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Synthesis and Properties of Optically Active Phosphine-Boranes Possessing an *l*-Menthyloxy Group

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ABSTRACT

(SP)-9-Anthryl(l-menthyloxy)phenylphosphine-borane and (SP)-(1-l-menthyloxy)benzo[b]phosphole-borane were synthesized, and their structures were characterized by X-ray crystallographic analysis. The latter compound was reduced by lithium naphthalenide at −78°C with cleavage of the P–O bond, and the subsequent reaction with electrophiles afforded the corresponding tertiary phosphine-boranes possessing good to excellent enantiomeric excesses.

INTRODUCTION

Optically active tertiary phosphines possessing a chirality center at phosphorus play important roles, not only in the area of catalytic asymmetric reactions, but also in the study of the stereochemistry of reactions occurring at phosphorus [1]. Despite their enormous utility, syntheses of these types of compounds with high enantiomeric excesses have been achieved only with difficulty by the previously existing methods [2]. On the other hand, we reported that diastereomerically pure phosphine-boranes possessing an *l*-menthyloxy group were converted to *P*-chiral tertiary phosphines with excellent enantiomeric excesses via stereospecific transformations of optically active phosphine-boranes [3]. Based on these facts, we intended to synthesize new optically pure tertiary phosphines that have a 9-anthryl group or involve a phosphole moiety. For this purpose, it was desired to prepare diastereomerically pure 9-anthryl (*l*-menthyloxy)phenylphosphine-borane and (1-*l*-menthyloxy)benzo[*b*]phosphole-borane as the key intermediates. In this article, we report syntheses, X-ray crystallographic analyses, and some chemical properties of these compounds.

RESULTS AND DISCUSSION

Synthesis and Properties of (S_P)-9-Anthryl(l-menthyloxy)phenylphosphine-borane

Our initial study was undertaken by the synthesis of optically pure 9-anthryl(*l*-menthyloxy)-phenylphosphine-borane **1** with the ultimate aim of preparation of sterically hindered optically active tertiary phosphines. The synthesis of compound **1** was carried out by the reactions shown in Scheme 1. Thus, dichlorophenylphosphine was treated successively with 9-anthryllithium, lithium *l*-men-

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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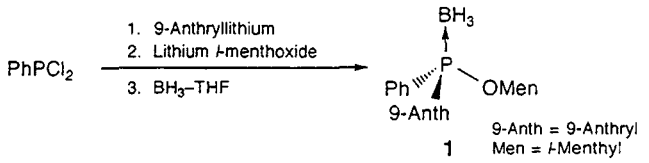


SCHEME 1

thoxide, then borane-THF complex, and a crystalline compound was isolated from the reaction mixture. This compound was identified as one of the expected diastereomers from spectroscopic data together with elemental analysis.

The structure of the compound was unequivocally determined by X-ray crystallographic analysis. The ORTEP drawing, which indicates the *S* configuration of the chiral phosphorus, is shown in Figure 1. Selected bond distances and bond angles are also listed in Table 1.

X-ray crystal data indicate the following characteristic features of this compound. (1) The phenyl group and the 9-anthryl group are located in a face-edge manner. (2) The B(1)–P(1)–C(1) bond angle (123.5°) is unusually large, indicating steric repulsion between the boranato group and the hydrogen atom attached at the C(3) atom of the 9-anthryl group.

It is particularly notable that one of the methyl groups of the isopropyl group shows its signal at 0.00 ppm. This unusual high-field shift is ascribed to the large anisotropy effect of the 9-anthryl group,

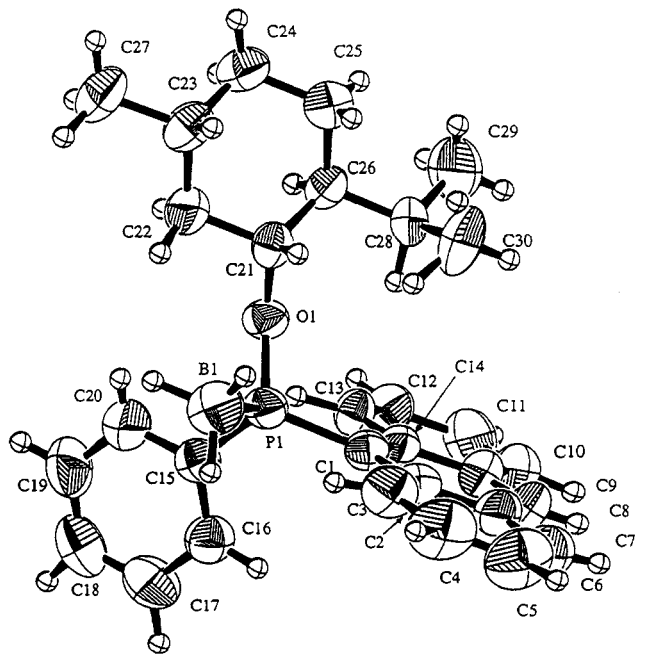


FIGURE 1 Molecular structure of compound **1**.

TABLE 1 Selected Bond Distances (Å) and Angles (°) for Compound **1**

Bond distances			
P(1)–B(1)	1.92(1)	P(1)–O(1)	1.614(6)
P(1)–C(1)	1.842(8)	P(1)–C(15)	1.801(9)
Bond angles			
B(1)–P(1)–C(1)	123.5(6)	B(1)–P(1)–C(15)	106.5(6)
B(1)–P(1)–O(1)	112.1(6)	C(1)–P(1)–C(15)	105.1(4)
C(1)–P(1)–O(1)	106.4(3)	O(1)–P(1)–C(15)	100.7(4)

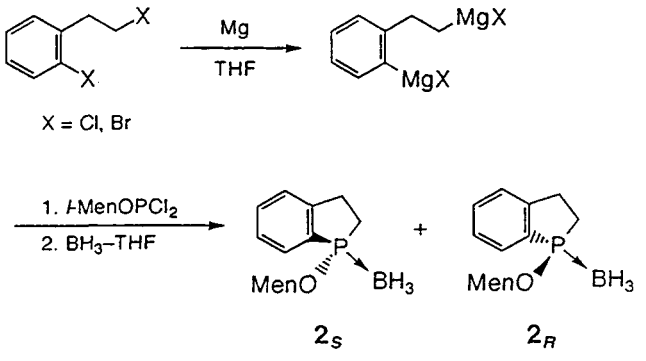
since the methyl group is located closely to a center of the anthracene ring.

The large steric repulsion also affects the stability of this compound. It was thermally unstable, particularly in solution, and it gradually decomposed with liberation of borane to give 9-anthryl(*l*-menthyloxy)phenylphosphine and its oxidation product [4].

Synthesis and Properties of (S_P)- *and* (R_P)-(*1-l-menthyloxy*)*benzo*[*b*]*phosphole-boranes* (**2**$_S$) *and* (**2**$_R$)

Synthesis of (S_P)- and (R_P)-(1-*l*-menthyloxy)-benzo[*b*]phosphole-boranes (**2**$_S$ and **2**$_R$) was carried out according to Scheme 2. Thus, *o*-(2-bromoethyl)bromobenzene [5] or *o*-(2-chloroethyl)chlorobenzene [6] was converted to the corresponding bis-Grignard reagent on treatment with magnesium in THF [7]. The Grignard reagent was allowed to react successively with dichloro(*l*-menthyloxy)phosphine and borane-THF complex to afford a diastereomeric mixture of the desired phosphole-boranes in moderate yield. The mixture was subjected to fractional recrystallizations from methanol to provide two types of crystalline form [cubes (mp 100–101°C) and plates (mp 113–114°C)].

The crystal structure of one diastereomer (mp 100–101°C) was studied by X-ray crystallography. The ORTEP drawing and the selected bond distances and angles are shown in Figure 2 and Table 2, respectively. It is clear from the ORTEP draw-



SCHEME 2

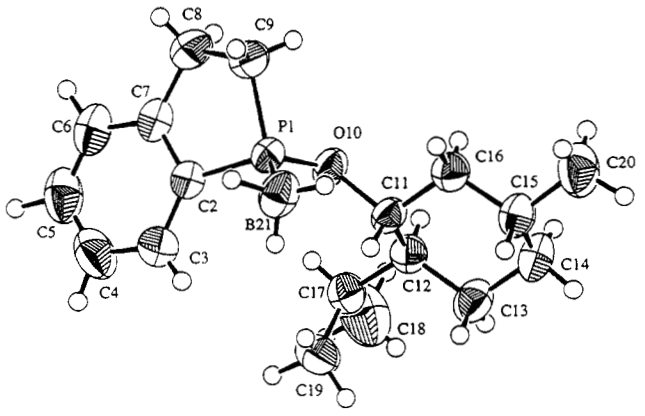


FIGURE 2 Molecular structure of compound **2s**.

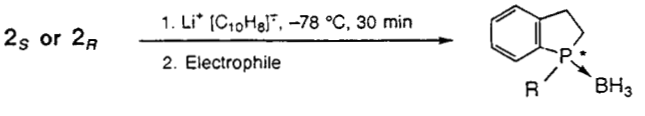
ing that this compound has the *S* configuration at chiral phosphorus and, therefore, the other diastereomer (mp 113–114°C) must possesses the *R* configuration. One of the notable structural characteristics is indicated in the bond angle of C(2)–P(1)–C(9); this bond angle (93.1°) is remarkably distorted from the bond angles that are usually observed for four-coordinate phosphorus compounds.

Some Reactions of Compounds $\mathbf{2_S}$ *and* $\mathbf{2_R}$

We tried to prepare some optically active phosphine-boranes possessing a phosphole moiety using $\mathbf{2_S}$ or $\mathbf{2_R}$. These compounds were reduced by lithium naphthalenide at −78°C, and the resulting reaction mixture was treated with an electrophile, such as iodomethane (Scheme 3) [8]. The results are summarized in Table 3.

Phosphole-borane $\mathbf{3_S}$, which has a P–H bond, was obtained in almost quantitative yield by treating the reduction mixture with dilute hydrochloric acid (Entry 1). Unfortunately, however, this compound was stereochemically unstable, and its optical purity gradually decreased on standing at room temperature. In contrast, the reaction of the reduction products with alkyl iodides provided the corresponding alkylation products in excellent enantiomeric excesses (Entries 2–4).

A zero-valent palladium-catalyzed cross-coupling reaction of the reduction product with *o*-iodoanisole was also examined using $Pd(PPh_3)_4$ as the catalyst, and compound $\mathbf{6_S}$ was isolated in 48% yield. Although the enantiomeric excess of the product was not high (65%), it was increased to 95% ee by recrystallization from hexane.



SCHEME 3

TABLE 2 Selected Bond Distances (Å) and Angles (°) for Compound $\mathbf{2_S}$

Bond distances			
P(1)–B(21)	1.898(4)	P(1)–O(10)	1.596(2)
P(1)–C(2)	1.796(3)	P(1)–C(9)	1.820(3)
Bond angles			
B(21)–P(1)–C(2)	115.6(2)	B(21)–P(1)–C(9)	117.5(2)
B(21)–P(1)–O(10)	116.9(1)	C(2)–P(1)–C(9)	93.1(1)
C(2)–P(1)–O(10)	106.1(1)	O(10)–P(1)–C(9)	104.5(1)

EXPERIMENTAL

General

Infrared spectra were obtained by use of a Hitachi-215 spectrophotometer. ^{1}H-NMR spectra were recorded on JEOL FX-270, JEOL GSX-400, and JEOL GSX-500 spectrometers. ^{13}C NMR, ^{31}P NMR, and ^{11}B NMR spectra were obtained by a use of a JEOL GSX-400 spectrophotometer. Chemical shifts of ^{31}P and ^{11}B NMR are reported in δ units from 85% H_3PO_4 and trimethyl borate, respectively. Microanalysis and mass spectroscopic analysis were performed on Perkin-Elmer 240B and JEOL JMS HX-110 instruments at the Chemical Analysis Center of Chiba University. Optical rotations were measured with a JASCO DIP-370 digital polarimeter with a 100-mm-long cell. Optical purities were determined by HPLC analysis performed on a Hitachi L-6000 pump and Hitachi L-4000 UV detector with an appropriate chiral column. Gas chromatographic analysis was carried out on a Shimadzu-GC 6A instrument.

Tetrahydrofuran was distilled from sodium-benzophenone ketyl under a dry argon atmosphere prior to use. Magnesium powder (50 mesh) was purchased from Aldrich. 2-Iodoethyl methyl ether was prepared from 2-chloroethyl methyl ether and sodium iodide. Other simple chemicals were purchased and used without further purification.

Synthesis of (S_P)*-9-Anthryl(l-menthyloxy)phenylphosphine-Borane* (**1**)

A solution of 9-bromoanthracene (6.43 g, 25 mmol) in THF (200 mL) was cooled to −78°C, and to this solution was added *tert*-butyllithium (34 mL of 1.5 mol/L pentane solution, 51 mmol) during 20 minutes. The resulting reaction mixture was added to a solution of dichlorophenylphosphine (3.39 mL, 25 mmol) in THF (50 mL) at −78°C with vigorous stirring over a period of 45 minutes. The temperature was gradually increased to 0°C, and then a solution of lithium *l*-menthoxide, prepared from *l*-menthol (3.91 g, 25 mmol) and *n*-butyllithium (16 mL of 1.6 mol/L hexane solution), was added. The

TABLE 3 Reactions of 2_S or 2_R with Lithium Naphthalenide and Electrophiles

Entry	*Substrate*	*Electrophile*	*Product*	*Yield*[a] (%)	*ee*[b] (%)
1	2_S	H_2O	3_S (R = H)	99	44
2	2_S	CH_3I	4_S (R = CH_3)	95	99
3	2_R	CH_3I	4_R (R = CH_3)	96	97
4	2_S	$CH_3OCH_2CH_2I$	5_S (R = $CH_3OCH_2CH_2$)	78	99
5	2_S	*o*-$MeOC_6H_4I$[c]	6_S (R = *o*-$MeOC_6H_4$)	48	65

[a]Isolated yield.
[b]The ee's were determined by HPLC analysis with CHIRALCEL OJ column (hexane/2-propanol = 9/1 as an eluent).
[c]The reaction was carried out in the presence of a catalytic amount of $Pd(PPh_3)_4$ at −78°C through to room temperature.

reaction mixture was slowly warmed to 45°C and was kept at the same temperature for 1 hour. The flask was immersed in an ice bath, and borane-THF complex (35 mL of 1.0 mol/L THF solution) was slowly added. After having been allowed to stand at ambient temperature for 10 hours, the reaction mixture was carefully added to ice-water with stirring. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to chromatography on silica gel using toluene-hexane (1:8) as the eluent. The product was purified by recrystallization from methanol to give colorless prisms (560 mg, 5%). Mp 155–157°C (dec); $[\alpha]^{27}D$ −185° (*c* 1.0, $ClCH_2CH_2Cl$), R_f = 0.34 (AcOEt/hexane = 1/20); IR (KBr) 2925, 2395, 1065, 980, 735 cm^{-1}. ^1H NMR (500 MHz) ($CDCl_3$) δ 0.00 (d, *J* = 6.87 Hz, 3H), 0.19 (d, *J* = 6.88 Hz, 3H), 0.99 (d, *J* = 6.59 Hz, 3H), 0.8–2.6 (m, 12H), 4.53 (m, 1H), 7.28–7.49 (m, 9H), 8.02 (m, 2H), 8.67 (s, 1H), 8.98 (d, *J* = 8.25 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.90, 20.49, 22.22, 22.57, 25.38, 31.68, 34.14, 44.11, 48.84, 48.87, 81.14, 81.17, 123.86, 124.23, 125.07, 126.66, 127.68, 127.74, 128.27, 128.85, 128.90, 129.15, 129.65, 129.75, 130.30, 131.12, 131.19, 134.55, 135.17, 135.24, 137.80, 138.40; ^{31}P NMR (162 MHz) ($CDCl_3$) δ 103.1; ^{11}B NMR (128 MHz) ($CDCl_3$) δ −49.9; HRMS (FAB) calcd for $C_{30}H_{33}BOP$(M-3): 451.2354; found: 451.2351. Anal. calcd for $C_{30}H_{36}BOP$: C, 79.30; H, 7.98. Found: C, 79.44; H, 7.95.

X-ray Crystallographic Analysis of Compound **1**

A well-shaped monoclinic crystal of compound **1** was obtained by recrystallization from ether: $C_{30}H_{36}BOP$; space group $P2_1$; *Z* = 4; *D* = 1.137 g/cm^3; cell constant *a* = 10.367(1), *b* = 15.866(3), *c* = 16.327(1), β = 98.715(7); *V* = 2654.4(5). Lattice constants and intensity data for **1** were measured using graphite-monochromated Cu *Kα* radiation on a Rigaku AFC-5S diffractometer. The data were collected at a temperature of 23 ± 1°C using the ω-2θ scanning method with a 2θ scan speed of 32°/min to 120.1°. Of the 4382 reflections that were collected, 4127 were unique (R_{int} = 0.024). The structure was solved by the SHELXS86 system based on direct methods. Approximate positions for all hydrogen atoms were found in subsequent difference Fourier syntheses. Final refinement cycles utilizing anisotropic thermal parameters for all nonhydrogen atoms resulted in *R* = 0.058.

Preparation of Dichloro(l-menthyloxy)phosphine

A solution of *l*-menthol (78.3 g, 0.50 mol) in THF (80 mL) was added to a solution of phosphorus trichloride (53 mL, 0.60 mol) in THF (50 mL) during 10 minutes at room temperature. The mixture was heated at 80°C for about 2 hours until HCl gas was no longer evolved. After the solvent was removed, the residual oil was distilled under reduced pressure to give 107 g (83%) of a colorless oil: bp 120–122°C (3 mm Hg). Pure product was obtained by further distillation and was stored in an ampule under an argon atmosphere: bp 103–104°C (1 mm Hg). $[\alpha]^{24}D$ − 93.4° (*c* 0.6, benzene).

(S_P)-(1-l-Menthyloxy)benzo[b]phosphole-Borane (2_S) *and (R_P)-(1-l-Menthyloxy)benzo[b]phosphole-Borane* (2_R)

A solution of *o*-(2-chloroethyl)chlorobenzene (21.0 g, 0.12 mol) in THF (50 mL) was added dropwise during 30 minutes to magnesium powder (8.7 g, 0.3 mol) in THF (20 mL) with gentle refluxing. The mixture was vigorously stirred at reflux for more than 5 hours. The reaction was monitored by gas chromatographic analysis with an OV-17 column. After completion of the reaction, the mixture was diluted with dry THF (150 mL) and the supernatant liquid was transferred to a dropping funnel. The solution was added to an ice-cold solution of dichloro(*l*-menthyloxy)phosphine (23.1 g, 0.09 mol) in THF (40 mL) during a 30 minute period, and stirring was continued for an additional 1 hour at ambient temperature. The reaction flask was immersed in an ice-water bath again, and then borane-THF (1.0 mol/L, 95 mL, 95 mmol) was added

by use of a syringe. The reaction mixture was concentrated to half its volume, and then it was poured into ice-water (100 mL). The aqueous layer was extracted with ethyl acetate, and combined extracts were washed with aqueous $NaHCO_3$ solution and brine. The solvent was removed and the residual oil was triturated with methanol at ca. −10°C to afford a crystalline solid (14 g, 51%). Recrystallization of the crude product from methanol gave two kinds of crystals (cubes and plates), which were completely separated by further fractional recrystallizations. **2_S**: colorless cubes; mp 100–101°C (MeOH); $[\alpha]^{23}D$ −40.8° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.6–1.6 (m, 3H), 0.78 (d, *J* = 11.5 Hz, 3H), 0.80 (d, *J* = 11.2 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 2.22–2.29 (m, 2H), 3.22–3.26 (m, 1H), 3.35–3.40 (m, 1H), 4.07–4.12 (m, 1H), 7.33–7.40 (m, 2H) 7.44–7.52 (m, 1H) 7.69–7.75 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.8, 20.9, 22.1, 22.8, 25.5, 28.2, 28.5, 30.8, 31.4, 34.1, 43.4, 48.6, 48.6, 79.1, 79.1, 125.9, 126.0, 127.4, 127.5, 129.4, 129.5, 132.5, 133.2, 133.7, 148.1, 148.3; ^{31}P NMR (162 MHz) ($CDCl_3$) δ 133.6; ^{11}B NMR (128 MHz) ($CDCl_3$) δ −58.8 (d, J_{BP} = 60.4 Hz); IR (KBr) 2900, 2850, 2350, 1440, 1020, 980, 660 cm^{-1}. Anal. calcd for $C_{18}H_{30}BOP$: C, 71.07; H, 9.94. Found: C, 71.05; H, 10.04. **2_R**: colorless plates; mp 113–114°C (MeOH); $[\alpha]^{23}D$ −70.8° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.6–1.6 (m, 3H), 0.78 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 2.22–2.32 (m, 2H), 3.16–3.24 (m, 1H), 3.34–3.49 (m, 1H), 4.04–4.09 (m, 1H), 7.34–7.40 (m, 2H), 7.45–7.51 (m, 1H), 7.72–7.79 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.9, 21.0, 22.1, 22.9, 25.8, 27.0, 27.5, 30.5, 30.5, 31.5, 34.1, 43.7, 48.6, 48.6, 79.3, 79.4, 125.9, 126.0, 127.5, 127.6, 129.4, 129.5, 132.4, 133.7, 134.4, 148.2, 148.4; ^{31}P NMR (162 MHz) ($CDCl_3$) δ 133.2; ^{11}B NMR (128 MHz) ($CDCl_3$) δ −58.9 (d, J_{BP} = 61.0 Hz); IR (KBr) 2900, 2850, 2350, 1440, 1020, 1000, 660 cm^{-1}. Anal. calcd for $C_{18}H_{30}BOP$: C, 71.07; H, 9.94. Found: C, 71.06; H, 10.00.

X-ray Crystallographic Analysis of Compound **2_S**

A well-shaped monoclinic crystal of compound **2_S** was obtained by recrystallization from methanol: $C_{18}H_{30}BOP$; space group $P2_12_12_1$; *Z* = 4; *D* = 1.07 g/cm^{-3}; cell constant *a* = 15.055(1), *b* = 15.255(2), *c* = 8.2033(8), *V* = 1884.0(3). Lattice constants and intensity data for **2_S** were measured using graphite-monochromated Cu K_α radiation on a Rigaku AFC7R diffractometer. The data were collected at a temperature of 25 ± 1°C using the ω − 2θ scan technique at a speed of 16.0° to a maximum 2θ value of 120.1°. Of the 3294 reflections that were collected, 1647 were unique (R_{int} = 0.024). The data were corrected for Lorentz and polarization effects, and the structure was solved by and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 1528 observed reflections ($I > 3.00\ \sigma(I)$) and 311 variable parameters and converged with unweighed and weighed agreement factors of *R* = 0.030 and R_w = 0.043.

Reduction of **2_S** *or* **2_R** *with Lithium Naphthalenide and Subsequent Reactions with Electrophiles: A Typical Procedure*

A preformed THF solution of lithium naphthalenide (ca. 0.2 mol/L) was added dropwise to a solution **2_S** (150 mg, 0.5 mmol) in THF (2 mL) at −78°C until the typical deep green color persisted. After 30 minutes, iodomethane (0.3 mL, 2.5 mmol) was added and the temperature was allowed to increase to 0°C. The reaction mixture was mixed with 1 mol/L HCl, and the organic compounds were extracted with ether. The combined extracts were dried and concentrated. The residue was subjected to medium pressure liquid chromatography (Wakogel C-300, $CHCl_3$/hexane = 1/2 as an eluent) to give 78 mg of (*S*)-1-methylbenzo[*b*]phosphole-borane (**4_S**) (95%). The enantiomeric excess of the product was determined by HPLC analysis with CHIRALCEL OJ (Daicel Chemical Industries, Ltd., hexane/2-propanol = 9/1).

(S)-Benzo[b]phosphole-Borane (**3_S**)

Oil (44% ee); ^1H NMR ($CDCl_3$) δ 0.10–1.50 (m, 3H), 2.09–2.21 (m, 1H), 2.50–2.61 (m, 1H), 3.26–3.40 (m, 2H), 5.84 (J_{PH} = 370 Hz, 1H) 7.34–7.40 (m, 2H) 7.46–7.49 (m, 1H) 7.68–7.74 (m, 1H); IR (neat) 2350, 1440, 1060, 920, 750 cm^{-1}.

(S)-1-Methylbenzo[b]phosphole-Borane (**4_S**)

Colorless needles; mp 89.5–90.5°C (hexane); $[\alpha]^{24}D$ −52.5° (*c* 0.94, $CHCl_3$) (95% ee); ^1H NMR ($CDCl_3$) δ 0.20–1.06 (m, 3H), 1.47 (d, *J* = 10.5 Hz, 3H), 2.11–2.36 (m, 2H), 3.27–3.35 (m, 2H), 7.32–7.37 (m, 2H), 7.40–7.46 (m, 1H), 7.60–7.66 (m, 1H); IR (KBr) 2900, 2350, 1060, 920, 800, 780 cm^{-1}. Anal. calcd for $C_9H_{14}BP$: C, 65.92; H, 8.60. Found: C, 65.94; H, 8.64.

(R)-1-Methylbenzo[b]phosphole-Borane (**4_R**)

Colorless needles; mp 89–90°C (hexane); $[\alpha]^{24}D$ + 51.6° (*c* 1.0, $CHCl_3$) (96% ee); ^1H NMR ($CDCl_3$) δ 0.20–1.40 (m, 3H) 1.47 (d, *J* = 10.5 Hz, 3H), 2.13–2.34 (m, 2H), 3.27–3.36 (m, 2H), 7.32–7.37 (m, 2H), 7.40–7.47 (m, 1H), 7.61–7.67 (m, 1H); IR (KBr) 2900, 2350, 1060, 920, 800, 780 cm^{-1}; HRMS calcd for $C_9H_{13}BP$ (M − 1) 163.0854. Found 163.0854.

(S)-1-(2-Methoxyethyl)benzo[b]phosphole-Borane (**5_S**)

Oil; $[\alpha]^{24}D$ −16.7°C (*c* 1.0, $CDCl_3$) (95% ee); ^1H NMR ($CDCl_3$) δ 0.40–1.40 (m, 3H), 2.03–2.08 (m, 2H), 2.26–

2.40 (m, 2H), 3.20–3.30 (m, 2H), 3.28 (s, 3H), 3.52–3.67 (m, 2H), 7.34–7.62 (m, 4H); IR (neat) 2900, 2350, 1450, 1120, 1090, 780 cm^{-1}.

Reaction of $\mathbf{2_S}$ *with o-Iodoanisole in the Presence of* $Pd(PPh_3)_4$

Compound $\mathbf{2_S}$ (90.3 mg, 0.3 mmol) was reduced by treatment with lithium naphthalenide (0.6 mmol) at −78°C for 30 minutes. *o*-Iodoanisole (0.2 mL, 1.5 mmol) and $Pd(PPh_3)_4$ (20 mg, 5 mol%) were added to the mixture at the same temperature. The temperature was gradually elevated to room temperature with vigorous stirring during 3 hours. The reaction mixture was worked up in the usual manner to give (1-*o*-methoxyphenyl)benzo[*b*]phosphole-borane ($\mathbf{6_S}$) (36 mg, 48%, 65% ee) [9]. Recrystallization of the product from hexane provided colorless needles: mp 78.5–79.5°C; $[\alpha]^{24}D$ +31.8° (*c* 1.0, $CHCl_3$) (95% ee); ^1H NMR ($CDCl_3$) δ 0.40–1.60 (m, 3H), 2.33–2.45 (m, 1H), 2.61–2.75 (m, 1H), 3.28–3.38 (m, 2H), 3.69 (s, 3H), 6.84–6.89 (m, 1H), 6.95–6.99 (m, 1H), 7.28–7.35 (m, 2H), 7.38–7.47 (m, 2H), 7.54–7.60 (m, 2H); IR (KBr) 2900, 2350, 1580, 1460, 1250, 760 cm^{-1}.

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REFERENCES

[1] For representative reviews, see C. R. Hall, T. D. Inch, *Tetrahedron, 36,* 1980, 2059; D. Valenine: in J. D. Morrison, J. W. Scott (eds): *Asymmetric Synthesis,* Academic Press, New York, vol. 4, ch. 3 (1984); H. B. Kagan, M. Sasaki: in F. R. Hartley (ed.): *Chemistry of Organophosphorus Compounds,* vol. 1, pp. 1–52 (1990); T. Imamoto: in R. Engel (ed): *Handbook of Organophosphorus Compounds,* Marcel Dekker, New York, pp. 1–53 (1992).

[2] For an excellent review, see K. Michal Pietrusiewicz, M. Zablocka, *Chem. Rev., 94,* 1994, 1375.

[3] T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc., 112,* 1990, 5244; T. Imamoto, T. Oshiki, T. Onozawa, M. Matsuo, T. Hikosaka, M. Yanagawa, *Heteroatom. Chem., 3,* 1993, 563; T. Imamoto, M. Matuo, T. Nonomura, K. Kishikawa, M. Yanagawa, *Heteroatom. Chem., 4,* 1993, 475.

[4] We attempted to isolate another diastereomer. However, the expected diastereomeric compound was extremely unstable at room temperature and was gradually converted into 9-anthryl(*l*-menthyloxy)phenylphosphine with liberation of borane.

[5] S. Ueno, T. Mizutani, A. Yoshitake, A. Ito, *Yakugaku Zasshi, 84,* 1964, 458.

[6] J. F. Bunnett, Joseph A. Skorcz, *J. Org. Chem., 27,* 1962, 3836.

[7] *o*-(2-Bromoethyl)bromobenzene was readily converted to the corresponding bis-Grignard reagent by the standard procedure. On the other hand, the reaction of *o*-(2-chloroethyl)chlorobenzene with magnesium turnings was very sluggish under ordinary conditions, and the preparation of the desired bis-Grignard was accomplished at refluxing temperature using magnesium powder (see the Experimental section).

[8] T. Oshiki, T. Hikosaka, T. Imamoto, *Tetrahedron Lett., 32,* 1991, 3371.

[9] The enantiomer excess was determined by HPLC analysis using CHIRALCEL OC column (Daicel Chemical Industries Co. Ltd. hexane/2-propanol = 9/1 was used as an eluent).