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Palladium-Catalyzed Asymmetric Reduction of Allylic Esters with a New Chiral Monodentate Ligand, 8-Diphenylphosphino-8'-methoxy-1,1'-binaphthyl

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Abstract: A new chiral monodentate ligand, 8-diphenylphosphino-8'-methoxy-1,1'-binaphthyl (8-MeO-MOP), was used for palladium-catalyzed reduction of allylic carbonates with formic acid. Various methylcarbonates of 3,3'-disubstituted allylic alcohols were converted to the corresponding optically active 1-olefins with this ligand. © 1998 Elsevier Science Ltd. All rights reserved.

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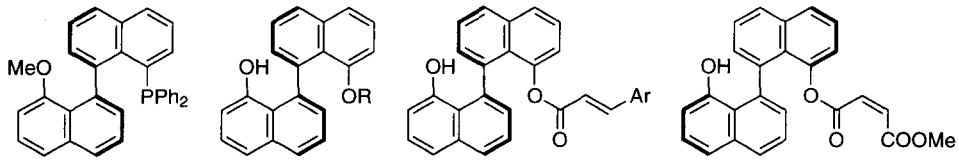
The palladium-catalyzed reduction of allylic esters with formic acid requires a monodentate phosphine ligand.[1] Hayashi and his coworkers reported an asymmetric version of this reaction by using optically active monodentate phosphine ligands such as 2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (MeO-MOP)[2] and 3-diphenyl-phosphino-3'-methoxy-4,4'-biphenanthryl.[2,3] We report here the asymmetric hydrogenolysis of allylic esters using a novel chiral phosphine ligand, 8-diphenylphosphino-8'-methoxy-1,1'-binaphthyl (8-MeO-MOP, **1**). A highly dissymmetric environment is created around the substituents at C-8 and C-8' in **1**, since one side of each substituent is completely blocked by another naphthyl ring in the molecule.[4]



1 **2**: R = H; **3**: R = $OCONEt_2$ **4** **5**

Recently, we demonstrated the potential use of 8,8'-dihydroxy-1,1'-binaphthyl (**2**) in asymmetric protonation with carbamate **3**,[5] in the highly enantioselective synthesis of β-substituted ketones *via* tandem 1,4- and 1,2-addition of Gilman reagents to half-esters **4**,[6] and in the diastereoselective Diels-Alder reactions of **5**.[7] Recently, Meyers *et al.* reported interesting behavior to atropisomerization of an 8,8'-dioxazolynyl-1,1'-binaphthyl and its use for the copper-catalyzed asymmetric cyclopropanation of styrene by ethyl diazoacetate.[8] The highly dissymmetric environment of **2** was also demonstrated in the chiral recognition of amino acid derivatives.[9] Although the lone pair of the phosphorous atom in **1** seems to be too hindered to coordinate to the palladium, the activity of racemic **1** as a ligand for a palladium-catalyzed reaction has been proven.[10] Since the

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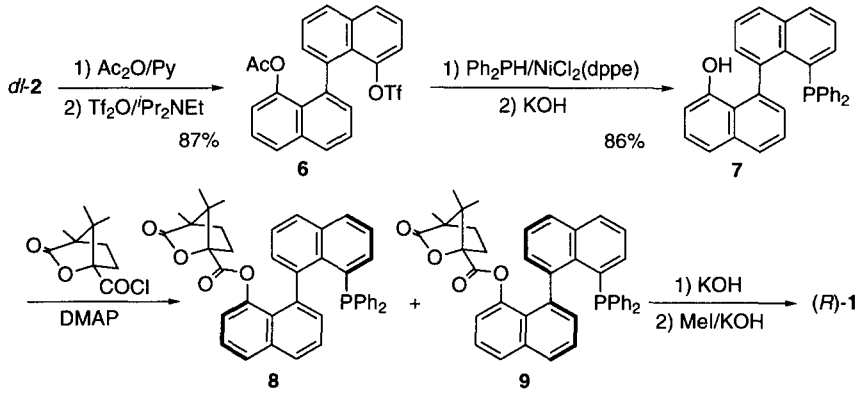
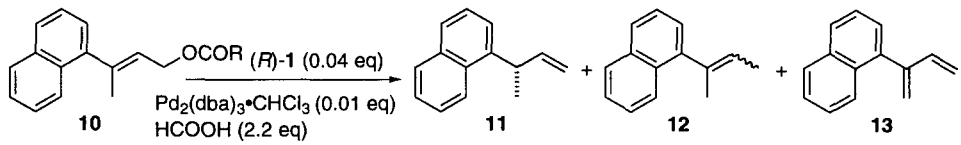
attempted synthesis of optically active 8-MeO-MOP (**1**) via a phosphine oxide by a route similar to that reported for the synthesis of the corresponding 2,2'-series by Hayashi *et al.*[11] encountered complete racemization at the phosphinoylation step,[12] we adopted a nickel-catalyzed coupling reaction between diphenylphosphine and racemic triflate **6** derived from racemic **2** (Scheme 1). The coupling reaction followed by hydrolysis gave the

Scheme 1. Synthesis of Optically Active 8-MeO-MOP (**1**)



phosphine **7**, which was converted into a mixture of diastereomers **8** and **9** upon acylation with (1*S*)-camphanic chloride in quantitative yield. Chromatographic separation of this mixture gave pure **8** and **9** in respective yields of 49%. The absolute configuration of the binaphthyl moiety in **9** was determined to be of *R* by an X-ray analysis.[13] Basic hydrolysis of **9** followed by methylation gave (*R*)-**1**[14] in 54% overall yield after recrystallization from ^{i}PrOH.

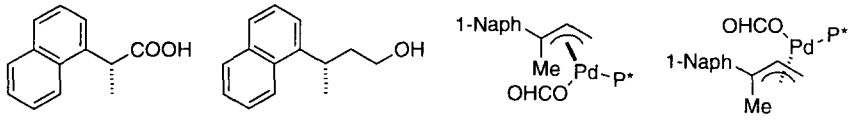
Table 1. Palladium-Catalyzed Asymmetric Reduction of **10** with (*R*)-**1** as a Chiral Ligand.



entry	R	solvent	reaction time (h)	**11** : **12** : **13**	yield of **11** %	% ee of **11**
1	OPh	DMF	20	95 : 2 : 3	92	73
2	O^{t}Bu	DMF	258	92 : 5 : 3	54[a]	61
3	Me	DMF	333	-	b	-
4	NHTs	DMF	244	93 : 7 : 0	51	77
5	OMe	DMF	38	94 : 2 : 4	80	77
6	OMe	NMP[c]	35	94 : 2 : 4	79	82
7	OMe	CH_3CN	41	98 : 1 : 1	85	67
8	OMe	CH_2Cl_2	42	90 : 1 : 9	76	59
9	OMe	THF	135	85 : 1 : 14	69	77
10	OMe	toluene	272	76 : 1 : 23	42[d]	67

[a]A 34% of starting material was recovered. [b]A 95% of starting material was recovered. [c]1-Methyl-2-pyrrolidone. [d]A 36% of starting material was recovered.

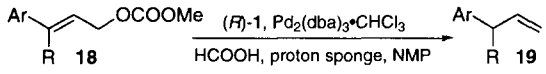
Palladium-catalyzed hydrogenolysis was performed using **10** as a standard substrate. The results are listed in Table 1. The *S*-configuration and the enantiomeric excess (ee) of **11** were determined for **14**[15] obtained by oxidation with $KMnO_4$-$NaIO_4$ and **15** obtained by hydroboration. Phenylcarbonate and methylcarbonate gave the desired product **11** in good yield (entries 1, 5-8). 1-Methyl-2-pyrrolidone (NMP) was a solvent of choice (entry 6). Hünig's base gave a yield comparable to the proton sponge. A standard procedure for asymmetric hydrogenolysis derived from the above studies was applied to substrates **18** with an aromatic ring at C-3. The results are summarized in Table 2. A higher ee was observed on allylic esters with an *ortho*-substituent on the aromatic ring (entries 1, 4-6).

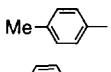


14 **15** **16** **17**

According to the accepted mechanism[16,17] a key intermediate in the hydrogenolysis of **10** is the π-allylpalladium formate **16** or **17**, which in turn affords *S*-**11** or *R*-**11**, respectively, via intramolecular hydride transfer. Although the attempted isolation of the palladium complex **16** or **17** was unsuccessful, crystals of $PdCl(\eta^3\text{-allyl})$(8-MeO-MOP)•1/2$Et_2O$ (**20**) were obtained when a mixture of $[PdCl(\pi\text{-allyl})]_2$ and (*R*)-**1** was kept for four weeks in THF under an atmosphere of Et_2O. The X-ray crystal structure of **20** is shown in Figure 1. The crystal turned out to be racemic, even though we used optically pure (*R*)-**1** as a starting material. Since C(36) is more hindered than C(34), the unsubstituted terminal should be located cis to the phosphine ligand. Since (*S*)-**11** was obtained from the reaction with (*R*)-**1** as a ligand, the possible intermediate should be **16** rather than **17**. These considerations suggest that the absolute configuration of **19** must be *S*, although there is no direct chemical evidence.

Table 2. Palladium-Catalyzed Asymmetric Reduction of Allylic Esters.



entry	Ar	R	reaction time (h)	yield %	% ee
1		Et	160	67	84
2		Me	23	58	41
3		Me	44	41	55
4		Me	156	54	84
5		Me	19	80	69
6		Me	96	65	86

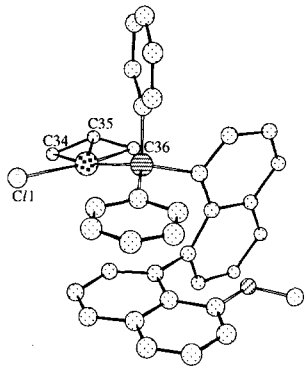


Figure 1. X-ray Crystal Structure of **20**. A molecule of ether and all hydrogen atoms have been omitted.

In conclusion, we have introduced the basic structure of a new chiral ligand for palladium-catalyzed hydrogenolysis, although fine-tuning by structural modification is required to improve the ee and to extend its usefulness.

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13. Crystal structure analyses: **9:** $C_{42}H_{35}O_4P$, orthorhombic, $P2_12_12_1$, a = 16.458(2) Å, b = 22.265(6) Å, c = 9.363(2) Å, V = 3431(2) Å^3, Z = 4, ρ_{calcd} = 1.229 g cm^{-3}, R = 0.043. **20**•Et_2O: $C_{38}H_{35}ClO_{1.5}PPd$, prismatic, $P1$, a = 10.4305(6) Å, b = 15.7679(9) Å, c = 9.7065(6) Å, V = 1580.3(2) Å^3, Z = 2, ρ_{calcd} = 1.447 g cm^{-3}, R = 0.043. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101232. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).
14. Mp. 79-80 °C; $[\alpha]_D^{17}$ -452.9 (c, 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 3.04, (s, 3H), 6.55 (dd, J = 1.2, 7.7 Hz, 1H), 6.65-6.89 (m, 5H), 7.04-7.52 (m, 13H), 7.79 (dd, J = 1.5, 8.6 Hz, 1H), 7.87 (dt, J = 1.4, 8.0 Hz, 1H), 7.94 (dd, J = 1.4, 8.1 Hz, 1H). 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. Enantiomeric excess was determined to be >99% by HPLC (CHIRALCEL OD, hexane : ^{i}PrOH = 99.8 : 0.2).
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