Tetrahedron Letters, Vol.32, No.28, pp 3387-3390, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

ASYMMETRIC DOUBLE HYDROBORATION OF 1,3-DIENES CATALYZED BY CHIRAL PHOSPHINE-RHODIUM COMPLEXES

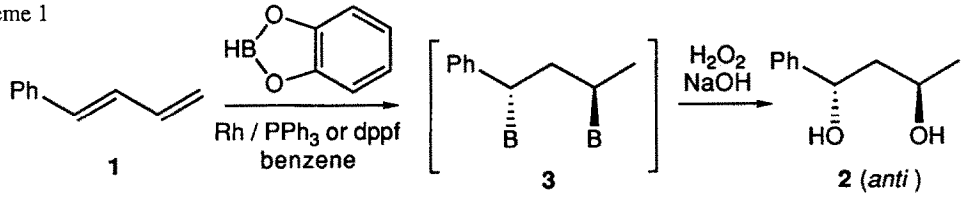
Yonetatsu Matsumoto and Tamio Hayashi*
Catalysis Research Center and Graduate School of Pharmaceutical Sciences
Hokkaido University, Kitaku, Sapporo 060, Japan

Summary: Reaction of 1-phenyl-1,3-butadiene with catecholborane in the presence of a rhodium catalyst bearing triarylphosphine ligand such as PPh_3 or dppf proceeded regioselectively to give, after oxidation, *anti*-1-phenyl-1,3-butanediol in a good yield. Use of (*R*)-BINAP as a chiral ligand for the catalytic hydroboration gave optically active (1*S*,3*R*)-1-phenyl-1,3-butanediol of up to 67% ee.

Recent reports on rhodium-catalyzed hydroboration of olefins have demonstrated its great potential in organic synthesis.[1] We have previously reported that asymmetric hydroboration of substituted styrenes with catecholborane in the presence of a cationic rhodium-phosphine catalyst proceeded regiospecifically to give, after oxidation, optically active 1-arylethanols of over 90% ee.[2] Here we report a new type of catalytic asymmetric hydroboration where the addition of two molecules of catecholborane to 1-phenyl-1,3-butadiene takes place with high regio- and stereoselectivity.

Reaction pathway of catalytic hydroboration of 1-phenyl-1,3-butadiene (**1**) with catecholborane was found to be strongly dependent on the phosphine ligand coordinated with rhodium (Scheme 1). Thus, the reaction of **1** with 2.5 eq of catecholborane in the presence of a triphenylphosphine-rhodium complex, $RhCl(PPh_3)_3$ or a mixture of $[RhCl(COD)]_2$ and PPh_3, in benzene at room temperature for 3 h gave, after oxidation with alkaline hydrogen peroxide, 1-phenyl-1,3-butanediol (**2**) in 73% yield, whose stereochemistry is *anti* with over 90% purity.[3] The selective formation of diol **2** was also observed with dppf[4] which is a bidentate triarylphosphine ligand, though the *anti*-selectivity was lower. The monohydroboration products that are possible intermediates to the double-hydroboration product **3** were not observed in ^1H NMR studies of the catalytic hydroboration in C_6D_6, indicating that the second hydroboration is fast compared with the first one. Reaction of **1** with 1 eq of catecholborane gave double-hydroboration product **2**, with half of the starting diene recovered.

Scheme 1



1 **3** **2** (*anti*)

On the other hand, the double hydroboration was not observed in the reaction with dppe[5] ligand, which lead to the selective formation of terminal alcohols, consisting of 4-phenyl-3-butenol (**4**) as a main isomer and a

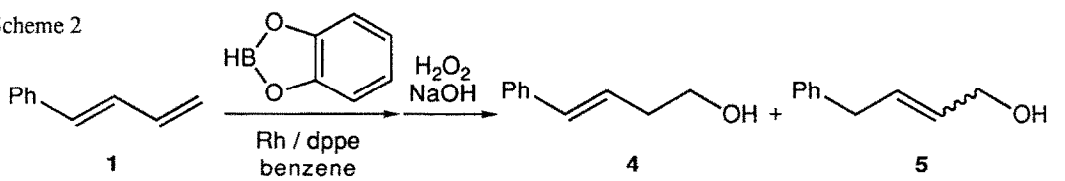
Table 1. Hydroboration of 1-Phenyl-1,3-butadiene (**1**) with Catecholborane Catalyzed by Rhodium-Phosphine Complexes.[a]

catalyst	ligand[b]	time (h)	**2** (%)[c]	**2** (*anti*/*syn*)[d]	**4** and **5** (%)[c,e]
$RhCl(PPh_3)_3$		3	73	10 / 1	<5
$1/2[RhCl(COD)]_2$	$2PPh_3$	1.5	73	10 / 1	<5
	dppe	1.5	0	–	60
	dppb	1.5	20	2 / 1	33
	dppf	1.5	68	3 / 1	<5
$[Rh(COD)_2]ClO_4$	$2PPh_3$	1.5	65	10 / 1	<5
	dppe	1.5	0	–	52
	dppb	1.5	31	2 / 1	20
	dppf	1.5	60	3 / 1	12

[a] Carried out with 2.5 eq of catecholborane and 1 mol% of a rhodium catalyst in benzene at room temperature. [b] Rh/P = 1/2. [c] Isolated yield by preparative TLC. [d] Determined by ^1H and ^{13}C NMR spectra. [e] **4**/**5** = 3/1 ~ 5/1.

small amount of 4-phenyl-2-butenol (**5**), even in the reaction with an excess of catecholborane (Scheme 2). Use of dppb[6] as a ligand gave both diol **2** and terminal alcohol **4** in comparable amounts. The selectivity forming **2** or **4** was not affected by the use of cationic rhodium catalysts.[7] The reaction conditions and results are summarized in Table 1.[8,9]

Scheme 2



1 **4** **5**

Catalytic asymmetric hydroboration forming optically active 1-pheny-1,3-butanediol (**2**) was carried out in the presence of cationic rhodium complexes coordinated with chiral phosphines (Scheme 3). (*R*)-BINAP,[10] (*R*)-(*S*)-BPPFA,[11] and (+)-DIOP[12] ligands gave diol **2** selectively. Of these phosphine ligands, BINAP gave the highest enantioselectivity (Table 2). The double hydroboration of diene **1** with 1 mol% of rhodium catalyst, generated in situ by mixing $[Rh(COD)_2]ClO_4$ with (*R*)-BINAP in THF, at 0 °C for 52 h, followed by oxidation of the reaction mixture with alkaline hydrogen peroxide gave 77% yield of optically active diols, *anti*-(–)-**2** of 48% ee and *syn*-(+)-**2** of 43% ee, the ratio of *anti* isomer to *syn* isomer being 3 to 1 (entry 2). Higher enantiomeric purity of *anti*-**2** (61% ee in THF and 67% ee in dichloromethane) was obtained at a lower reaction temperature (entries 3 and 7). The enantiomeric purities of **2** were determined by HPLC analysis of their dicarbamates, prepared by the reaction of **2** with $3,5\text{-}(NO_2)_2C_6H_3NCO$, with a chiral stationary phase column (Sumichiral OA-1100), and the absolute configurations of *anti*-(–)-**2** and *syn*-(+)-**2** were determined to be (1*S*,3*R*) and (1*R*,3*R*), respectively, by comparison of their optical rotation values with those of authentic samples derived from known

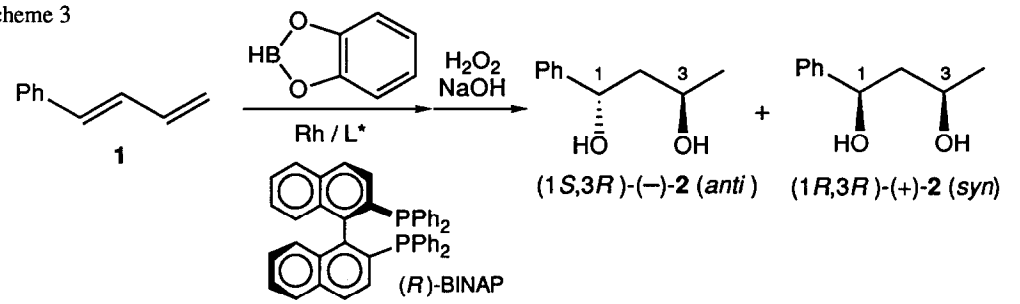
Table 2. Asymmetric Hydroboration of **1** Catalyzed by Chiral Phosphine-Rhodium Complexes.[a]

entry	ligand	solvent	reaction conditions temp (°C)	time (h)	yield of **2**[b] % (*anti*/*syn*)	% ee (configuration) *anti*-**2**	*syn*-**2**
1	(*R*)-BINAP	THF	20	10	62 (3/1)	40 (1*S*,3*R*)	44 (1*R*,3*R*)
2			0	52	77 (3/1)	48 (1*S*,3*R*)	43 (1*R*,3*R*)
3			–20	36	42 (3/1)	61 (1*S*,3*R*)	35 (1*R*,3*R*)
4		DME	20	10	57 (3/1)	46 (1*S*,3*R*)[c]	40 (1*R*,3*R*)[d]
5		benzene	20	15	68 (3/1)	47 (1*S*,3*R*)	36 (1*R*,3*R*)
6[e]		CH_2Cl_2	20	15	60 (3/1)	55 (1*S*,3*R*)	11 (1*R*,3*R*)
7[e]			–20	48	36 (3/1)	67 (1*S*,3*R*)	11 (1*R*,3*R*)
8	(*R*)-(*S*)-BPPFA	benzene	20	22	65 (2/1)	2 (1*S*,3*R*)	15 (1*R*,3*R*)
9	(+)-DIOP	benzene	20	4	62 (2/1)	8 (1*S*,3*R*)	2 (1*R*,3*R*)

[a] Carried out with 2.5 eq of catecholborane in the presence of 1 mol% of catalyst prepared from $[Rh(COD)_2]^+ClO_4^-$ and a phosphine ligand. [b] Isolated yield by preparative TLC. [c] $[\alpha]_D^{20}$ –32.4° (*c* 0.9, $CHCl_3$). [d] $[\alpha]_D^{20}$ +18.2° (*c* 1.2, $CHCl_3$). [e] **4** and **5** were also isolated (entry 6: 34%, entry 7: 28%).

(*R*)-4-phenyl-4-hydroxy-2-butanone ((*R*)-**6**).[13,14] It follows that the diastereoisomeric diols have the same configurations at 3 position and opposite ones at 1 position.

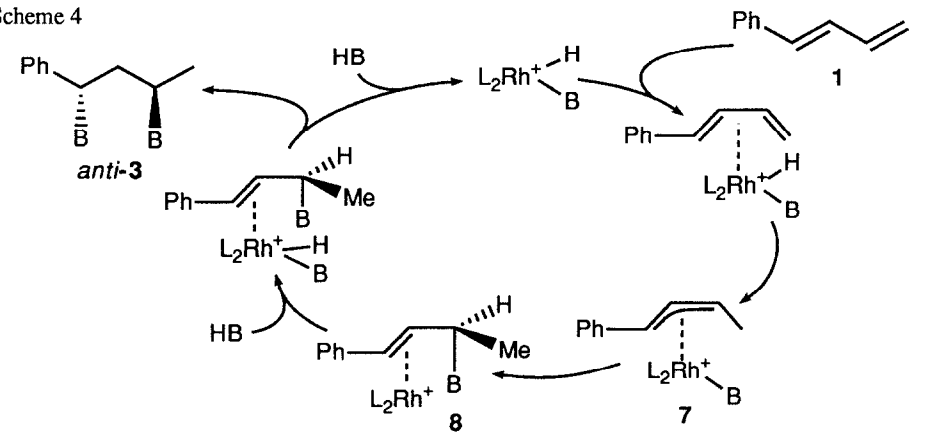
Scheme 3



The catalytic cycle proposed for the double hydroboration that produces *anti*-diol **2** preferentially is shown in Scheme 4.[15] Coordination of diene **1** in *cisoid* conformation with a hydrido(boryl)rhodium species followed by migration of the hydride to the terminal carbon forms π-allylrhodium complex **7**. Transfer of boron from rhodium to π-allyl carbon leads to rhodium complex **8** where allylborane is coordinated to rhodium. Rhodium-mediated hydroboration of the double bond in **8** from the same side as rhodium will release the double hydroboration product with the observed stereochemistry.

We thank the Ministry of Education, Japan for Grant-in-Aid for Scientific Research (Grant No. 02453089) and the Naito Foundation for partial financial support of this work.

Scheme 4



References and Notes

1 a) D. Männing and H. Nöth, *Angew. Chem., Int. Ed. Engl.*, **24**, 878 (1985). b) D. A. Evans, G. C. Fu, and A. H. Hoveyda, *J. Am. Chem. Soc.*, **110**, 6917 (1988). c) K. Burgess and M. J. Ohlmeyer, *J. Org. Chem.*, **53**, 5178 (1988). d) K. Burgess and M. J. Ohlmeyer, *Tetrahedron Lett.*, **30**, 395 (1989). e) K. Burgess and M. J. Ohlmeyer, *Tetrahedron Lett.*, **30**, 5857 (1989). f) K. Burgess and M. J. Ohlmeyer, *Tetrahedron Lett.*, **30**, 5861 (1989). g) M. Satoh, Y. Nomoto, N. Miyaura, and A. Suzuki, *Tetrahedron Lett.*, **30**, 3789 (1989). h) M. Sato, N. Miyaura, and A. Suzuki, *Tetrahedron Lett.*, **31**, 231 (1990). i) D. A. Evans and G. C. Fu, *J. Org. Chem.*, **55**, 2280 (1990). j) J. M. Brown and G. C. Lloyd-Jones, *Tetrahedron Asymmetry*, **1**, 869 (1990).

2 T. Hayashi, Y. Matsumoto, and Y. Ito, *J. Am. Chem. Soc.*, **111**, 3426 (1989).

3 The *syn*/*anti* stereochemistry of **2** was determined by ^{13}C NMR: S. Kiyooka, H. Kuroda, and Y. Shimasaki, *Tetrahedron Lett.*, **27**, 3009 (1986).

4 1,1'-Bis(diphenylphosphino)ferrocene: T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, and K. Hirotsu, *J. Am. Chem. Soc.*, **106**, 158 (1984).

5 1,2-Bis(diphenylphosphino)ethane.

6 1,4-Bis(diphenylphosphino)butane.

7 The use of a cationic rhodium catalyst is essential for the asymmetric hydroboration of styrenes (ref. 2).

8 The catalytic double hydroboration forming diol was observed only with 1-phenylbutadiene. Rhodium-catalyzed hydroboration of 1,3-decadiene and 1-vinylcycloheptene gave terminal allylic and homoallylic alcohols analogous to **4** and **5**.

9 Uncatalyzed reaction of **1** with 2.2 eq of 9-BBN in THF at 20 °C gave 74% of 1-phenyl-1,4-butanediol and 16% of **4**.

10 (*R*)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl: H, Takaya, K. Mashima, K. Koyano, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa, and R. Noyori, *J. Org. Chem.*, **51**, 629 (1986).

11 (*R*)-*N*,*N*-Dimethyl-1-[(*S*)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine: T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, and M. Kumada, *Bull. Chem. Soc. Jpn.* **53**, 1138 (1980).

12 (+)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane: H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972).

13 T. Hayashi, Y. Matsumoto, and Y. Ito, *J. Am. Chem. Soc.*, **110**, 5579 (1988).

14 Reduction of (*R*)-**6** ($[\alpha]_D^{23}$ +53.6° (c 1.6, chloroform), 71% optical purity) with $LiAlH_4$ in THF at 0 °C gave *anti*-(+)-**2** ($[\alpha]_D^{20}$ +50.7° (*c* 0.6, chloroform)) and *syn*-(+)-**2** ($[\alpha]_D^{20}$ +38.4° (*c* 1.0, chloroform)) in a ratio of 29 : 71, which should have (1*R*,3*S*) and (1*R*,3*R*) configurations, respectively.

15 A catalytic cycle for rhodium-catalyzed hydroboration of simple olefins has been proposed (ref. 1a and 1i).

(Received in Japan 15 February 1991)