, 8.4 Hz), 1.60 (s, 3H), 1.68 (s, 3H), 1.91—2.20 (m, 3H), 4.89—5.14 (m, 3H), 5.70 (ddd, 1H, J = 7.5, 10.3, 17.6 Hz).

Hydrosilylation of Styrene. Typical Procedure in Table 2 A mixture of styrene (1.0 ml, 8.7 mmol), trichlorosilane (1.1 ml, 11 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (1.6 mg, 4.4 mmol) and **8** (8.2 mg, 17 mmol) was stirred at 40 °C for 8 h. The reaction mixture was distilled under reduced pressure (88—89 °C/3—4 mmHg) to give 1-phenyl-1-trichlorosilylethane (1.5 g, 74%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.62 (d, 3H, J = 7.2 Hz), 2.89 (q, 1H, J = 7.5 Hz), 7.20—7.38 (m, 5H).

Hydroboration of 2-Methyl-1-buten-3-yne A mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (2.2 mg, 2.1 mmol) and **8** (3.9 mg, 8.3 μmol) in $CHCl_3$ (4 ml) was stirred at room temperature for 1.5 h, then 2-methyl-1-buten-3-yne (0.20 ml, 2.1 mmol) and catecholborane (**11**, 0.27 ml, 2.5 mmol), were added. The whole was stirred at room temperature for 1.5 h, then cooled with a dry ice-acetone bath, and benzaldehyde (0.30 ml, 3.0 mmol) was added. The mixture was allowed to warm to room temperature. It was stirred for 2.5 h, the mixture was poured into water and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane : ether = 9 : 1) to give 2,2-dimethyl-1-phenyl-3-butyn-1-ol (40 mg, 11%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.11 (s, 3H), 1.28 (s, 3H), 2.28 (s, 1H), 4.52 (s, 1H), 7.28—7.46 (m, 5H).

References and Notes

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11) The MacroModel/MM2 (version 4.5) force field was used.
12) Crystal data: Monoclinic, space group $P2_1/c$, a = 8.658(3) Å, b = 12.733(6) Å, c = 23.235(2) Å, β = 97.86(2)°, V = 2537(1) Å^3, Z = 4, D_{calc} = 1.226 g/cm^3. The structure was refined to R = 0.052, R_w = 0.049, and S = 1.23. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.